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Low nitrate contamination of shallow groundwater in spite of intensive dairying: the effect of reducing conditions in the vadose zone–aquifer continuum

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Abstract

The Toenepi catchment is in a long-established dairying area near Morrinsville, in the Waikato (New Zealand). To investigate the effect of land use on the contamination of the underlying shallow groundwater with nitrogen, seven well transects were established in this rolling downlands catchment. The monitoring wells were typically only 2.5 to 3.0 m deep, as shallow groundwater was expected to best reflect the most recent land-use intensity. The 34 wells were sampled monthly from December 2002 to December 2004 and analysed for inorganic N. Relative to the land-use intensity on the dairy farms (avg. 3.1 cows ha^{-1}, 99 kg ha^{-1} yr^{-1} N fertiliser), NO_3-N concentrations in the shallow groundwater were generally very low. Eighty percent of the 843 samples had concentrations below the ANZECC trigger value for eutrophication of surface water (0.44 mg NO_3-N L^{-1}). We investigated the hypothesis that substantial nitrate reduction could be occurring in the vadose zone–aquifer continuum in this catchment. Vadose zone pore water NO_3-N concentrations were monitored, soil pit profiles and bore-hole samples were visually inspected for indications of reducing conditions, and additional field (e.g., dissolved oxygen) and laboratory analyses (e.g., dissolved Mn and Fe) were undertaken on groundwater samples. The results indicated that nitrate reduction through heterotrophic and/or autotrophic denitrification is widespread in this catchment in the vadose zone and/or in the shallow aquifer. Estimates of NO_3-N leaching from the root zone of the pasture, as provided by nutrient budget models, are thus not sufficient to evaluate the effect of leaching losses on ground and surface waters in catchments such as this, where nitrate reduction can occur below the root zone.

Keywords

Nitrogen, dissolved oxygen, dissolved Fe, denitrification, redox, leachate, water quality, dairy farming

Introduction

During the past 25 years, dairy cattle numbers have risen in New Zealand from 2.9 million in 1981 to 5.2 million in 2006. While there was a particularly strong growth on the South Island (from 0.2 to 1.5 million), the Waikato

remains by far the most important dairying region, with 1.7 million dairy cattle or 33% of the national herd (Statistics New Zealand, 2007). Parallel to the increase in dairy cattle numbers and the corresponding increase in the land area used for dairying, there also have been substantial productivity increases, in part due to increased application of fertilisers and increased use of supplementary feed. As a result, the average amount of milk solids produced per effective hectare of dairy land has increased by 39% between 1992/93 and 2005/06, from 653 to 907 kg (LIC, 2006). This ongoing expansion and intensification has the potential to further increase the contamination of ground and surface waters with nutrients that is often associated with intensive dairying (e.g., Selvarajah *et al.*, 1994; Ledgard *et a*l., 1996; Monaghan *et al.*, 2007, Wilcock *et al.*, 2007).

While the water quality of Toenepi Stream had been comprehensively investigated since 1995 (Wilcock *et al.*, 2006), little was known about the groundwater quality in this catchment. In 2002 we installed 34 shallow groundwater monitoring wells that are predominantly only 2-3 m deep. We focused on shallow groundwater, as that was expected to better reflect the most recent land-use intensity rather than the deeper groundwater. This approach differs from most groundwater studies in New Zealand, as most of the latter are based on the sampling of existing production or domestic wells, most of which are dozens of metres deep and located in reasonably high-producing aquifers (e.g., Selvarajah *et al.*, 1994; Rosen, 2001; Hadfield *et al.*, 2001; Hanson, 2002; Kensington *et al.*, 2004; Morgenstern *et al.*, 2004).

From the beginning, our monitoring results showed very low nitrate concentrations in shallow groundwater relative to the land-use intensity in the Toenepi catchment. As high nitrate reduction rates had previously been reported for lowlands and riparian areas (e.g., Trudell *et al.*, 1986; Martin *et al.*, 1999), we concomitantly started investigating the hypothesis that substantial nitrate reduction might be occurring in the vadose zone–aquifer continuum in this rolling downlands catchment. We define here vadose zone as the variably saturated zone between the ground surface and the permanently saturated zone.

Nitrate reduction has often been reported to occur in the root zone of soils (e.g., Luo *et al.*, 1998; Ledgard *et al.*, 1999), but can also occur deeper in the vadose zone (e.g., Jarvis and Hatch, 1994; Clough *et al.*, 1999; Barkle *et al.*, 2007). Since the 1970s, it also has become evident that nitrate can also be reduced in the aquifer, provided sufficient electron donors are available (e.g., Trudell *et al.*, 1986; Hiscock *et al.*, 1991; Korom, 1992; Appelo and Postma, 2005). Soils featuring prolonged wetness are particularly conducive for nitrate reduction, as they typically provide restricted O_2 availability and sufficient electron donors (e.g., Well *et al.*, 2005). Prolonged wetness may be caused by a slowly permeable layer within the soil profile (e.g., perch-gley soils) or by a groundwater table (e.g., gley and peat soils).

Depending on the redox status of the vadose zone–aquifer continuum and its composition (e.g., organic matter and FeS_2 contents), several microbially catalysed or abiotic processes can result in the reduction of nitrate leached from the root zone (Korom, 1992; Stumm and Morgan, 1996; Appelo and Postma, 2005; Burgin and Hamilton, 2007). While some processes can occur at low rates abiotically, significant nitrate reduction rates generally require microbial catalysis (e.g., Appelo and Postma, 2005). Abiotic reduction of nitrate has particularly been reported to occur in the presence of minerals containing Fe^{2+} in their structure. Appelo and Postma (2005) noted that these processes, which can reduce nitrate either to N_2 or to NH_4, are probably most important in fine-grained sediments with slow groundwater transport rates.

Heterotrophic denitrification, i.e., the dissimilatory reduction of nitrate (NO_3^-) and nitrite (NO_2^-) to gaseous nitrogen forms (NO, N_2O, and N_2), occurs under mildly reducing conditions when dissolved oxygen (DO) becomes limited and facultative microbes switch to using nitrate (and nitrite) as alternative electron acceptors during the decomposition of organic matter (e.g., Paul and Clark, 1989; see Eq. 2). The potential for heterotrophic denitrification is restricted by the availability of organic carbon. Korom (1992) reports that, as a rule of thumb, one unit mass of organic carbon typically can reduce less than one unit mass of NO_3-N. Substantial heterotrophic denitrification in aquifers has been observed particularly under shallow water table conditions, where short vadose zone travel times result in sufficient input of DOC from root exudates and from decomposition of plant residues and soil organic matter into the aquifer (e.g., Hiscock *et al.*, 1991; Korom, 1992, Starr and Gillham, 1993; Davis *et al.*, 2007). In contrast, at sites with a groundwater table deeper than 2-3 m, most DOC is mineralised aerobically in the vadose zone (e.g., Starr and Gillham, 1993), resulting in groundwater DOC concentrations of typically < 2 mg L^{-1}. Any heterotrophic denitrification occurring in deeper aquifers is considered to be fuelled by typically small amounts of resident particulate organic matter in the aquifer material (e.g., Starr and Gillham, 1993).

Dissimilatory nitrate reduction to ammonium is another nitrate reduction process involving organic matter decomposition (e.g., Korom, 1992; Paul and Clark, 1989; Burgin and Hamilton, 2007). It has traditionally been thought to occur only in highly reducing environments capable of maintaining sustained anaerobic metabolism (anaerobic sludge, anoxic sediments, rumen), but has more recently also been reported for tropical forest soils (Silver *et al.*, 2001). Tiedje *et al.* (1982) hypothesised that dissimilatory nitrate reduction to ammonium is favoured when nitrate supplies are limiting, while denitrification is favoured when carbon supplies are limiting.

Autotrophic denitrification can occur when nitrate leaches into an environment that is more strongly reduced and contains reduced forms of manganese (Mn^{2+}), iron (Fe^{2+}), or sulphur (S^{2-}) that autotrophic bacteria oxidise to derive their energy requirements (see e.g. Eq. 8 below).

The development of reducing conditions in the aquifer is essentially determined by the relative rate of consumption and replenishment of dissolved oxygen. Replenishment from the atmosphere strongly depends on the depth, porosity and water content of the vadose zone, as the O_2 diffusion coefficient in water is approx. 10^4 times lower than in air. If aerobic decomposition of organic matter (Eq. 1) becomes limited due to decreasing oxygen levels, bacteria can use a series of other electron acceptors instead of O_2 for further decomposition of organic matter (Eqs. 3 -5). In thermodynamic equilibrium, these processes would strictly follow the order NO_3^- reduction (heterotrophic denitrification), closely followed by Mn^{4+} reduction, then Fe^{3+} reduction, and finally almost simultaneously SO_4^{2-} reduction and methane fermentation (Stumm and Morgan, 1996). However, thermodynamic equilibrium does not normally exist in natural systems and the following redox reactions can thus occur concurrently (e.g., Korom, 1992):

Aerobic decomposition

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \quad (1)$$

Heterotrophic denitrification

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + H_2CO_3 + 2H_2O \quad (2)$$

Manganese (IV) reduction

$$CH_2O + 2MnO_2 + 3H^+ \rightarrow 2Mn^{2+} + HCO_3^- + 2H_2O \quad (3)$$

Ferric iron (III) reduction

$$CH_2O + 4Fe(OH)_3 + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 10H_2O \quad (4)$$

Sulfate reduction

$$CH_2O + ½\ SO_4^{2-} \rightarrow ½\ HS^- + HCO_3^- + ½\ H^+ \quad (5)$$

Methane fermentation

$$2CH_2O + H_2O \rightarrow CH_4 + HCO_3^- + H^+ \quad (6)$$

As mentioned, besides organic matter, pyrite (FeS_2) is the other important solid phase electron donor for nitrate reduction (Hiscock *et al.*, 1991; Appelo and Postma, 2005). Pyrite can be found in aquifers, finely dispersed in clayey sediments formed under anaerobic conditions, and in dark-coloured zones of reductimorphic soils. In the presence of pyrite, autotrophic bacteria can catalyse reactions in which nitrate is reduced directly by pyrite (Eq. 7) as well as by the ferrous iron (Fe^{2+}) resulting from the sulphide oxidation (Eq. 8):

Sulfide oxidation

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 5Fe^{2+} + 10SO_4^{2-} + 2H_2O \quad (7)$$

Ferrous iron oxidation

$$5Fe^{2+} + NO_3^- + 7H_2O \rightarrow 5FeOOH + ½\ N_2 + 9H^+ \quad (8)$$

Ferrous iron (Fe^{2+}) can thus result from sulphide oxidation (Eq. 7) or from reductive dissolution of ferric iron (Fe^{3+}) in iron oxides, provided there is an abundant supply of organic matter (Eq. 4). The latter mechanism explains the high concentrations of Fe^{2+} typically found under peat (e.g., on the lower Hauraki Plains). The potential for autotrophic denitrification to occur in New Zealand groundwaters is demonstrated by the concentrations of dissolved Fe and Mn documented in an analysis of groundwater data from 15 local government bodies and the National Groundwater Monitoring Programme (Daughney, 2003). Apart from groundwater affected by point-source pollution (e.g., land-fill leachates), many groundwaters never reach the stage of sulphate reduction or even methane production (Appelo and Postma, 2005).

The following (or similar) groundwater parameter concentrations have previously been used as trigger values indicating reducing conditions: Mn^{2+} > 0.25 mg L^{-1}, Fe^{2+} > 0.10 mg L^{-1} and NH_4-N > 0.10 mg L^{-1} (e.g., Selverajah *et al.*, 1994; Rosen, 2001; Hadfield *et al.*, 2001; Morgenstern *et al.*, 2004). Any DO concentration below the O_2 solubility in water (10. 1 mg L^{-1} at 15°C and 1013 hPa) indicates a depletion of O_2, generally due to aerobic decomposition of organic matter, while heterotrophic denitrification is considered to proceed at concentrations of < 2 mg L^{-1} (Gillham and Cherry, 1978, as cited in Korom, 1992). Detectable concentrations of the rather unstable intermediate nitrite can indicate current denitrification activity, but it can also be produced during nitrification (Firestone and Davidson, 1989; Appelo and Postma, 2005). NH_4-N concentrations greater than approx. 0.10 mg L^{-1}, particularly if found together with enhanced dissolved Fe and Mn, can indicate reducing conditions (Rosen, 2001). Enhanced NH_4-N concentrations can result from restricted nitrification due to O_2 deficiency (Rosen, 2001) or under highly reducing conditions from dissimilatory nitrate reduction (e.g., Paul and Clark, 1989; Korom, 1992). However, enhanced groundwater NH_4-N concentrations can also occur under aerobic conditions if large amounts of ammonium (e.g., from urine patches or effluent irrigation) are rapidly leached into shallow groundwater from soils prone to bypass flow. Consequently, all these indicators of reducing conditions should only be interpreted collectively, as individual indicators may be affected by factors not related to the redox status (Chapelle *et al.*, 1995; Appelo and Postma, 2005).

This paper focuses on monitoring work undertaken between December 2002 and December 2005 to investigate the temporal and spatial variation of nitrate concentrations in shallow groundwater in a dairying catch-

ment with intensive land use. Additional vadose zone and groundwater analyses were undertaken (2004–2007) to investigate the hypothesis that nitrate reduction in the vadose zone–aquifer continuum was responsible for the unexpectedly low groundwater nitrate concentrations measured in the catchment.

Catchment characteristics

Physical setting

The Toenepi catchment is situated in a long-established dairying area near Morrinsville, Waikato, in the North Island of New Zealand. The elevation of the 15.1 km^2 large catchment ranges from approx. 40 to 130 m above mean sea level, and it lies in the transition zone between the central alluvial plains of the Hauraki basin and the western uplands (Fig. 1). The catchment comprises low rolling downlands in the headwater area and along the southwestern and northeastern boundaries, while the central corridor alongside Toenepi Stream and the catchment outlet in the northwest form part of the alluvial plains (Fig. 2).

The downlands are characterised by 1-2 m Holocene to late Pleistocene volcanic ash beds of silt loam to fine sandy loam textures,

Figure 2 – Topographic map of the Toenepi catchment. Groundwater monitoring well transects shown as existing in 2005.

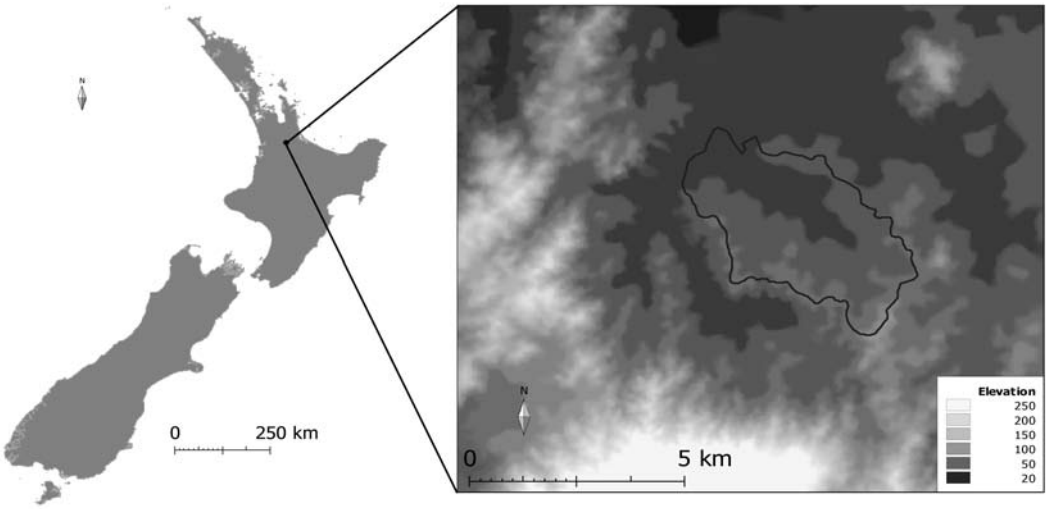

Figure 1 – Physical setting of the Toenepi catchment.

overlying older strongly argillised Pleistocene volcanic ash beds ('Hamilton Ash'). The younger ash beds contain allophanic clays and volcanic glass and are friable under field conditions. The older ash deposits consist of beds of sticky and plastic halloysite and allophane clays. The alluvial plains have developed on Pleistocene rhyolitic alluvium with a varying thin cover of Holocene rhyolitic and andesitic volcanic ash. The subsoils are dominantly sandy and consist of cross-bedded sands and gravelly sands with occasional lenses of peat, silts and clays (Wilson, 1980).

In the 1:50000 Piako County map by Wilson (1980), three soil groups, differing distinctly in their hydrological characteristics, are shown for the catchment:

Topehaehae soils (Typic Recent Gley Soils) have developed from recent alluvium on river flood plains and are characterized by a naturally high water table. Mole and tile drainage is typically installed to enable year-round grazing on these poorly drained soils. The distribution of Topehaehae soils is restricted to typically narrow bands in the lowest lying areas adjacent to Toenepi stream and its small tributaries, covering approx. 13% of the catchment area (Wilson, 1980). A subsequent survey of the distribution of Topehaehae soils at a higher spatial resolution concluded that Topehaehae soils cover approx. 9% of the catchment area (Singleton and Addison, 1996).

The very similar Kereone and Kiwitahi soils (Typic Orthic Allophanic Soils) have both developed on the younger ash beds. These allophanic soils are well drained due to their good soil physical properties (e.g., high porosity and aggregate stability). They occur on easy rolling to rolling slopes and on freely drained levees of the plains (Wilson, 1980) and account for approx. 47% of the soils in the catchment.

Morrinsville soils (Typic Orthic Granular Soils) make up the remaining approx. 40% of the catchment. They have developed on the more weathered, clay textured, strongly argillised 'Hamilton Ash' and are characterised by their clay-illuvial B horizon. They are consequently less well drained than the former group. Morrinsville soils occur predominantly on rolling slopes where the younger ash was eroded (Wilson, 1980).

Land use

Land-use data were obtained through a farm survey conducted in 2003 (McGowan, AgResearch, pers. communication, 2005). Of the 24 farms in the catchment, 18 were dairy farms, with the balance being dry-stock farms and a horse stud. The average stocking rate of all dairying land was 3.1 cows ha^{-1}, ranging from 2.5 to 4.3 cows ha^{-1} on individual farms. Annual N fertiliser application on the dairy farms varied from 28 to 227 kg N ha^{-1}, resulting in an overall average of 99 kg N ha^{-1} for the dairying land. Additional nutrients were imported into the catchment through supplementary feed, mainly pasture and maize silage. Average milk solids production was 1060 kg ha^{-1} yr^{-1}, which was approx. 12% above the regional average (LIC, 2004).

Climate

Meteorological data have been recorded in the catchment as part of this study since October 2002. Annual rainfall between 2003 and 2006 ranged from 1177 to 1379 mm, while annual potential evapotranspiration (PET) ranged from 842 to 917 mm, resulting in an annual rainfall surplus of 260 to 537 mm.

Methods

Groundwater monitoring transects

December 2002–December 2004

Seven transects, consisting of 4 to 6 wells each, were installed in 2002 perpendicular to Toenepi Stream or one of its small tributaries (Fig. 2). To ensure representative sampling

of the shallow groundwater, these transects were distributed in the catchment, taking the different soil types into account (Fig. 3). Naturally poorly drained Topehaehae Gley soils dominate along the transects T2, T9 and T17, and were mapped for some well locations close to surface waters in several other transects (Fig. 3). While most transects go across different soil types, the transects T16 and T18 lie almost exclusively in areas mapped as well-drained Kiwitahi soils (Fig. 3e). It should be noted that the soil type found at a particular site during well installation can differ from the soil type shown on the available soil map (Singleton and Addison, 1996), which is based on the 1:50000 map by Wilson (1980). In contrast to the soil map (Fig. 3), Topehaehae soil was identified at well sites T1-6, T2-1, T17-6, and T23-2. Well site T9-1 was considered to have Kereone rather than Topehaehae soil. Individual wells are denoted by Tx-y, with x being the transect number and y the well number within that transect.

Wells made of slotted PVC pipe (17.7 mm internal diameter, slot width 0.45 mm) were installed directly into tightly fitting holes created by a 25 mm diameter direct push-probe drilling system (Geonor, Norway). With the exception of wells T2-3 (3.8 m), T18-4 (4.3 m), and T23-1 (5.0 m), all wells were installed to a depth of 2.5 to 3.0 m below the ground surface. The wells were subsequently developed by repeatedly pumping them dry until the water became clear. These 34 wells were sampled at monthly intervals from December 2002 until December 2004.

January 2005–December 2005

Five of the transects were extended in length in December 2004 by installing a total of 9 additional 'distal' wells further away from Toenepi Stream or its tributary at the transect in question (T1-7, T1-8, T9-0, T16-7, T16-8, T17-6, T17-7, T18-5, T18-6; see Fig. 3). These new wells (internal diameter 40 mm, depth 2.1 to 4.2 m) were installed using a 70 mm hand auger and had drainage metal filled into the annular gap. A bentonite plug on top of the drainage metal sealed the wells against the surface. These wells were monitored during 2005, together with a selection of the wells previously monitored.

May 2007 well sampling campaign

A comprehensive set of field and laboratory parameters (see below) was analysed on samples from 18 wells in May 2007 to evaluate the redox status of shallow groundwater in the catchment. Twelve of the sampled wells had previously formed part of the monitoring programme (2002–2005). Changes of the analysed parameters with increasing depth below the water table were investigated by sampling 6 additional wells (inner diameter 50 mm) that belonged to three well clusters established in 2006. These well clusters were located at sites that represent Kereone (Ke), Morrinsville (Mv), and Topehaehae (To) soils (Fig. 3c, e). Note that after comprehensive field investigations, the Kereone well cluster was established at a site that is shown on the soil map as boundary between Topehaehae and Morrinsville soils (Fig. 3c). These wells were screened for the bottom 50 cm of the well. Well depths were 470 cm for Ke-1 and Mv-1, 410 cm for Ke-3 and Mv-3, 170 cm for To-3 and 390 cm for To-1.

Monitoring of vadose zone pore water NO_3-N concentrations

The dynamics of NO_3-N in the vadose zone was monitored at a naturally poorly drained Topehaehae site (NP1, Fig. 3e) and a well-drained Kereone site (NP3, Fig. 3c) from July 2004 until October 2005. Ceramic suction cup samplers (Type 653X02-B01M3, Soilmoisture Equipment Corp., USA) were installed in six replicates in multiple depths below the ground surface (30, 60, 90, 120 cm; also 150 cm at the Kereone site). The samplers were installed horizontally from

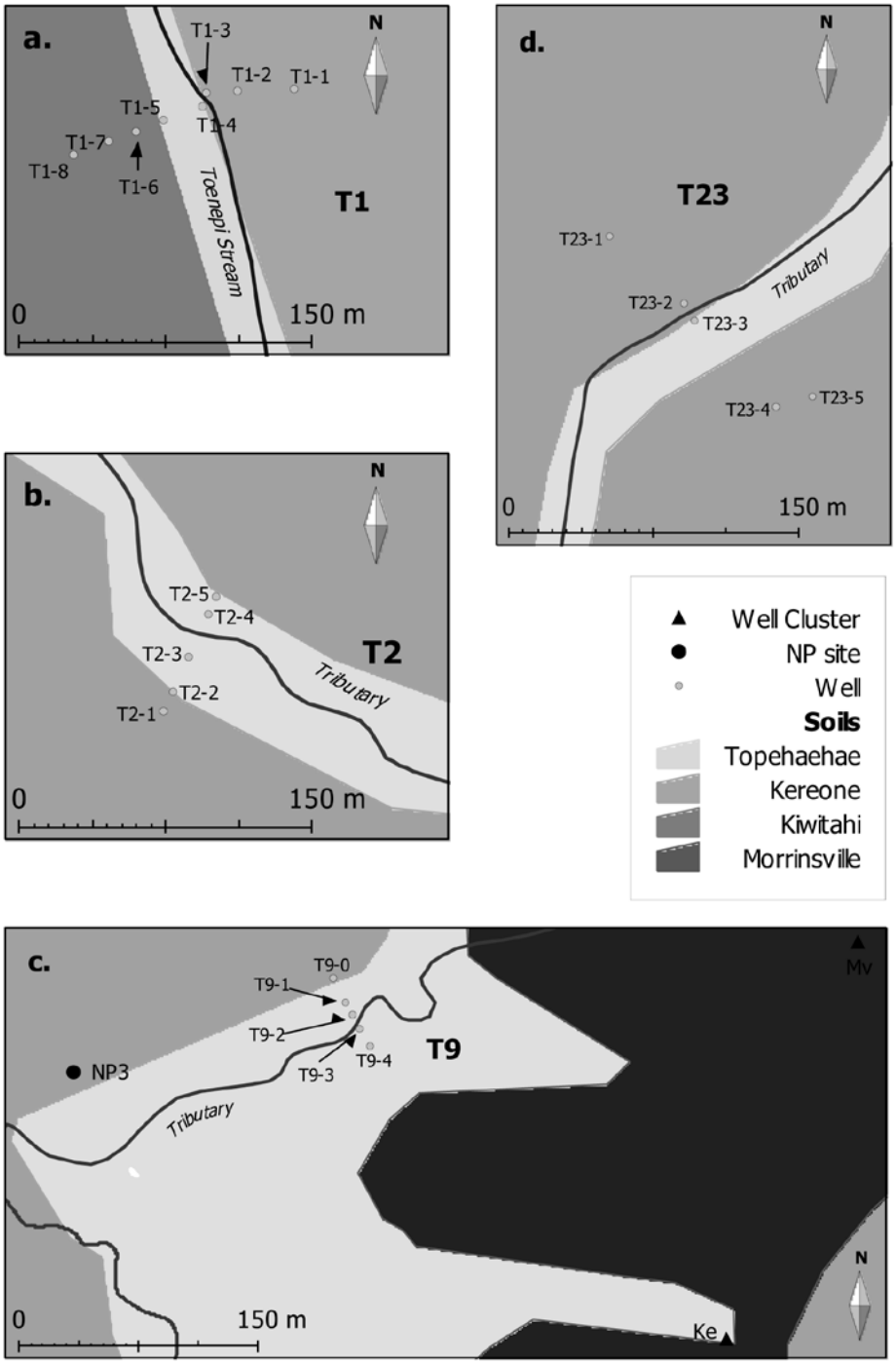

Figure 3a-d – Soil types at groundwater monitoring well transects T1, T2, T9 and T23 (Singleton and Addison, 1996). Kereone vadose zone monitoring site (NP3) and well cluster (Ke and Mv) are also shown in Figure 3c.

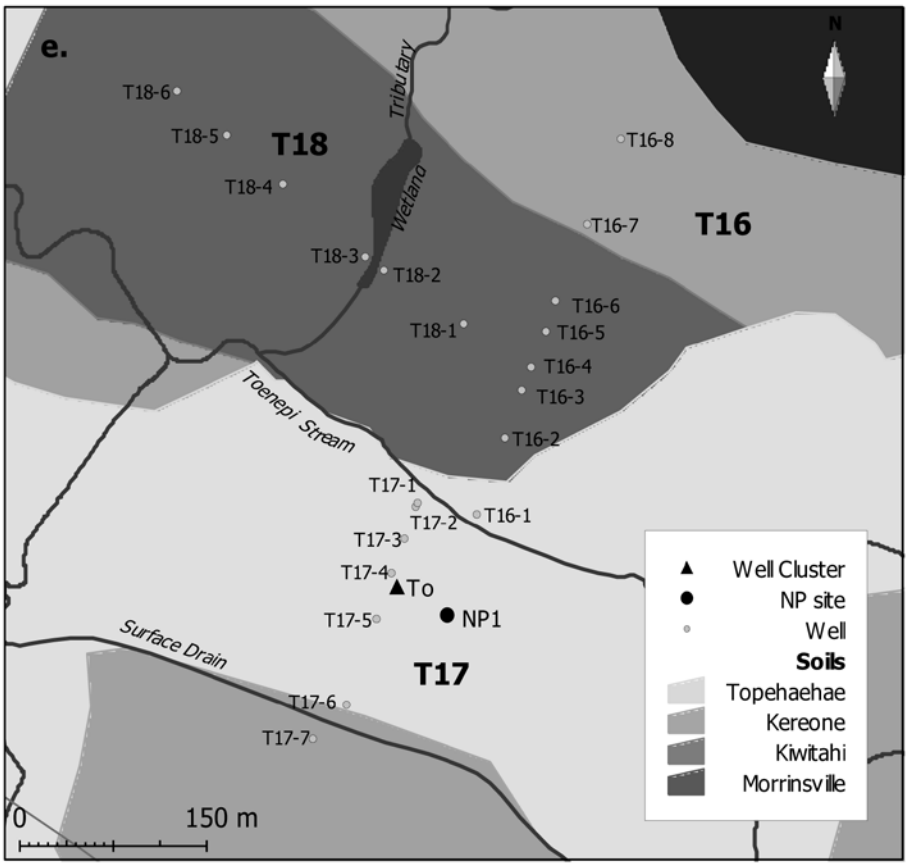

Figure 3e – Soil types at the groundwater monitoring well transects T16, T17, and T18 (Singleton and Addison, 1996). Topehaehae vadose zone monitoring site (NP1) and well cluster (To) also shown.

soil pits into the surrounding vadose zone. A suction of 30 kPa was applied using the 'falling head method' and the accumulated sample was collected on the next day through tubing routed to the ground surface (Wilson *et al.*, 1995).

Collection of groundwater samples (2002–2005)

Due to the generally slow recharge into the purged monitoring wells, sampling of these wells was a two-day procedure. Water levels were measured on the first day using an acoustic water level meter. Wells were subsequently purged by pumping the wells dry, which typically equated to less than two times the volume of the standing water column. A 60 mL water sample was collected on the second day. Samples were chilled in the field and either delivered directly to the laboratory or stored in a freezer prior to analysis.

Laboratory analysis of vadose zone pore water and groundwater samples

December 2002 to December 2005

Samples were analysed for ammonia N (the sum of NH_4-N and NH_3) and total oxidised nitrogen (NO_x-N). The former is in the following denoted NH_4-N, as NH_3 accounts

for less than 0.1% at pH < 6.5. NO_x-N is in the following denoted nitrate nitrogen (NO_3-N), as based on literature (e.g., Close *et al.*, 2001; Kensington *et al.*, 2004) and our own results (see below) any possibly occurring nitrite nitrogen (NO_2-N) was considered negligible.

May 2007 well sampling campaign

In addition to NH_4-N and NO_3-N, nitrite nitrogen (NO_2-N), dissolved Kjeldahl nitrogen (DKN), dissolved inorganic carbon (DIC), dissolved total carbon (DTC), and dissolved Fe and Mn were measured on 18 groundwater samples collected in May 2007. The concentration of organic nitrogen was calculated as N_{org} = TKN – NH_4-N and the concentration of dissolved organic carbon as DOC = DTC – DIC. The samples for the analysis of dissolved Fe and Mn were filtered in the field using a 0.45 µm cellulose acetate syringe-tip filter into a nitric acid preserved container. This procedure ensures that dissolved Fe and Mn can be used synonymously with Fe^{2+} and Mn^{2+}, respectively. Detection limits were 0.002 mg L^{-1} for NO_3-N and NO_2-N, 0.01 mg L^{-1} for NH_4-N, 0.02 mg L^{-1} for dissolved Fe, 0.0005 mg L^{-1} for dissolved Mn, 0.1 mg L^{-1} for DKN, and 0.5 mg L^{-1} for DOC (Hill laboratories, Hamilton).

Field analysis of groundwater samples in May 2007

At the May 2007 well sampling campaign, dissolved oxygen (DO), pH and electrical conductivity were measured on site at 18 wells directly prior to sampling for the laboratory analyses outlined above. The field analyses were undertaken using a TPS 90-FLMV field lab (TPS, Springwood, Australia). A well sampling procedure based on the guidelines and stability criteria of the 'National Protocol for State of the Environment Groundwater Sampling in New Zealand' (Daughney *et al.*, 2006) was used. As outlined earlier, the requirement to remove three times the volume of water in the well directly prior to sampling for laboratory analysis could frequently not be met, as the recharge of shallow groundwater into the wells was too low to achieve the necessary volumes within a feasible timeframe. Most of our wells were therefore pumped dry on the day prior to sampling to provide sufficient time for water level recovery and particular attention was given on the following day to the stability of the field parameters measured prior to sampling for laboratory analysis. To demonstrate the stability of these field parameters, we report the arithmetic mean and standard deviation of 17 values recorded in 30 second intervals during the last 8 minutes of purging prior to the commencement of sampling for laboratory analysis. Supporting this procedure is the conclusion by Daughney *et al.* (2007) that it is more appropriate to assess the adequacy of purging based on the stabilisation of field parameters than on the total volume of water that has been purged.

OVERSEER® leachate concentration estimates

As the nutrient budget model OVERSEER® is increasingly being used to evaluate the effect of nutrient losses from agricultural land use on the receiving environment (e.g., Waikato Regional Plan Variation 5 – Lake Taupo Catchment; Wheeler *et al.*, 2006), the groundwater NO_3-N concentrations measured between December 2002 and December 2004 were compared with OVERSEER® results. The OVERSEER® results were calculated by AgResearch (Costall, pers. communication, 2005), based on input data from the 2003 farm survey (McGowan, AgResearch, pers. communication, 2005). Detailed information on the OVERSEER® model is available at the web site http://www.agresearch.co.nz/overseerweb/environment.aspx and in Wheeler *et al.*, (2006).

Results and discussion

Nitrate and ammonium nitrogen in shallow groundwater

Monitoring results

December 2002–December 2004

NO_3-N concentrations were predominantly very low, with 80% of the 843 analysed samples lying below the ANZECC trigger value for eutrophication of surface water (0.44 mg NO_3-N L^{-1}; ANZECC, 2000). Only 3% of all samples were above the WHO drinking water guideline (11.3 mg NO_3-N L^{-1}). These elevated samples (11-45 mg NO_3-N L^{-1}) all came from well T23-1. Given that this well had concentrations substantially higher than any other well in the catchment and OVERSEER® results (see below), we assume that it was affected by an unidentified point source (Table 1). The overall mean and median of all samples analysed from the 34 wells were 1.47 and 0.03 mg NO_3-N L^{-1}, respectively. The overall mean decreased to only 0.53 mg NO_3-N L^{-1} when data from the outlier well T23-1 was excluded from the analysis (Table 1).

NO_3-N concentrations in four well transects (T2, T17, T1, T16) were almost always below the trigger value for eutrophication, while concentrations in T9 and T23 were below the trigger value in more than 50% of all samples (Table 1). Only concentrations in T18 exceeded the trigger value in the majority of samples. Occasional NH_4-N peaks and greenish-brown colour of groundwater samples indicated that irrigation of dairy farm effluent was the reason for the relatively high NO_3-N concentrations observed in that transect. The lowest NO_3-N concentrations were measured in the only transect (T2) with exclusively drystock farming upslope of the transect. However, very similar concentrations were also found in transects on farms with medium- to high-intensity dairy farming (e.g., T17 and T1). Additionally, quite different nitrate N concentrations were found in the neighbouring transects T16 and T18, which are located in the same effluent irrigation block. These observations suggest that factors other than land-use intensity are responsible for the spatial variation of the generally very low nitrate concentrations found in the transects.

While low groundwater nitrate concentrations were also found under Kereone/Kiwitahi soils (e.g., T16-2 to T16-5, T23-4 and T23-5), most data sets showing consistently very low concentrations came from sites that, based on the soil map and/or field evidence, were considered to be Topehaehae sites (e.g., T1-4 to T1-6, T2-2 to T2-4, T17). Heterotrophic denitrification is the most likely reason for these particularly low nitrate concentrations, as these poorly drained Gley soils are characterised by high water contents and thus poor aeration close to the root zone of the pasture, where organic matter is abundant and which is the microbially most active part of the vadose zone.

Following Starr and Gillham (1993), the similarly low groundwater nitrate concentrations measured at some sites under well-drained Kereone/Kiwitahi soils could be the result of denitrification occurring in the shallow aquifer. All but one of the 34 wells had a mean water table of less than 2.5 m, and 13 had a mean water table of less than 1 m below ground surface (data not shown). Consequently, sufficient DOC might leach into the aquifer to sustain heterotrophic denitrification of any NO_3-N not already reduced in the vadose zone. To investigate this hypothesis, a comprehensive well sampling campaign was undertaken in May 2007 (see below).

It is evident in the data presented in Table 1 that NO_3-N concentrations in a few wells varied considerably over the 25-month monitoring period (T23-1, T18-4,

Table 1 – Summary statistics for nitrate nitrogen (NO_3-N) concentrations measured in shallow groundwater at 25 sampling dates between December 2002 and December 2004. All concentrations in mg L^{-1}; s = standard deviation.

	Individual well					Well transect	
	Mean	**s**	**Median**	**Min**	**Max**	**Mean**	**Median**
T1-1	0.20	0.16	0.17	0.00	0.54	0.09	0.01
T1-2	0.25	0.10	0.25	0.04	0.42		
T1-3	0.03	0.05	0.01	0.00	0.19		
T1-4	0.01	0.04	0.00	0.00	0.18		
T1-5	0.01	0.04	0.00	0.00	0.19		
T1-6	0.01	0.04	0.00	0.00	0.19		
T2-1	0.04	0.06	0.02	0.00	0.21	0.03	0.01
T2-2	0.02	0.04	0.00	0.00	0.18		
T2-3	0.02	0.05	0.00	0.00	0.18		
T2-4	0.03	0.05	0.00	0.00	0.18		
T2-5	0.04	0.07	0.01	0.00	0.24		
T9-1	2.91	1.07	3.11	0.64	5.00	0.88	0.17
T9-2	0.35	0.87	0.03	0.00	3.53		
T9-3	0.02	0.04	0.00	0.00	0.19		
T9-4	0.25	0.24	0.21	0.00	0.92		
T16-1	0.03	0.05	0.00	0.00	0.18	0.22	0.03
T16-2	0.09	0.11	0.07	0.00	0.47		
T16-3	0.06	0.10	0.02	0.00	0.43		
T16-5	0.01	0.04	0.00	0.00	0.19		
T16-6	0.86	0.56	0.78	0.02	1.83		
T17-1	0.02	0.04	0.00	0.00	0.18	0.06	0.00
T17-2	0.05	0.08	0.01	0.00	0.23		
T17-3	0.09	0.28	0.00	0.00	1.20		
T17-4	0.03	0.12	0.00	0.00	0.58		
T17-5	0.12	0.12	0.08	0.00	0.44		
T18-1	1.37	0.54	1.28	0.27	3.31	2.70	1.39
T18-2	3.26	2.94	2.34	0.01	9.78		
T18-3	0.13	0.18	0.05	0.00	0.65		
T18-4	5.95	1.95	5.86	1.02	10.48		
T23-1	33.21	7.49	32.07	11.24	45.35	6.88	0.20
T23-2	0.58	1.09	0.15	0.00	3.87		
T23-3	0.05	0.11	0.01	0.00	0.51		
T23-4	0.38	0.18	0.39	0.00	0.73		
T23-5	0.17	0.17	0.11	0.00	0.81		
All wells (n = 34)	1.47	5.77	0.03	0.00	45.35		
T23-1 excluded (n = 33)	0.53	1.40	0.03	0.00	10.48		

T18-2 and T9-1), while in 59% of all wells the range of measured concentrations did not exceed 0.5 mg L^{-1}. The wells with more variable concentrations generally also had higher mean concentrations than those wells with more consistent concentrations and were located at well-drained sites. Possible explanations for this observation are discussed below, including the data from the extended transects sampled during 2005.

The vast majority of groundwater samples contained only non-detectable or minute amounts of ammonia nitrogen (NH_4-N). Of the 843 analysed samples, 58% had concentrations below the detection limit (0.01 mg L^{-1}) and 78% below 0.10 mg NH_4-N L^{-1}, a concentration sometimes considered a trigger value indicating reducing conditions (e.g., Rosen, 2001). Enhanced NH_4-N concentrations coincided in most instances with very low NO_3-N concentrations, which is in agreement with the presumption of reducing conditions at these sites at the time of sampling (e.g., T2-4, T9-2, T9-3, T17-4, T17-5, T23-3). In contrast, sporadically occurring NH_4-N peaks (up to 4.1 mg L^{-1} NH_4-N) in wells T18-2 and T18-4 are more likely the result of NH_4-N leaching through the vadose zone after effluent irrigation, as indicated by the sometimes greenish-brown colour of groundwater samples and their concomitantly enhanced NO_3-N concentrations. Of all samples analysed, 98% were below 0.90 mg NH_4-N L^{-1}, which is the 95% protection level from toxicity in surface water (ANZECC, 2000).

In four well transects (T1, T9, T16, T17), the highest NO_3-N concentrations were frequently found in those wells that were located the furthest away from Toenepi Stream or its tributary at the well transect in question (e.g. T9-1, T16-6, T17-5). To ascertain whether higher NO_3-N concentrations exist at a greater distance from the surface waters, additional 'distal' wells were installed in these transects and sampled during 2005.

Monitoring results January–December 2005

The NO_3-N concentrations measured during 2005 confirmed for transects T1, T16, and T17 the expectation of finding the highest concentrations at the distal end(s) of the transect (Table 2). This is where typically better-drained soils were found, even if the mapped soil type remained the same (Fig. 3). No explanation can be offered for the observation that only very low concentrations were found at the most distal well of the T9 transect (T9-0). The extremely high concentrations (up to 111 mg NO_3-N L^{-1}) found at T16-8 are considered to be caused by a second unidentified point source (similar to T23-1 during 2002/04). The NH_4-N concentrations measured in the new distal wells were similar to or lower than those measured in the old wells (data not shown).

To gain a better understanding of the variability of nitrogen concentrations in shallow groundwater underlying an effluent irrigation block, well transect T18 was also extended by two wells (Fig. 3e). The mean NO_3-N concentrations measured in the new wells T18-5 and T18-6 (5.37 and 7.00 mg L^{-1}, respectively) indicated that the range of concentrations previously found in T18-2 and T18-4 was more representative for this part of the effluent block than the lower concentrations found in T18-1 (closest to T16) and particularly T18-3 (Tables 1 and 2). The consistently very low NO_3-N concentrations measured at T18-3 reflect reducing conditions, which presumably result from the vicinity of this well to an extended wetland area (Fig. 3e). The overall groundwater flow direction is towards the catchment outlet in the north-west. Water table data indicate that well T18-3 may receive input from the wetland, while the groundwater with higher concentrations

Table 2 – Summary statistics for nitrate nitrogen (NO_3-N) concentrations measured in shallow groundwater at 16 sampling dates between January and December 2005. All concentrations in mg L^{-1}; s = standard deviation; New 'distal' wells marked '*'.

Well	Mean	s	Median	Min	Max
T1-1	0.23	0.27	0.12	0.00	0.99
T1-4	0.01	0.02	0.01	0.00	0.10
T1-7*	0.20	0.22	0.15	0.00	0.71
T1-8*	1.04	1.48	0.80	0.00	6.16
T9-0*	0.13	0.24	0.01	0.00	0.84
T9-1	2.10	1.26	2.23	0.00	4.26
T9-2	1.17	1.86	0.04	0.00	6.27
T16-1	0.01	0.02	0.01	0.00	0.10
T16-6	1.06	0.66	1.27	0.00	1.80
T16-7*	3.57	2.91	3.96	0.00	9.84
T16-8*	50.35	27.39	48.55	12.40	111.00
T17-1	0.02	0.05	0.00	0.00	0.16
T17-5	0.53	0.88	0.20	0.00	3.43
T17-6*	0.46	0.89	0.11	0.00	2.93
T17-7*	1.40	0.82	1.82	0.00	2.39
T18-3	0.06	0.11	0.04	0.00	0.46
T18-4	8.65	3.04	9.78	3.00	11.80
T18-5*	5.37	3.61	6.24	0.00	13.00
T18-6*	7.00	7.51	4.68	0.00	24.10

sampled at well T18-2 discharges into the wetland (Table 1). The highest of all NH_4-N peaks was observed in well T18-5 in autumn 2005, amounting to 10.8 mg L^{-1} NH_4-N.

Combined monitoring results December 2002–December 2005 for the well transects in the effluent irrigation block

Over the whole monitoring period, quite different NO_3-N concentrations were measured in neighbouring well transects T16 and T18 (Tables 1 and 2), even though both transects were within the same effluent irrigation block, with well-drained Kiwitahi soils (Fig. 3e). Ignoring well T18-3, mean NO_3-N concentrations in the T18 transect were amongst the highest measured in the catchment (1.37–8.65 mg NO_3-N L^{-1}). In contrast, NO_3-N concentrations in wells T16-1 to T16-5 were amongst the lowest, while concentrations in wells T16-6 and T16-7 were moderately enhanced (0.86–3.57 mg NO_3-N L^{-1}). The consistently much lower NO_3-N concentrations at T16 were particularly surprising, as according to the farmer the surrounding paddocks received more effluent than those around T18. While being generally lower, the mean concentrations observed in the T18 wells are not too dissimilar to the long-term average leachate concentration of 9 mg NO_3-N L^{-1} estimated for that effluent irrigation block using the OVERSEER® nutrient budget model (Costall, AgResearch, pers. communication, 2005).

In four of the six wells in T18 (not in T18-1 and T18-3) and in the two distal wells in T16 (T16-6, T16-7) NO_3-N concentrations tended to decrease with increasing depth to the water table (Fig. 4). The remaining wells had consistently low (T18-1) or very low NO_3-N concentrations (T16-1 to T16-5, and T18-3) independent of their water table dynamics. Linear regression equations relating NO_3-N concentrations to the depth to the water table had the highest gradients (25.5 and 6.2 mg NO_3-N m^{-1} water table change) and the highest coefficients of determination (R^2 = 0.59 and 0.61) for wells T18-6 and T18-4, respectively. An increasing groundwater NO_3-N concentration with rising water table demonstrates that there must have been a significant amount of NO_3-N residing in the deeper vadose zone. In contrast, no response of the groundwater NO_3-N concentration to rising water tables would suggest that concentrations in the

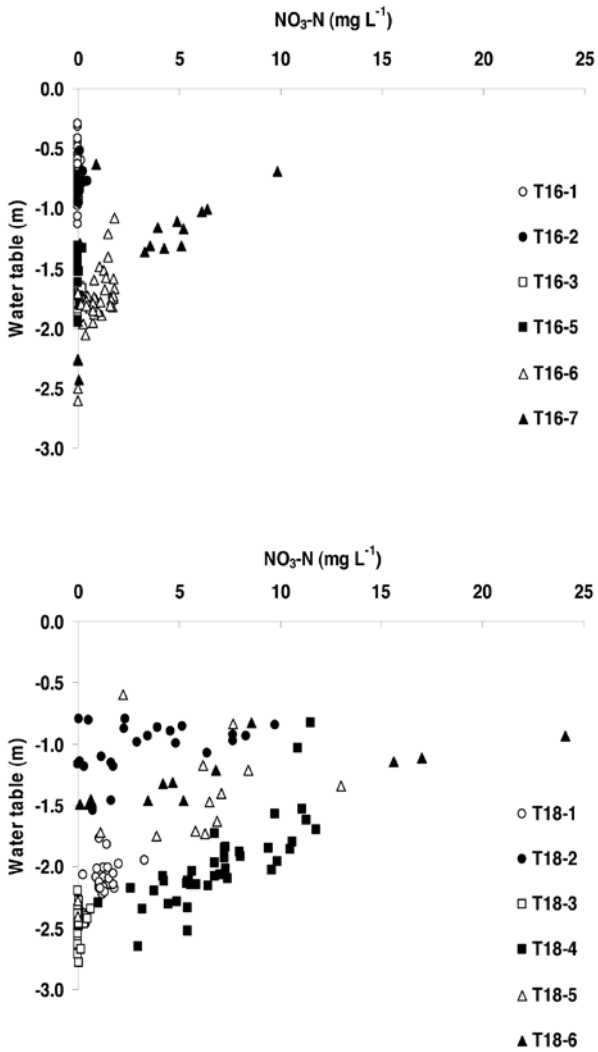

Figure 4 – NO3-N concentrations versus water table depth (in m below ground level) for well transects T16 (top) and T18 (bottom) in the effluent irrigation block (all data from December 2002 to December 2005; outlier well T16-8 omitted).

vadose zone were not higher than the low concentrations measured in the groundwater.

Circumstantial evidence from well drilling supported the hypothesis that reducing conditions below the soil zone may be causing the differences between these two transects. At T16 more material of greyish-white colour (resulting from reductive dissolution of Fe and Mn oxides) was observed deeper in the vadose zone than at T18, where brownish colours prevailed.

For the sites with consistently very low NO_3-N concentrations (T16-1 to T16-5, T18-3) this would suggest that nitrate reduction is occurring in the vadose zone. While nitrate reduction may already be occurring within the soil zone at T16-1 (poorly drained Topehaehae soils), it presumably occurs deeper in the vadose zone at all other sites (well-drained Kiwitahi soils). In contrast, no (or at least substantially less) nitrate reduction appears to occur at the remaining sites where NO_3-N concentrations were generally higher and tended to rise with rising water table (e.g. T16-6, T16-7, T18 wells apart from T18-1 and T18-3).

Comparison of monitoring results with OVERSEER® estimates

The average NO_3-N concentrations in the leachate at the bottom of the root zone estimated using OVERSEER® ranged from 7–11 mg L^{-1} for the dairy farms and was 3 mg L^{-1} for the drystock farm. These estimates are substantially higher than the concentrations measured in the shallow groundwater for 32 out of 34 wells monitored from December 2002 to December 2004 (Table 2). The two exceptions were an outlier well considered to be affected by a point source (T23-1) and one of the wells in transect T18 affected by effluent-irrigation (T18-4). This result was confirmed in 2005, where the new wells installed in the effluent block (T18-5, T18-6) had mean concentrations (5.4 and

7.0 mg NO_3-N L^{-1}, respectively) not much lower than the OVERSEER® estimate of 9 mg L^{-1}. A second outlier well presumably affected by a point source (T16-8) had a mean concentration approx. 4 times higher than the OVERSEER® estimate.

It should be remembered that OVERSEER® estimates are not directly comparable to the groundwater measurements as OVERSEER® estimates the long-term average concentration of the leachate leaving the root zone of the pasture, i.e., in approx. 0.6 m depth. In contrast, the well transect concentrations were measured over a 2-year period in shallow groundwater, with median water tables ranging from 0.7 to 2.1 m below ground surface.

Provided OVERSEER® estimates are realistic for the bottom of the root zone, the significant differences to our monitoring data would support the hypothesis that substantial nitrate reducing processes must be occurring in the deeper part of the vadose zone or in the shallow aquifer.

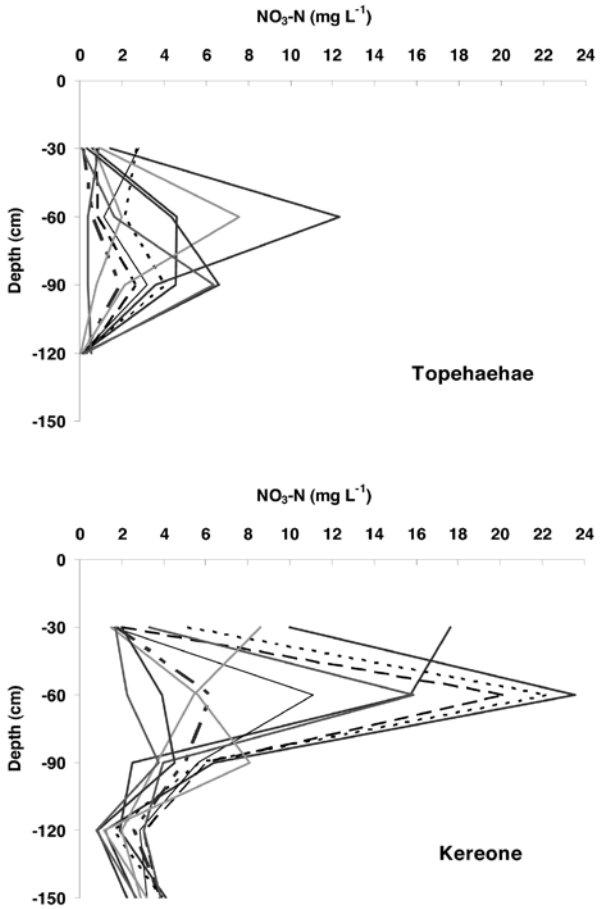

Figure 5 – Vadose zone NO_3-N profiles at a poorly drained Topehaehae site (NP1) and a well-drained Kereone site (NP3). Mean of 6 replicates shown for 11 sampling dates between July 2004 and October 2005.

Monitoring of vadose zone pore water NO_3-N concentrations

NO_3-N concentrations varied substantially between the six replicate samples per depth, with average standard deviations ranging from 0.2 to 4.2 mg L^{-1} at the Topehaehae site and 1.3 to 17.6 mg L^{-1} at the Kereone site (Fig. 5). Average NO_3-N concentrations in 30 cm and 60 cm depth were predominantly substantially lower at the Topehaehae site as compared to the Kereone site (Fig. 5). Apart from possibly slightly lower land-use intensity, denitrification occurring within the root zone of the pasture is one of the possible reasons for the low NO_3-N concentrations at this Gley soil site. The water table at the site is generally shallow (summer minimum approx. 150 cm) and very dynamic during winter and spring (quickly varying between approx. 90 and 40 cm in response to rain). The decreases in NO_3-N concentrations, observed at some sampling dates between 60 cm and 90 cm depth, and always between 90 cm and 120 cm depth, could therefore be caused by dilution with groundwater of lower concentration, as well as by denitrification.

In contrast, dilution can be excluded as possible mechanism explaining the substantially decreasing NO_3-N concentrations between 60 cm and 120 cm depth in the Kereone profile (Fig. 5), as the water table was predominantly deeper than 140 cm depth.

Examination of the Kereone vadose zone profile in an excavated pit confirmed denitrification occurring below the root zone as the most likely reason for these decreasing NO_3-N concentrations. While the top 80 cm of the profile consisted of well-drained reddish-brown soil, redox-mottling resulting from periodically occurring reducing conditions was evident from approx. 80–130 cm depth. The predominantly greyish colours of the clay found below 130 cm depth indicated more persistent reducing conditions due to longer-lasting saturation.

These results support the hypothesis that reducing conditions occurring below the soil zone, particularly in the strongly argillised older volcanic ash beds underlying the soils and their parent material, could explain the observation that very low groundwater NO_3-N concentrations were found even in transects where the soils were mapped (to approx. 1 m depth) as well-drained Kiwitahi or Kereone soils.

May 2007 well sampling campaign

As found during 2002–2005, most wells sampled in May 2007 showed very low NO_3-N concentrations (Table 3). A notable exception was well T16-8 (49.7 mg NO_3-N L^{-1}) that already had been suspected during 2005 as being affected by an unidentified point source.

Evidence of reducing conditions

Apart from the electrical conductivity in well T16-8, all field parameters were very stable and well within published stability criteria, demonstrating that the wells had been sufficiently purged. The combination of the indicators for reducing conditions analysed demonstrates that some degree of reducing conditions existed in all but a few groundwater samples (Table 3). Concentrations of dissolved oxygen (DO) were below 2 mg L^{-1} in 10 of the 18 groundwaters, indicating that oxygen was sufficiently depleted for heterotrophic denitrification to occur. The range of DO concentrations observed in our wells (Table 3) was similar to that found in shallow groundwater of an American lowland catchment with fine-grained soils and geologic materials where substantial denitrification was observed (Mehnert *et al.*, 2007). Only 4 groundwaters exceeded the trigger value indicating Mn reduction (0.25 mg L^{-1}), but twelve groundwaters had dissolved Fe concentrations above the trigger value for Fe reduction (0.10 mg L^{-1}), demonstrating potential for autotrophic denitrification to occur. Only well Ke-1 exceeded an NH_4-N concentration of 0.15 mg L^{-1}, which demonstrates that dissimilatory nitrate reduction to ammonium and abiotic nitrate reduction to ammonium were not relevant pathways for nitrate reduction in the shallow groundwater. The predominantly low NO_3-N concentrations measured are therefore considered to be caused by heterotrophic and/or autotrophic denitrification.

In our data set, no NO_3-N concentrations greater than 0.20 mg L^{-1} were observed if the concentrations of dissolved Mn and Fe were greater than 0.04 and 0.07 mg L^{-1}, respectively, or the concentration of DO was smaller than approx. 3.5 mg L^{-1} (Fig. 6). However, due to the small sample size (n=18) and one outlier in the dissolved Fe data, these boundaries should be considered indicative only. Although boundaries may vary, the general pattern of mutual exclusivity of high NO_3-N and high dissolved Fe concentrations, which results from autotrophic denitrification, has commonly been found in

Table 3 – Field and laboratory analyses of the May 2007 well sampling campaign. DO, dissolved oxygen; EC, electrical conductivity; Diss. Fe and Mn, dissolved iron and manganese, respectively. DON, dissolved organic nitrogen; DOC and DIC, dissolved organic and dissolved inorganic carbon, respectively. WL, water level (in cm below ground surface). Arithmetic mean and standard deviation (s) of 17 consecutive measurements (30 sec intervals) within 8 minutes given for DO, EC, pH and temperature.

	DO		EC		pH		Temp.		Diss. Fe	Diss. Mn	NO_3-N	NO_2-N	NH_4-N	DON	DOC	DIC	WL
	mean	s	mean	s	mean	s	mean	s									
	(mg L^{-1})		(µS cm^{-1})		(-)		(°C)		(mg L^{-1})								(cm)
T1-1	5.35	0.07	84	1	4.84	0.01	17.8	0.1	0.39	0.01	0.926	<0.002	0.030	0.20	1.40	5.2	167
T1-5	0.94	0.04	247	0	5.18	0.01	19.3	0.1	2.81	2.05	0.018	<0.002	0.090	<0.10	1.30	7.4	108
T1-7	6.17	0.12	99	1	4.27	0.00	18.6	0.1	0.19	0.03	0.038	<0.002	0.020	0.10	0.90	2.7	332
T2-2	0.36	0.05	150	0	5.37	0.02	17.4	0.1	4.60	0.19	0.005	0.004	0.110	<0.10	2.90	15.7	78
T2-4	0.88	0.03	152	1	4.91	0.01	16.3	0.1	0.05	0.05	0.045	<0.002	<0.010	0.10	3.00	11.3	89
T16-8	7.04	0.02	918	41	4.50	0.00	17.4	0.2	<0.02	0.04	49.700	<0.002	<0.010	<0.10	1.10	5.3	207
T17-1	0.72	0.02	161	0	5.68	0.00	18.3	0.1	6.31	0.19	0.006	<0.002	0.100	<0.10	3.00	15.6	41
T17-5	0.65	0.06	267	0	4.97	0.01	17.5	0.1	1.11	0.29	0.072	<0.002	0.130	0.10	1.70	7.9	129
T17-7	6.39	0.10	105	0	4.92	0.01	20.6	0.1	0.04	0.02	2.430	<0.002	0.010	<0.10	0.70	4.5	292
T18-3	1.42	0.06	114	0	5.57	0.02	18.7	0.1	9.76	0.84	0.004	0.008	0.100	<0.10	2.30	9.3	261
T23-3	0.58	0.04	111	3	5.41	0.00	17.5	0.1	1.03	0.03	<0.002	<0.002	0.150	<0.10	2.40	10.3	80
T23-4	6.20	0.03	65	0	5.32	0.01	17.0	0.0	<0.02	0.00	0.558	<0.002	<0.010	<0.10	<0.50	4.5	90
Ke-3	3.45	0.10	175	0	5.21	0.00	17.9	0.1	0.07	0.02	7.000	0.045	0.020	0.10	<0.50	3.7	330
Ke-1	1.64	0.01	233	5	5.92	0.01	18.3	0.2	4.73	1.20	<0.002	<0.002	2.230	<0.10	4.60	14.9	333
Mv-3	1.57	0.03	111	0	5.27	0.01	18.5	0.1	<0.02	0.07	0.039	<0.002	<0.010	<0.10	<0.50	8.6	291
Mv-1	3.21	0.03	119	0	5.41	0.02	18.1	0.1	0.29	0.05	0.004	<0.002	0.010	<0.10	<0.50	8.6	458
To-3	1.49	0.08	145	0	5.01	0.03	18.7	0.1	2.91	0.19	0.112	<0.002	0.130	<0.10	2.60	10.3	140
To-1	3.70	0.01	71	1	4.90	0.01	20.1	0.1	0.12	0.07	0.008	<0.002	0.140	<0.10	1.20	6.2	372

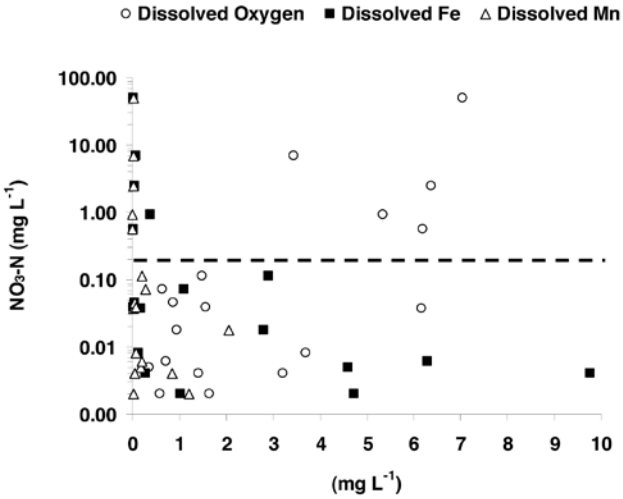

Figure 6 – Relationship between NO_3-N and dissolved oxygen, iron, and manganese in groundwater samples (n = 18). Note the logarithmic scale of the *y*-axis.

groundwater world wide (see, e.g., Korom, 1992) and in New Zealand. Selvarajah *et al.* (1994) reported that over 90% of the bores in the Waikato region with dissolved Fe concentrations > 0.2 mg L^{-1} had NO_3-N concentrations < 1 mg NO_3-N L^{-1}. Similarly, of the seven groundwater samples from the Lake Taupo catchment with dissolved Fe concentrations > 0.1 mg L^{-1} reported by Hadfield *et al.* (2001), all but one had NO_3-N concentrations < 1 mg L^{-1}.

DO concentration alone did not always provide a reliable indicator of the degree of reducing conditions, as relatively high DO concentrations could coincide with substantially enhanced concentrations of dissolved Fe and/or Mn, e.g., in well Ke-1 (Table 3). Appearance of dissolved Mn and Fe while there is still appreciable DO could indicate that groundwater is typically not in thermodynamic equilibrium and more than one electron acceptor can be utilized at any one time (e.g., Korom, 1992; Chapelle *et al.*, 1995). Co-occurrence of DO and dissolved Fe was also noted by Mehnert *et al.* (2007), who suggested it could have been the result of pumping a mixture of shallow oxic and deeper anoxic water. However, this explanation is less likely to apply to well Ke-1, as it is only screened over a length of 50 cm. Denitrification occurring in microenvironments is given by Mehnert *et al.* (2007) as a possible explanation for clear isotopic evidence for denitrification, in spite of DO concentrations of approx. 6 mg L^{-1}. Referring to similar findings, Korom (1992) pointed to the uncertainty regarding trigger DO concentrations for various types of denitrifiers.

Spatial variation of redox conditions

Apart from a moderate depletion in DO concentrations, groundwater from wells T16-8, T17-7, and T23-4 showed no indication of reducing conditions and only weak indications for reducing conditions were found for wells Ke-3 and T1-1. Well-drained Kereone soils are mapped at all these sites (Fig. 3). The observation that only groundwater from these five wells had NO_3-N concentrations > 0.5 mg L^{-1} demonstrates the dominating effect of reducing conditions on the level of groundwater NO_3-N concentrations found in the catchment.

The combination of all analysed indicators suggested that the strongest reducing conditions occurred in wells Ke-1 and T23-3, with NO_3-N concentrations being below the detection limit (Table 3). Supporting the analytical data was, in both instances, a very unpleasant smell noted during sampling and at well T23-3 considered to have been H_2S resulting from sulphate reduction (see Eq. 5). While well T23-3 is located in a naturally poorly drained area with Topehaehae soil close to a small tributary to Toenepi Stream (Fig. 3d), well

Ke-1 is the deeper of the two wells of the Kereone well cluster (Fig. 3c, see below for further discussion).

While there is substantial variation in the data, they generally indicate that more reducing conditions are associated with shallower groundwater tables (e.g., T23-3, T2-2, T17-1; all < 80 cm), whereas aerobic conditions were more frequently observed at locations where the depth to the groundwater table was deeper (e.g., T16-8, T17-7, Ke-3; all > 200 cm). The measured DOC concentrations ranged from 2.40 to 3.00 mg L^{-1} in the above-mentioned wells with shallow water tables, but were less than 1.10 mg L^{-1} in the corresponding wells with deeper water tables (Table 3). This observation supports the hypothesis that microbial decomposition of DOC leached from the root zone is responsible for inducing reducing conditions at these sites with a shallow water table. It may appear as an anomaly that a DOC concentration < 0.50 mg L^{-1} but no signs of reducing conditions were found in well T23-4 in spite of a water table at only 90 cm below ground surface (Table 3). However, while most wells with a shallow water table are located in areas with Topehaehae Gley soil, well T23-4 is located in an area with Kereone soil. Aerobic decomposition of leached DOC in the well-drained soil appears to be sufficient to reduce the concentration of DOC substantially before it reaches the groundwater.

Two wells with deeper water tables showed high DOC concentrations and strongly reducing conditions, well Ke-1 (discussed below) and well T18-3 (water table at 261 cm). As reported earlier, well T18-3 is located on a high streambank above a wetland area; the abundant carbon supply from the grassy wetland vegetation is assumed to induce reducing conditions in the groundwater sampled at this well (Fig. 3e).

Apart from higher DOC concentrations, the data presented in Table 3 suggest that strongly reducing groundwater also tends to have higher concentrations of dissolved inorganic carbon (DIC) than non-reducing groundwater. Higher DIC concentrations presumably reflect the production of bicarbonate (HCO_3^-) during the decomposition of organic matter (e.g., Trudell *et al.*, 1986; Davis *et al.*, 2007; see Eqs. 2-6). DIC concentrations in the wells with more strongly reducing conditions were not only higher than in the non-reducing wells, but typically also 3–5 times higher than the DOC concentrations measured in the more reducing wells. This observation could indicate that substantial decomposition of organic matter has already occurred in these waters and the remaining DOC, while still enhanced relative to the non-reducing wells, might only be the more recalcitrant residue of the organic material that induced the reducing conditions.

Variation of redox conditions with depth

Sampling of two adjacent wells with well screens in different depth ranges allowed at three sites to obtain some information on the vertical distribution of redox conditions within the aquifer. The deep well at the Kereone site (Ke-1, Fig. 3c), mentioned above for its particularly strong reducing conditions and NO_3-N below the detection limit, is screened in 420 cm to 470 cm depth in a zone with numerous layers of loamy sand to silt texture material of greyish, olive-brown or nearly black colour. While no chemical analyses have been undertaken on the very light material of nearly black colour, it appeared to consist mainly of organic matter, which could explain the highest of all measured DOC concentrations (4.60 mg L^{-1}). This sample concomitantly also had by far the highest NH_4-N concentration (2.23 mg L^{-1}), which could reflect restricted nitrification of ammonium produced by

ammonification of organic matter, or by dissimilatory nitrate reduction to ammonium. The latter would be in agreement with the hypothesis that under strongly reducing conditions dissimilatory nitrate reduction to ammonium is favoured when nitrate supply is limiting, while denitrification is favoured when carbon supply is limiting (Tiedje *et al.*, 1982). Reducing conditions do not appear to occur higher up in the profile, although the detectable nitrite in well Ke-3 (screened in 360 cm to 410 cm depth; 7.00 mg NO_3-N L^{-1}) could be interpreted as indicating heterotrophic denitrification activity (Table 4). The results from these wells and observations made during well installation suggest that in this catchment, which is characterised by intensive layering as a result of alluvial and/or volcanic deposits, resident organic matter sufficient to induce denitrification may be available in thin layers well below the ground surface (e.g., peat lenses, buried soil horizons).

Apart from the DO concentrations, the results from the Morrinsville well cluster (Fig. 3c) also indicated non-reducing conditions in the shallower well Mv-3 (screened in 360 cm to 410 cm depth) as compared to somewhat reducing conditions in the deeper well Mv-1 (screened in 420 cm to 470 cm depth). In contrast to the more reducing conditions at greater depth observed at the Kereone and Morrinsville sites, a different situation was observed at the Topehaehae Gley soil cluster (Fig. 3e). The shallower well To-3 (screened in 120 cm to 170 cm depth) clearly showed more signs of reducing conditions than the deeper well To-1 (screened in 340 cm to 390 cm depth). Circumstantial evidence from well installation at that site (and along the T17 transect up to T17-6) indicates that the water sampled in To-3 stems from a perched groundwater body caused by a grey-coloured aquitard that starts approx. 170 cm depth below ground surface. In contrast, the deeper well is screened in a confined aquifer underlying the aquitard. That groundwater is envisaged to infiltrate on higher ground further away from Toenepi Stream where well-drained Kereone soils prevail (see, e.g.; T17-7 results in Table 3) and then flow laterally below the aquitard towards Toenepi Stream.

Summary and conclusions

The predominantly very low NO_3-N concentrations measured in shallow groundwater from December 2002 to December 2004 suggested that substantial nitrate reduction is occurring in this downlands catchment. Results from additional wells monitored during 2005 supported the hypothesis that nitrate concentrations in shallow groundwater underlying well-drained vadose zones tended to be higher than in groundwater under less well-drained conditions. Monitoring of NO_3-N concentrations in a well-drained Kereone soil underlain by poorly drained material deeper in the vadose zone demonstrated that nitrate reduction can occur below the root zone. Visual inspection of borehole samples confirmed that reducing conditions deeper in the vadose zone could explain unexpectedly low NO_3-N concentrations in groundwater transects in areas with well-drained soils (e.g., T16). The combination of field (e.g., DO) and laboratory parameters (dissolved Mn and Fe) analysed in 2007 demonstrated that some degree of reducing conditions existed in all but a few monitored wells. Apart from well Ke-1, NH_4-N concentrations were $\leq$ 0.15 mg L^{-1}, indicating that dissimilatory nitrate reduction and abiotic nitrate reduction to ammonium were not relevant pathways for nitrate reduction in this catchment. Heterotrophic and/or autotrophic denitrification are thus considered to be responsible for the low nitrate concentrations observed in the groundwaters. Independent of the exact processes involved,

it is apparent that nitrate reduction below the root zone is widespread in the catchment. Estimates of NO_3-N leaving the root zone of the pasture, as provided by nutrient budget models like OVERSEER®, are thus not sufficient to evaluate the effect of leaching losses on ground and surface waters in catchments like this, where nitrate reduction can occur below the root zone.

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