

FATE OF A DAIRY COW URINE PULSE IN A LAYERED VOLCANIC VADOSE ZONE

G.F. Barkle*, R. Stenger[†], Th. Wöhling[†], B. Moorhead[†], A. Wall[†], and J. Clague[†].

**Aqualinc Research Ltd, Ruakura Research Centre, Hamilton
Private Bag 14-041, Enderley, Hamilton 3252
Email: G.Barkle@Aqualinc.co.nz*

[†] Lincoln Agritech, Private Bag 3062, Hamilton 3240.

Abstract

Nitrate-N leaching from dairy cow urine patches has been identified as one of the major contributors to groundwater contamination and degradation of surface waters in dairying catchments. To investigate the transport and transformations of nitrogen (N) originating from urine, fresh dairy cow urine was collected, amended with the conservative tracer chloride (Cl) and applied onto a loamy sand topsoil, underlain by gritty coarse sands and pumice fragments in the lower part of the vadose zone. The fluxes of the different N components and the conservative tracer leaching from the urine application were measured at five different depths in the vadose zone using three Automated Equilibrium Tension Lysimeters (AETLs) at each depth (max. 5.1 m). The uppermost part of the saturated zone was also monitored for the leached N and Cl fractions from the urine application.

Textural changes and hydrophobicity in the vadose zone materials resulted in heterogeneous flow patterns and a high variability in the N and Cl masses captured. All three forms of potentially leachable N from the urine – organic-N (org-N), ammonium-N (NH₄-N) and nitrate-N – were measured at the bottom of the root zone at 0.4 m depth. At the 1.0 m depth, effectively all of the captured N was in the mobile nitrate-N form. In the lower part of the vadose zone at 4.2 m, 33% of the applied urine-N was recovered as nitrate-N. This fraction was not significantly different from the corresponding fraction measured at the bottom of the root zone, indicating that no substantial assimilation of the nitrate-N being leached from the root zone was occurring in this vadose zone.

Introduction

Nitrogen (N) and phosphorus losses from agricultural land use are considered responsible for the increasing degradation of water quality in catchments dominated by farming (Monaghan et al., 2005). N losses from grazed pastoral systems can largely be attributed to the temporal discrepancy between the high instantaneous N load resulting from urination events and the concomitant substantially lower N uptake rate by pasture. This discrepancy creates an excess of mobile nitrate-N in the root zone, which is subsequently available to be leached (Di and Cameron, 2002; Cichota and Snow, 2011). Consequently, dairy cow urine has been recognised as one of the major sources of non-point-source nitrate-N pollution from agricultural land use in New Zealand.

N leaching from dairy cow urine patches has been measured at the base of the root zone in numerous studies using various measurement techniques: soil sampling and extraction (Ledgard and Saunders, 1982; Carran et al., 1982), barrel lysimeters (Fraser et al., 1994; Di and Cameron, 2002; Silva et al., 1999), and ceramic soil suction samplers combined with

drainage estimates from either barrel lysimeters (Shepherd et al., 2011) or models (Shepherd et al., 2010). However, no published studies have reported on the transport and transformation of urine-N through the vadose zone and into the underlying groundwater zone.

Urine-N, when excreted, consists of 60–90% org-N as urea (Whitehead and Raistrick, 1993). Urea is hydrolysed rapidly to $\text{NH}_4\text{-N}$ when in contact with soil (Pakrou and Dillon, 1995). The $\text{NH}_4\text{-N}$ is then subject to various transformations and pathways, including: adsorption onto cation adsorption sites in the soil, immobilisation into organic matter, nitrification into nitrate-N, gaseous losses by volatilisation, leaching as $\text{NH}_4\text{-N}$ and root water uptake. The initial transport of the urea pulse, the transformation of urea into $\text{NH}_4\text{-N}$, the nitrification into nitrate-N and the competing pathways for these N products make the fate of the N in urine challenging to measure.

Regulators and others grappling with setting nutrient load limits for freshwater quality are forced into assuming that root zone N losses will either travel through the vadose and saturated zone and enter receiving surface waters (a) unabated, or (b) apply a reduction factor, to account for nitrate-N assimilation that could possibly be occurring along the subsurface conduit from the root zone to the receiving surface water. In addition, lag times of N travelling through the vadose zone (and saturated zone) are often ignored.

Differences between the root zone losses of N in a catchment and the N load measured in surface waters can arise due to at least three reasons. Firstly, not all leachate generated within the topographical catchment boundaries necessarily reaches the surface monitoring site. Some N may bypass the monitoring site in deeper groundwater flow lines and the groundwater catchment boundaries may not be congruent with the topographical catchment boundaries (Bidwell et al., 2008). Secondly, differences can be due to long mean residence times in the groundwater system, which can result in the current surface water N concentration reflecting root zone losses generated under different historical land use intensity. Thirdly, attenuation processes (predominantly denitrification) may remove N along the flow path from the bottom of the root zone to the discharge location into surface waters (Böhlke et al., 2007; Puckett and Cowdery, 2002; Stenger et al., 2008).

Stenger et al. (2012) reported for a small catchment (15 km²) dominated by dairying that root zone N losses estimated with the Overseer[®] nutrient balance model (Shepherd and Wheeler, 2012) were approximately twice as high as the load measured at the surface water monitoring site at the catchment outlet. Water balance calculations indicated that streamflow accounted for nearly all the water exported from the catchment, i.e. the groundwater is predominately discharged to the stream. In a modelling study of the Taupo Lake catchment (3,500 km²), the average predicted flow-weighted nutrient concentrations at various surface water sites were in reasonably good agreement with measured data when an attenuation factor of approximately 60% was assumed (Elliot and Stroud, 2001). Clothier et al. (2007) derived an attenuation factor of approximately 50% for a large catchment study on the Manawatu River (5944 km²). This factor was computed by comparing Overseer[®] root zone N loss estimates and measured surface water N loads in two sub-catchments. Alexander et al. (2002) reported in a SPARROW modelling study of five catchments in the Waikato Region, ranging in size between 2,686 and 13,517 km², that the N load in the surface water load was between 25 and 61% of what was estimated leaving the root zone.

However, there is little quantitative evidence published to identify where, when and how much nitrate-N lost from the root zone can be attenuated along the subsurface pathway below

the root zone, and particularly within the vadose zone. Two of the major reasons for this deficiency in our knowledge are the absence of fundamental and reliable data on the physical properties of the vadose zone materials, and the inherent difficulty of measuring actual water and contaminant fluxes in this zone (Kowall, 2001; Holt and Nicholl, 2004; Halford, 2004). To respond to this specific need for measuring and understanding the temporal dynamics of contaminant fluxes and potential assimilation processes in the vadose zone, the “Spydia” monitoring and experimental facility was installed within the Lake Taupo catchment (Wöhling et al., 2009; Barkle et al., 2011). The Spydia facility has been designed and built to accurately measure water and contaminant fluxes through the vadose zone using Automated Equilibrium Tension Lysimeters (AETLs). In addition to the AETLs, tensiometers and time-domain reflectometer probes for measuring pressure heads and water contents respectively were installed at the base of the root zone and at various depths down to the water table.

Wöhling et al. (2012) reported that the high variability in measured tracer mass recoveries in the AETLs throughout the vadose zone was primarily due to the variability in drainage volumes. In particular, the variability at a given depth was not due to differences in measured concentrations. These tracer recoveries confirmed and quantified the variability observed due to unsaturated heterogeneous transport in earlier dye studies conducted at the site (Werisch, 2010). The heterogeneous transport occurring in the coarse volcanic sand materials was attributed to textural discontinuities between different strata and a temporal variable degree of hydrophobicity (Werisch, 2010).

To investigate the transformation and transport of urine-N through the vadose zone, dairy cow urine was collected and amended with a conservative tracer (Cl) and applied on the surface area above and around the AETLs. Previous laboratory studies (Barkle et al., 2007; Clague et al., 2012) have determined that significant denitrification capacity exists in the materials occurring throughout the vadose zone profile at this site. Comparing the time series of the N species measured at different depths of the vadose zone allows us to determine the transport and fate of urine-N through this vadose zone, and to investigate the degree to which the reported denitrification capacity of the subsurface has been realised during this experiment.

Methods

Vadose zone

The Spydia field site was established on a sheep and beef station within a sub-catchment of Lake Taupo. The modern soil at the site belongs to the Oruanui loamy sand series within the Podzolic Orthic Pumice Soil subgroup (New Zealand soil classification) and is a mesic Andic Haplorthod according to the United States soil taxonomy (Rijkse, 2005). The majority of the vadose zone profile is developed from deposits of the Taupo eruption approximately 1.8 ka BP and is commonly found in the Lake Taupo catchment. As a comprehensive description of the vadose zone profile has already been presented in Wöhling et al. (2008) and Barkle et al. (2011), only a short summary is given here. The A horizon soil

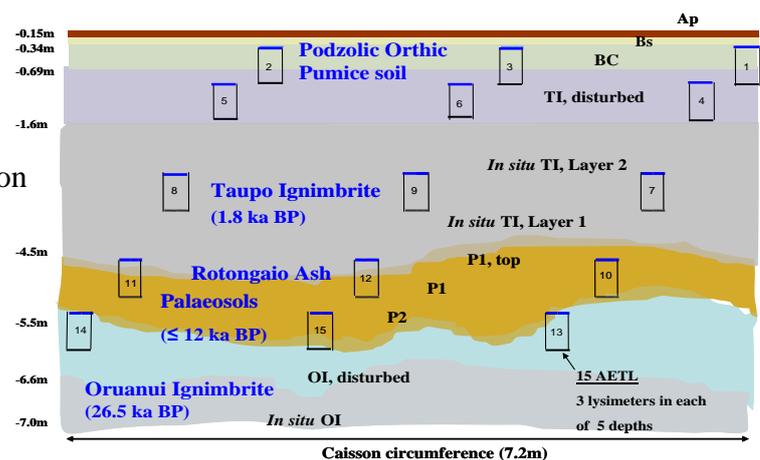


Figure 1: Schematic of the materials in the vadose zone profile and AETLs location around the circumference of the installed caisson.

texture is loamy sand, changing into a gritty coarse sand at 0.15 m depth. Gravelly coarse sand follows at 0.34 m and becomes stony coarse sand at approximately 1.6 m. Below this depth the vadose zone material is described as being coarse pumice fragment and fines down to the Palaeosol depth at approximately 4.2 m (Fig. 1).

Spydia monitoring facility

The experimental facility has been described comprehensively by Wöhling et al. (2008, 2009, 2012) and Barkle et al. (2011). Therefore, only a short précis is contained below.

The 15 sampling AETLs using porous stainless steel plates (0.9 m long by 0.22 m wide; 0.198 m²) are installed horizontally outward and sequentially stepped downwards at the depths of 0.4, 1.0, 2.6, 4.2 and 5.1 m from the ground surface. These AETLs are installed radially around a central access caisson: a 2.3 m diameter, 7.0 m deep steel pipe, excavated by hand through the undisturbed vadose zone materials down into the permanently saturated zone. To fulfil a minimum separation distance (Mertens et al., 2005) and reduce boundary effects, a spacer AETL of 0.45 m length is used to increase the radial distance of the sampling AETL from the central caisson. A reference tensiometer is installed at each of the sampling AETLs in the surrounding undisturbed vadose zone material. The control system matches the individually measured reference pressure head and the vacuum applied under the corresponding sampling AETL, with a tolerance of ± 0.2 hPa.

At each sampling depth there are three AETLs installed. At the 4.2 m depth, two of these AETLs (11 and 12) are installed in the base of the Taupo Ignimbrite (TI), while AETL10 is installed into Palaeosol layer 1 (Fig. 1). This installation pattern occurred due to the sloping nature of the Palaeosol layer intersecting with the vertical Spydia caisson. To enable samples to be collected from the permanently saturated zone beneath the Spydia, a well is installed through the floor of the caisson and screened from 7.0–8.75 m depth. A vented pressure transducer is installed in this monitoring well to provide continuous measurement of the water table location. When the water table raises to depths where AETLs are installed, a set of three saturated zone samplers (SZS-1 to SZS-3), screened between 5.8–6.3 m depth, allow groundwater samples to be collected.

Urine collection and application

Fresh urine (230 l) was collected from a Friesian dairy cow herd over ten days in early May 2010. The collected urine was frozen (-18°C) within an hour of collection. Prior to application the urine was unfrozen and the Cl concentration was increased to 4340 mg/l to ensure the Cl concentration remained easily detectable throughout the vadose zone.

As a large volume of urine was applied in one event, small steel frames pushed into the sod were used to limit the amount of redistribution of the urine on the soil surface. The frames extended 0.45 m beyond the dimensions of the AETLs. An equivalent of 2 mm of clean water was initially applied to wet-up the pasture before the urine application and another 2 mm of wash-off water was applied after application. The urine was surface applied on the 9th August, 2010 at the typical estimated loading depth of a dairy cow urine event of 10 mm (Hogg, 1981; Williams et al., 1990; Meneer et al., 2008).

Pasture

Pasture takes up Cl passively and N competitively into its root system via the soil water. Therefore, the pasture was cut in the areas where urine was applied, and accumulated Cl and

N was measured in the dry mass 67 days after application of the urine and tracer. The pasture was analysed using the method of Schnabel et al. (1995).

Hydrological conditions and leachate collection

The last leachate sample was collected in the AETLs at 4.2 m depth on 19th December, 2011, which was 497 days after the urine tracer was applied. Due to concern that the water table would rise and flood the lower AETLs before the complete breakthrough curve (BTC) data had been collected, the site was irrigated between 18th May and 1st August, 2011. The cumulative rainfall over the entire monitoring period was 2317 mm, with an additional 1071 mm of irrigation applied (Fig. 2). During the monitoring period the watertable depth peaked three times, the highest at -3.7 m in November 2010. The lowest recorded water table depth was -5.5 m in May 2011.

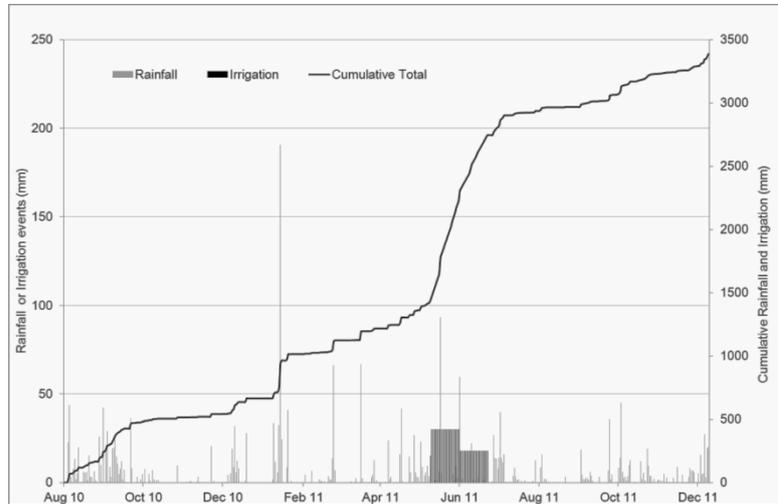


Figure 2: Rainfall and irrigation events (mm/day) and cumulative rain and irrigation depth (mm.)

Unfortunately, the high water table levels in 2010 resulted in the AETLs at the 4.2 m depth being flooded, rendering these AETLs inoperative for 66 days from 7th September to 12th November. This did not affect the measurement of tracer and nitrate-N concentrations from the urine as the pulse had yet to reach this depth. However, due to this data gap, the BTC data from these AETLs cannot be presented on the basis of cumulative drainage since tracer/urine application. The AETLs at 5.1 m depth were flooded for longer periods during this experiment. Consequently, the more continuous data from the saturated zone samplers are used to describe the dynamics of the tracers and nitrate-N at the base of the Spydya profile.

As background Cl and nitrate-N concentrations occur in the leachate due to rainfall deposition of Cl and net soil mineralisation with subsequent nitrification respectively, the measured leachate Cl and nitrate-N concentrations were corrected for background concentrations determined from the long term AETL monitoring data from the site.

Analytical methods

Cl and nitrate-N concentrations were determined using ion chromatography (APHA-4110B, 2005) which had detection limits 0.5 mg/l Cl and 0.05 mg/l nitrate-N respectively. NH₄-N was determined using phenol/hypochlorite colorimetric method (APHA-4500, 2005), which has a detection limit of 0.01 mg/l NH₄-N. The org-N concentration was established using the difference between the Kjeldahl-N concentration, determined from sulphuric acid digestion and phenol/hypochlorite colorimetric method (APHA-4500, 2005) and the NH₄-N concentration. All the carbon analysis used catalytic oxidation followed by inferred detection (APHA-5310 B, 2005).

Data analysis

BTC information from the AETLs is reported with respect to measured cumulative drainage, as opposed to time. The calculation of the drainage per unit area (mm) from the volume (l) of leachate measured by an AETL assumes that the surface area (m²) that contributes drainage to each AETL is known (Wöhling et al., 2012). The contributing surface area (m²) is determined by dividing the mass of Cl tracer (mg) recovered in an AETL by the application rate at which the tracer was applied onto the ground surface (mg/m² Cl).

The contributing area for each AETL is determined by calculating the fraction of the Cl tracer recovered, assuming the contributing area has a 1:1 correspondence with the plate area as per Equation 1. The plate area is then multiplied by this Cl recovery fraction to determine the equivalent contributing surface area for each AETL (Eq. 2).

$$Cl\ recovery\ fraction = \frac{\Sigma\ Concentration\ of\ Cl\ in\ event\ (mg/l) * Volume\ (l)\ of\ each\ event}{\{Applied\ Cl\ concentration\ (mg/m^2) * Plate\ area\ (m^2)\} - Plant\ uptake(mg)} \dots (Eq. 1)$$

$$Equivalent\ contributing\ area\ (m^2) = Plate\ area\ (m^2) * Cl\ recovery\ fraction \dots \dots (Eq. 2)$$

For this equivalent contributing area approach to be valid, the average of the tracer recoveries in the AETLs at a single depth must be close to 100%. This requires the measured variability in the Cl recoveries to have no systematic bias, which could be ascribed to Cl adsorption, and/or measurement error in the AETLs. If the AETL has a calculated Cl recovery (1:1 area correspondence) of less than 100%, then the AETL is sampling from a surface area less than the plate area of 0.198 m². Equally, if the Cl recovery is greater than 100% then the AETL is sampling from an area greater than that of the plate.

Results and Discussion

Urine

The urine was analysed for N, carbon and Cl concentrations and reported in Table 1 together with loadings on a per hectare basis. The equivalent urine-N application rate of 464 kg N/ha is lower than the range of 800–1000 kg N/ha that has typically been used in previous New Zealand dairy cow urine-N leaching studies (Shepherd et al., 2010; Silva et al., 1999; Di et. al., 2002). These higher rates have generally been referenced to the published work by Haynes and Williams (1993). While the application depth for dairy cow urine (10 mm) used in our work was also based on this reference, we had a substantially lower urine-N concentration of 4.64 g/l N compared to the concentration data reported by Haynes and Williams of 10 g /l N.

It is appreciated that there is a high variability in the dairy cow urine-N concentrations due to seasonal variation, daily temperatures, feed and pasture variability, cow breed and age, and time of day. However, the higher N concentrations reported by Haynes and Williams (1993) are reported from data collected in North Carolina in the U.S. (Safley, 1984) and England (Whitehead, 1970), and may not apply that well to current New Zealand conditions. The

Table 1: Average concentration of N and carbon components (mg/l) in urine (n=5) amended with Cl. Resulting loadings on a kg/ha basis with 10 mm application depth used.

| Species | Average concentration (mg/l) | Standard deviation (mg/l) | Average loading (kg/ha) |
|--------------------|------------------------------|---------------------------|-------------------------|
| Chloride (amended) | 4340 | 114.0 | 434.0 |
| Kjeldahl-N | 4540 | 89.4 | 454.0 |
| NH ₄ -N | 25.2 | 0.8 | 2.5 |
| Nitrate-N | 104.4 | 33.2 | 10.4 |
| Total-N (by sum) | 4644 | 116.2 | 464.4 |
| Total carbon | 6360 | 167 | 636.0 |
| Inorganic carbon | 500 | 0.0 | 50.0 |
| Organic carbon | 6000 | 200 | 600.0 |

urine-N concentration of 4.6 g/l N in this study agrees with other reported New Zealand data (which are generally lower than the 10 g/l N reported by Haynes and Williams): for example, 3.0 g/l N (Park, 1996), 5.5 g/l N (Williams et al., 1989), and 7.3 g/l N (Silva et al., 1999). In a recent comprehensive study on the seasonal and dietary effects on the concentration of urine-N from grazing dairy cows in New Zealand, Pacheco et al. (2010) reported the average total-N concentration in urine, for cows fed with either Perennial or Italian ryegrass, to be 4.5 g/l N. Accordingly, based on the 10 mm application depth, the 464.4 kg N/ha loading rate used in this study would appear to be a loading representative of current New Zealand conditions.

The predominant form of N in the applied urine was org-N (97%), which indicates that no significant urea hydrolysis to NH₄-N had occurred during collection and storage. However, the NH₄-N concentration was lower than expected; this may indicate that some volatilisation losses could have occurred.

Pasture uptake

The pasture sampled 67 days after the tracer was applied to the soil had an average Cl concentration of 694 mg/kg Cl of fresh grass. The average mass of pasture removed per AETL was 428 g fresh grass, resulting in an average Cl mass being taken up by the pasture of 297 mg Cl per surface area of AETL. The plant uptake equates to an average of 3.2% of the applied Cl. This reduction in the mass of conservative tracer available for transport through the vadose zone has been accounted for in the tracer recovery calculations.

The average N concentration measured in the pasture was 3.9% N, which equates to a mass of N accumulated by the pasture of 123 kg N/ha. If this was assumed to be entirely derived from the urine, it would represent 27% of the applied N. As urine-N is not a conservative tracer and plant N uptake is a significant and expected pathway, the mass of N applied was not adjusted for this N removed by the plant.

Recovery and BTCs of urine-N components and Cl

The average recovery of the Cl tracer at each depth over all measured sites is reasonably close to 100% (Table 2). With no bias in the recovery values evident, we calculated the equivalent contributing area for the individual AETLs and used it for subsequent analysis of the data. The variability in Cl recovery due to heterogeneous flow is high, with the overall CV being 69%.

The various N fractions contributing to the total-N being leached, namely org-N, NH₄-N and nitrate-N, are different for each AETL as reported in Table 3. The average total-N recovered at the 0.4 m depth was 24.5% of the applied urine-N, which equates to a mass of 114 kg N/ha. Org-N was measured in all three AETLs; this fraction was less than 1% of the total-N applied, and 2.0–3.5% of the total-N leached to this depth. NH₄-N accounted for 21–38% of the N leached to 0.4 m, which corresponds to 5.2–9.2% of the total-N applied. On average, 70% (std. 9.3%) of the N leached to 0.4 m was nitrate-N. The leached nitrate-N exhibited an inverse relationship with NH₄-N, i.e. the more NH₄-N, the less nitrate-N, so that the resulting total-N leached was similar in all the AETLs.

Table 2: Cl recoveries in individual AETLs, equivalent contributing areas, average and (std) with depth.

| AETL depth (m) | AETL number | Cl recovery (%) | Equivalent contributing area (m ²) |
|----------------|------------------------|------------------|--|
| | 1 | 100 | 0.198 |
| | 2 | 56 | 0.112 |
| | 3 | 202 | 0.400 |
| -0.4 | Ave (± std) | 119 (75) | 0.236 (0.15) |
| | 4 | 272 | 0.538 |
| | 5 | 21 | 0.041 |
| | 6 | 71 | 0.141 |
| -1.0 | Ave (±std) | 121 (133) | 0.241 (0.26) |
| | 7 | 98 | 0.194 |
| | 8 | 53 | 0.105 |
| | 9 | 105 | 0.207 |
| -2.6 | Ave (±std) | 85 (28) | 0.169 (0.06) |
| Pal. | 10 | 1.5 | n.a. |
| TI | 11 | 198 | 0.391 |
| TI | 12 | 65 | 0.129 |
| -4.2(TI only) | Ave (TI) (±std) | 132 (94) | 0.260 (0.19) |
| | Overall average | 113 (78) | |

As 97% of N applied in the urine is in the form of org-N, and recognising that org-N is rapidly hydrolysed to NH₄-N after application, it is unlikely that much of the applied org-N is leached. Moreover, the time window of opportunity is comparatively short, as confirmed by the corresponding breakthrough curves in Figure 3, which show that the majority of org-N mass is leached before the other N components and the Cl tracer. The greater variation in the leaching behaviour of the NH₄-N (Fig. 3) as compared to the Cl tracer is attributed to variability in the formation process of the NH₄-N, which requires hydrolysis of the urea in the applied urine. The NH₄-N is additionally subject to various competing processes and pathways, including plant uptake, cation adsorption, immobilisation, nitrification and leaching. In all cases the NH₄-N leaching occurred prior to the nitrate-N. This is to be expected as NH₄-N is the substance that is oxidized to the more mobile nitrate-N.

Table 3: Nitrate-N, NH₄-N and org-N recoveries in individual AETLs, average with std. by depth. Based on contributing area analysis

| AETL number | NO ₃ recovery (%) | NH ₄ recovery (%) | Org-N recovery (%) | Total-N recovery (%) |
|--------------------|------------------------------|------------------------------|--------------------|----------------------|
| 1 | 19 | 5.2 | 0.5 | 24.6 |
| 2 | 15 | 9.2 | 0.9 | 24.6 |
| 3 | 18 | 6.2 | 0.5 | 24.4 |
| Ave (±std) | 17 (2) | 6.9 (2.1) | 0.6 (0.2) | 24.5 (0.1) |
| 4 | 22 | 0.4 | | 22.3 |
| 5 | 21 | 0.0 | | 20.7 |
| 6 | 64 | 0.0 | | 63.9 |
| Ave (±std) | 36 (25) | 0.1 | | 36 (25) |
| 7 | 13 | | | |
| 8 | 14 | | | |
| 9 | 43 | | | |
| Ave (± std) | 23 (17) | | | |
| 11 | 18 | | | |
| 12 | 48 | | | |
| Ave(± std) | 33 (21) | | | |

The nitrate-N is also the net result of variable and competing processes, not only in its current nitrate-N form but also in the precursory forms starting with the transformation of urea and subsequently of NH₄-N, so variability is expected. The measured nitrate-N leaching data reflects the sizes of the pools of precursory materials in the root zone, i.e. NH₄-N, which itself has already undergone variable leaching. This relationship is demonstrated in AETL2, which captured the highest mass of NH₄-N and the lowest mass of nitrate-N. On the contrary, AETL1 captured the lowest NH₄-N and highest nitrate-N masses.

At the 1.0 m depth, only one of these three AETLs (AETL4) showed detectable concentrations of NH₄-N (Table 3). In the other two AETLs at this depth (AETLs 5 and 6), nitrate-N was the only consistent form of N leaching detected. The mass of NH₄-N recovered in AETL4 was 0.4% of the total urine-N applied, which is 1.6% of the N leached to this depth. The average mass of N leached as nitrate-N to the 1.0 m depth is 36% of the applied total-N, which is not significantly different (5% Sig. Lev.) from the total-N leached at the 0.4 m depth. In AETL6, the mass of nitrate-N recovered equates to 64% of the applied urine-N, which was the highest recovery of N in any AETL. Additionally, this AETL had the highest peak nitrate-N concentration at 98 mg/l.

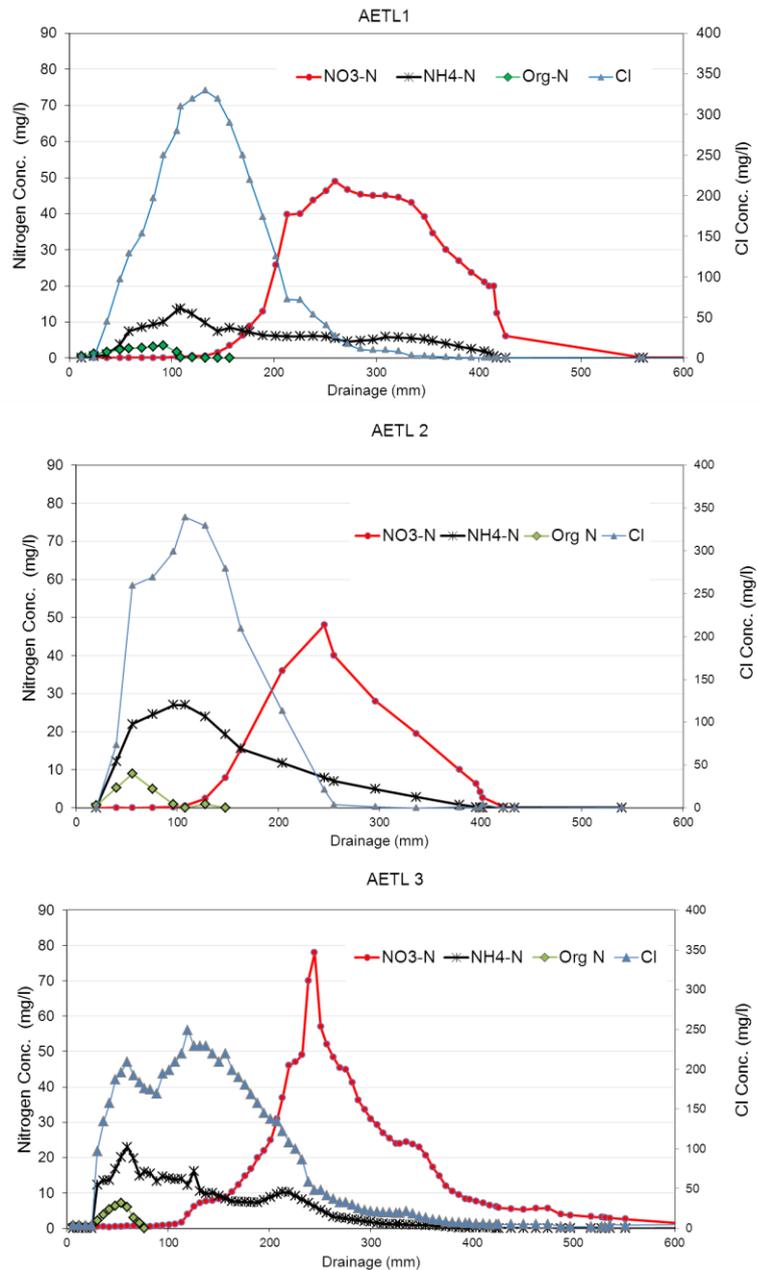


Figure 3a-c: BTCs for nitrate-N, NH₄-N, Org-N and Cl for three AETLs at 0.4 m depth.

The average mass of nitrate-N captured in the three AETLs at the 2.6 m depth (AETLs 7–9) is 107 kg N/ha, which is equivalent to 23% of the total-N applied in the urine. AETL9 measured over 2.5 times more nitrate-N (43% of applied N) when compared to the other two AETLs at this depth, which exhibit a similar recovery with an averaged of 17% applied urine-N.

The average mass of N as nitrate-N measured at the base of the TI at 4.2 m depth (AETLs 11 and 12) was 33 % of the total urine-N applied. This was not significantly different (5% Sig. Lev.) from the mass of total N leached from the bottom of the root zone. In contrast to these two AETLs, AETL10 located at the same depth but in the Palaeosol, showed no breakthrough of nitrate-N from the urine application. Additionally, AETL10 only recovered 1.5 % of the Cl tracer applied (Table 2; Fig. 4). This result suggests that lateral unsaturated flow is occurring at this stratigraphic boundary, and the vertical flow components into the Palaeosol layer are

relatively small. It should be noted, however, that the Palaeosol is not a contiguous layer at this site, and it could be expected that at some locations, vertical connection down to lower depths occurs. The result that there is no significant decrease in the N mass leached from the bottom of the root zone at 0.4 m down to the 4.2 m depth, suggests that there is no nitrate-N assimilation occurring in this vadose zone. This contradicts the denitrification capacity previously determined in lab incubations, but it is presumably caused by the lack of anaerobic conditions in the vadose zone under field conditions.

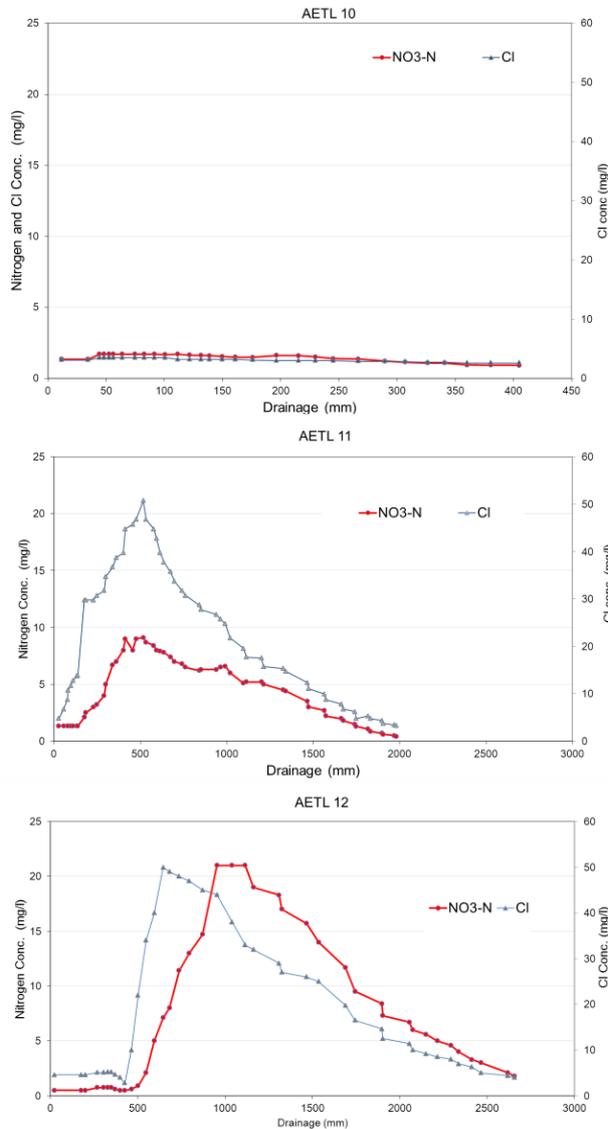


Figure 4 a-c: BTCs for nitrate-N, and Cl for three AETLs at 4.2 m depth. AETL 10 is in Palaeosol and AETL 11 and 12 are in TI.

nitrate-N or Cl occurred in the top of the saturated zone. However, more data with greater temporal resolution combined with groundwater flux estimates would be required to substantiate this finding.

The two AETLs in the base of the TI (AETLs 11 and 12) have similar shaped uni-modal BTCs. As discussed previously, due to the water table rising, the cumulative drainage data in the AETLs at 4.2 m commences only in April 2011. This was when the conservative tracer first became detectable at this depth. The centroid of mass of the nitrate-N in the BTCs at 4.2 m is comparatively closer, in cumulative drainage, to that of the Cl than at the 0.4 m depth. The org-N and $\text{NH}_4\text{-N}$ that were preferentially leached prior to the nitrate-N in the upper part of the vadose profile, and which then transformed into nitrate-N, were probably responsible for this relative shift in the centroid of nitrate-N mass earlier to that of the Cl. However this result could also occur if the nitrate-N is being preferentially transported as compared to the Cl.

Over the period from August 2010 to December 2011 only one of the three saturated zone samplers (SZS-3), located at the top of the saturated zone, displayed consistent and concomitant increases in nitrate-N and Cl (data not shown). Cl concentrations increased at the end of May 2011 from a baseline concentration of approximately 3.0 mg/l Cl to 4.7 mg/l Cl by mid-June. Concomitantly, nitrate-N increased by 0.3 mg/l to 1.5 mg/l. These results suggest that very little transport of

Conclusions

Under a dairy cow urine patch applied onto a loamy sand topsoil, the predominant form (70%) of N leached to 0.4 m depth is nitrate-N. The other important form of leached N to this depth is $\text{NH}_4\text{-N}$. By the 1.0 m depth, effectively all N leached from the urine is in the form of nitrate-N. The mass of N leached down to the lower part of the vadose zone at 4.2 m is 33% of the applied total-N in the urine. Judging by the observed contaminant fluxes at different locations and depths of the vadose zone, there is no evidence that nitrate-N is being assimilated by denitrification.

Assuming that all N measured in the pasture comes from the applied urine, the measured mass of N measured after 67 days represented 27% of the applied N. As the precursor N forms of nitrate-N in urine move at different rates, it is incorrect to use the ratios of the concentrations $\text{Cl}:\text{nitrate-N}$ to infer information on the fate of N from urine.

Due to heterogeneous flow in this vadose zone, the measured leaching volumes at the 0.2 m² sampling area are highly variable. When combined with spatially varying concentrations of nitrate-N, the resulting nitrate-N mass leaching patterns through the vadose zone are extremely variable. The spatially-different recovery of the conservative tracer applied on the soil surface with the urine confirms that one-dimensional uniform transport through the vadose zone cannot describe the measured leaching patterns.

Acknowledgements

This work was funded by the New Zealand Ministry for Science and Innovation (MSI). We gratefully acknowledge Landcorp Farming's permission to install and operate the Spydia facility on Waihora Station. We thank Mr Colin Armer, the current land owner, for enabling us to complete our research on the site.

References

- Alexander R.B., A. H. Elliott, U. Shankar, and G. B. McBride. 2002. Estimating the sources and transport of nutrients in the Waikato River Basin, New Zealand Water Resources Research Vol. 38 (12)1268:4-1 4-23.
- APHA. 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC. USA.
- Barkle G.F., T. Clough, R. Stenger R. 2007. Denitrification capacity in the vadose zone at three sites in the Lake Taupo Catchment, New Zealand. Australian Journal of Soil Research 45:91-99.
- Barkle G.F., Th. Wöhling, R. Stenger, J. Mertens, B. Moorhead, A. Wall and J Clague. 2011. Automated equilibrium pressure head lysimeters for measuring water fluxes through a layered, volcanic vadose zone profile in New Zealand. Vadose Zone J. 10(2):747-759.
- Bidwell, V., R. Stenger, G.F. Barkle. 2008. Dynamic analysis of groundwater discharge and partial-area contribution to Pukemanga stream, New Zealand. Hydrology and Earth System Science. 12:975-987.
- Böhlke, J.K., M.E.O'Connell and K.L. Prestegard. 2007. Groundwater stratification and delivery of nitrate to an incised stream under varying flow conditions. Journal of Environmental Quality 36, 664-680.

- Carran R. A., P. Roger Ball, P. W. Theobald and M. E. G. Collins. 1982. Soil nitrogen balances in urine-affected areas under two moisture regimes in Southland New Zealand *Journal of Agricultural Research*, 10:377-381.
- Cichota R. and V.O. Snow. 2011. Simplifying pastoral systems modelling – accounting for the effect of urine deposition on N leaching. In: Adding to the knowledge base for the nutrient manager. (Eds. L.D. Currie and C L. Christensen). Occasional Report No. 24. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. pp 788-794.
- Clague J. C., R. Stenger, and T. J. Clough. 2012. The impact of relict organic materials on the denitrification capacity in the unsaturated - saturated zone continuum of three volcanic profiles. *Journal of Environmental Quality* 42:145-154.
- Clothier B. E., A. Mackay, A. Carran, R. Gray, R. Parfitt, G. Francis, M. Manning, M. Deurer, and S. Green. 2007 *Farm Strategies for Contaminant Management: A report by SLURI for Horizons Regional Council*. AgResearch.
- Di H.J. and K.C. Cameron. 2002. The use of a nitrification inhibitor, dicyandiamide (DCD), to decrease nitrate-N leaching and nitrous oxide emissions in a simulated grazed and irrigated grassland. *Soil Use and Management* 18:395-403.
- Elliot A.H. and M.J. Stroud. 2001: Prediction of nutrient loads entering Lake Taupo under various land use scenarios. NIWA Client Report EVW01224. NIWA, Hamilton. Updated by Waikato Regional Council in January 2004
- Fraser P.M., K.C. Cameron, and R.R. Sherlock. 1994 Lysimeter study of the fate of nitrogen in animal urine returns to irrigated pasture. *European Journal of Soil Science* 45:439-447.
- Haynes R. J., and P.H. Williams. 1993: Nutrient cycling and soil fertility in the grazed pasture ecosystem. *Advances in Agronomy* 49:119-199.
- Halford K. 2004. More data required. *Groundwater* 42:477.
- Hogg D. E. 1981. A lysimeter study of nutrient losses from urine and dung applications on pasture. *New Zealand Journal of Experimental Agriculture*, 9:39-46.
- Holt R., and M. Nicholl. 2004. Uncertainty in vadose zone flow and transport predictions. *Vadose Zone J.* 3:480-484.
- Kowall J.S. 2001. United States Department of Energy: Vadose zone science and technology roadmap: A national program of research and development, Idaho National Engineering and Environmental Laboratory.
- Ledgard S. F. and W. M. H. Saunders. 1982. Effects of nitrogen fertiliser and urine on pasture performance and the influence of soil phosphorus and potassium status, *New Zealand Journal of Agricultural Research*, 25:4, 541-547
- Menneer J. C., M. S. Sprosen and S. F. Ledgard. 2008. Effect of timing and formulation of dicyandiamide (DCD) application on nitrate-N leaching and pasture production in a Bay of Plenty pastoral soil, *New Zealand Journal of Agricultural Research*, 51:3 377-385
- Mertens J., G.F. Barkle, and R. Stenger. 2005. Numerical analysis to investigate the effects of the design and installation of equilibrium pressure head plate lysimeters on leachate volume. *Vadose Zone J.* 4:488-499.

- Monaghan R.M., R.J. Paton, L.C. Smith, J.J. Drewry, and R.P. Littlejohn. 2005. The impacts of nitrogen fertilisation and increased stocking rate on pasture yield, soil physical condition and nutrient losses in drainage from a cattle-grazed pasture. *New Zealand Journal of Agricultural Research* 48:227–240.
- Pacheco D., K. Lowe, M.J. Hickey, J.L. Burke, and G.P. 2010. Seasonal and dietary effects on the concentration of urinary N from grazing dairy cows. In: *Meeting the Challenges for Pasture-Based Dairying*. Proceedings of the 4th Australasian Dairy Science Symposium, pp. 68-73. Lincoln University, Christchurch, New Zealand.
- Pakrou N., and P. Dillon. 1995. Preferential flow, nitrogen transformations and ^{15}N balance under urine-affected areas of irrigated and non-irrigated clover-based pastures. *Journal of Contaminant Hydrology* 20:329–347.
- Park S. 1996. The fate of urine-Nitrogen on two Waikato soils. MSc in Earth Science Thesis. University of Waikato.
- Puckett, L.J., and T.K. Cowdery. 2002. Transport and fate of nitrate in a glacial outwash aquifer in relation to groundwater age, land use practices, and redox processes. *Journal of Environmental Quality* 31:756-759.
- Rijkse W. 2005. Report on Oruanui loamy sand profile, Waihora Station. Prepared for Lincoln Ventures Ltd.
- Safley L. M. Jr., J. C. Barker and P. W. Westerman. 1984. Characteristics of fresh dairy manure. *Transactions of the ASAE* 27(4):1150-1153, 1162.
- Schnabel R.R., W.L. Stout, and J.A. Schaffer. 1995. Uptake of a hydrologic tracer (Bromide) by ryegrass from well and poorly drained soils. *J. Environmental Quality* 24:888-892.
- Shepherd, M. and Wheeler, D. 2012. OVERSEER® Nutrient Budgets – the next generation. In: *Advanced Nutrient Management: Gains from the Past - Goals for the Future*. (Eds. L.D. Currie and C L. Christensen). Occasional Report No. 25. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 9 pages.
- Shepherd M., P. Phillips, V. Snow, and C. Glassey. 2010. Mitigating nitrate-N leaching in dairy systems – which periods of urine deposition should we be targeting? In: *Farming's Future: Minimising Footprints and maximising margins*. (Eds. L D Currie and C L Lindsay), Occasional Report No. 23, Fertiliser Lime Research Centre, Massey University, Palmerston North, New Zealand pp. 174-182.
- Shepherd M.A., P. Phillip, and V. O. Snow. 2011. The challenge of late summer urine patches in the Waikato region. (Eds. L.D. Currie and C L. Christensen).\ Occasional Report No. 24. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand.
- Silva R.G., K.C. Cameron, H.J. Di, and T. Hendry. 1999. A lysimeter study of the impact of cow urine, dairy shed effluent, and nitrogen fertiliser on nitrate-N leaching. *Australian Journal of Soil Research* 37: 357-369.
- Stenger, R., Barkle, G.F., Burgess, C., Wall, A. and J. Clague (2008) Low nitrate contamination of shallow groundwater in spite of intensive dairying: the effect of reducing conditions in the vadose zone – aquifer continuum. *Journal of Hydrology (NZ)*, 47(1): 1-24.
- Stenger R., J. Clague, S. Woodward, B. Moorhead, L. Burberry, and H. Canard. 2012 Groundwater assimilative capacity – an untapped opportunity for catchment-scale nitrogen management ? *Advanced Nutrient Management: Gains from the Past - Goals for the*

- Future. (Eds L.D. Currie and C L. Christensen). Occasional Report No. 25. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand.
- Werisch S. 2010. Characterisation on non-uniform flow at the Spydia experimental site. Diplom Hydrologe Technische Universität Dresden.
- Whitehead D. C. 1970. The role of nitrogen in grassland productivity. *Commw. Bur. Pastures Field Crops*, 48.
- Whitehead D.C. and N. Raistrick. 1993. The volatilization of ammonia from cattle urine applied to soils as influenced by soil properties. *Plant Soil* 148:43-51
- Williams, P. H., M.J. Hedley, and P.E. Gregg. 1989. Uptake of potassium and nitrogen by pasture from urine-affected soil. *New Zealand Journal of Agricultural Research*, 32:415-421.
- Wöhling, Th., Vrugt, J.A. & Barkle, G.F. 2008. Comparison of three multiobjective algorithms for inverse modeling of vadose zone hydraulic properties. *Soil Science Society of America Journal*, 72, 305-319.
- Wöhling Th., N. Schütze, B. Heinrich, J. Simunek, and G. F. Barkle. 2009. Three-dimensional modeling of multiple Automated Equilibrium Tension Lysimeters to measure vadose zone fluxes. *Vadose Zone Journal*, 8(4), 1051–1063.
- Wöhling Th., V. Bidwell, and G. F. Barkle. 2012. Dual-tracer, non-equilibrium mixing cell modelling and uncertainty analysis for unsaturated bromide and chloride transport. *Journal of Contaminant Hydrology*, 104-141:150-163.