URINE NITROGEN IN HILL COUNTRY PASTURE SOILS

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ABSTRACT

In New Zealand the traditional way of building up nitrogen (N) fertility in pastures has been to apply phosphorus (P) fertilisers to provide adequate soil fertility for legume growth, which then provides N through biological N fixation. However, the marked responsiveness of hill pastures to N fertiliser indicates that this traditional approach may be placing a serious constraint on hill country production. At the same time, there is concern that the resulting elevated soil P levels may pose some environmental risk.

Although the importance of soil N availability to hill country pasture production has long been recognised, there is surprisingly little information available on N cycling in hill country pastures. This is because the limited research funding available has been directed mainly at determining the requirements for P and sulfur (S) fertilisers, which have constituted the bulk of fertiliser expenditure in hill country. In order to develop best practice in the use of fertiliser N in hill country, information is required on N flows in the soil-plant-animal system on the contrasting topographic land units that comprise hill pastures. The role of grazing animals and particularly the N transformations associated with urine patches are very important components of these N cycles.

In this study, two field experiments were conducted at contrasting locations in North Island hill country pastures to investigate the fate of urine N. These field experiments were then followed by a laboratory incubation experiment that sought to clarify the effect of soil properties on subsequent transformations of urine N. The experimental results were then used, together with data from the literature, to model the N cycle for hill country pasture. In addition, to assess the N availability in hill pastures, an *in situ* N measurement technique using ion exchange resin membrane spikes was developed and evaluated.

The first preliminary field experiment was carried out at the AgResearch Grassland hill country research site in Waipawa, North Island, New Zealand from 09 June 1999 to 29 October 1999. The major soil type was Waipawa Stony Silt Loam (Pallic Soil). Three synthetic urine treatments (0, 200, 400 kg N/ha) were applied in a randomised complete block design and the experiment was repeated in a flat campsite and a steep site. At 1

day after urine application (DAUA), the increase in the soil mineral N pool was close to or greater than the quantity of added urine N. The dominant form of mineral N throughout the experiment was NH_4^+-N. This suggested that nitrification rates were low and that leaching losses of NO_3^--N would therefore be low. Only 18-27% of the urine N was recovered by the pasture. Estimates of the loss of urine N by ammonia volatilisation were large, ranging from 21-34% of added urine N. At the end of the experiment (142 DAUA), 34 -50% of added urine N appeared to have been immobilized into complex organic matter.

The second field experiment was carried out at Ballantrae AgResearch hill country research station from 14 July 2000 to 12 December 2000. The soil was Ngamoko Silt Loam (Brown Soil). Three different rates (0, 280, 560 kg urine N/ha) of synthetic urine were applied as treatments and the experiment was repeated as a randomised complete block design on a flat campsite and a steep slope. Shortly after application, recovery of urine N as soil mineral N was greater than 100% (113-141%) in the flat site. This increase in mineral N corresponded to a decrease in mineralisable N, suggesting organic matter mineralisation after urine application. During the first month after urine application, NH_4^+-N was the dominant form of mineral N, but during the second month, NO_3^--N was the dominant mineral N form. At the end of the experiment (88 DAUA), urine N recovery as mineral N was very low, ranging from 0-3%. The rate of nitrification after urine application was higher in flat campsites than in steep slopes. Soil NO_3^--N levels in the 0-10 cm soil depth in urine-treated plots at both sites decreased considerably between 30 and 45 DAUA. A simple model developed in Microsoft Excel suggested that substantial leaching of urine N (9-33% of added urine N) was likely to have taken place. Urine N recovery by herbage in this experiment was low (1-14% of added urine N). Estimates of the loss of urine N through volatilisation were large, ranging from 24-51% of added urine N. At the end of the experiment the amounts of urine N estimated to have been immobilised into the soil organic matter ranged from 8-57% of that added.

A laboratory incubation experiment was conducted using four soils collected from the flat and steep sites of the field experiments at Waipawa and Ballantrae together with three other soils collected from lowland sites (Kairanga silt loam, Karapoti silt loam and Manawatu sandy loam (Fluvial Recent Soils)) that had received substantial quantities of

excretal N over several years. Field moist soil, equivalent to a weight of 100 g of dry soil, was placed in each of 36 small plastic cups for each soil type. Urine was collected from four cows during milking two weeks before the experiment. Urine was applied to 18 cups of each soil at the rate of 6 mL of urine/100 g dry soil (40 mg urine N/100 g dry soil). The remaining 18 cups were used as controls. No solution was added to the control cups.

In contrast to the field experiments, there was little evidence of an initial priming effect, with mineral N levels 3 DAUA ranging from 64-81% of added urine N. Nitrification rates were highly variable (0.3 to 18.3 μg NO_3^--N/g soil/day) across the seven soils. All lowland soils had higher nitrification rates than hill soils, while those soils collected from campsites had higher nitrification rates than soils collected from steep slopes. Although nitrification could account for most of the disappearance of soil NH_4^+-N from 3-45 DAUA, it was evident that mineralisable N and soil microbial biomass N also increased after urine application.

A simulation model of a hill country N cycle developed in Microsoft Excel confirmed the importance of urine N in hill country pastures. The model indicated that N outputs in animal products, together with losses through ammonia volatilisation and leaching from urine patches were likely to exceed the N inputs to hill pastures by legume N fixation, non symbiotic fixation and atmospheric deposition. This may be the reason for the observed high N responsiveness in hill country pastures. Pasture utilisation and excretal distribution in the paddock were the most important factors influencing the overall N balance in the paddock. More work is required to obtain information on these parameters in hill country pastures.

The *in situ* N measurement technique using ion exchange resin membrane spikes proved to be a useful approach to monitoring the continuous changes in soil mineral N in the field experiments as well as in the incubation experiment. Resin spikes were able to detect apparently real differences in the availability of soil N - even when the standard 2 M KCl extraction could detect no differences. The potential of resin spikes to detect spatial variability in soil N status was also demonstrated.

A simple model developed in Visual Basic in Microsoft Excel to simulate the N adsorption by resin spike in soils demonstrated that soil moisture, soil temperature, soil N concentration and the time the resin spike is in the soil are all major determinants of the amount of N adsorbed to resin in soil.

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INTRODUCTION

In New Zealand grazed pastures, nitrogen (N) fixation by clover is the traditional method of supplying N to the grasses that make up the bulk of the pasture sward. Nitrogen fixed by clovers is contained initially in the growth of the clover plant itself. Eventually however, most of the fixed N is recycled back into the soil, either through the breakdown of plant litter, roots and nodules, or by urine and faecal return from grazing animals. The N then becomes available for uptake by grasses.

The amount of nitrogen fixed by clovers is roughly proportional to clover growth (Ball and Field (1982). In many circumstances in hill country, this can be very low. In an experiment conducted at the AgResearch Ballantrae Research Station, the average quantity of N fixed by legumes in one year on a low-fertility, unimproved, North Island hill country site was estimated to be only 13 kg N/ha (Grant and Lambert, 1979). Although under summer-wet conditions, such as exist at Ballantrae, clover growth and N fixation can be increased markedly by increasing soil fertility, in summer-dry climates white clover may not persist because of moisture stress (Gillingham *et al.*, 1998) – despite high levels of soil P and S. In such situations pastures can be critically short of available N.

Recognising this problem, many experiments have been conducted in hill country pastures to assess possible N responses. The general conclusion has been that large N fertiliser responses are obtainable in most hill pastures (Luscombe, 1980; Ball *et a*l., 1982; Lambert and Clark, 1986; Clark and Lambert, 1989; Gillingham *et al.*, 1998; Blennerhassett, 2002). Gillingham *et al.* (1998) considered selective N fertiliser application, taking slope and aspect into account. They suggested that application of "normal" rates of P fertiliser to south aspects and moist north slopes and application of greatly reduced rates of P fertiliser, together with strategic applications of N fertiliser, on steep north- facing slopes, would be the most efficient fertiliser policy. Taking this concept further, Gillingham *et al.* (1999) suggested that the use of Global Positioning

Systems (GPS) and Geographic Information Systems (GIS) had the potential to improve greatly the efficiency of fertiliser use in hill country. These technologies also have the potential to reduce the environmental impacts of fertiliser use.

However, to adopt these types of advanced, differential fertiliser application on hill country farms requires more detailed information on pasture productivity and associated pasture responsiveness. In particular, more information is required on the N fertility on contrasting topographic land units.

Detailed studies of N flows in hill country pastures, especially in summer-dry hill pastures are scarce. The wide variation in microclimates and topographic units associated with hill country pastures make it difficult to achieve a complete picture of the N cycle in a single experiment. Therefore, in recent years more emphasis has been placed on detailed studies of individual aspects of the main N cycle in hill country.

The influence of fertiliser history and climate regime on pasture production and N accumulation in hill soils, was studied by Moir (2000). The constraints imposed on pasture growth by N deficiency in hill country, were studied by Blennerhassett (2002).

Nitrogen recycling through animal excreta has long been considered beneficial to the fertility of grazed pastures (Sears *et al.*, 1965; Levy, 1970). Nevertheless, recent research has indicated that grazing animals can cause substantial N outgoings from highly productive, flat land pastures through losses from urine patches (Ball *et al.*, 1979; Carran *et al.*, 1982; Ball and Keeney, 1983). In contrast, Sakadevan *et al.* (1993) indicated that N is conserved in urine patches of hill country pastures in New Zealand and Lambert *et al.* (1982a) also pointed out that hill soils are strongly N retentive because of their high C/N ratios.

The experiments described in this thesis attempt to clarify the apparently contrasting findings described in the previous paragraph, and to explore whether there are processes operating in urine patches of hill pastures that are different from those in more intensively farmed environments.

A major obstacle to gaining a good understanding of N dynamics in hill country pastures is the absence of a convenient way of measuring the pool of available soil N. The widely used extraction with 2 M KCl requires quick analysis after sampling. This is a constraint in experiments conducted at remote sites. In addition, the measure only gives a "snapshot" of the quantity of available N in the soil at the time of sampling. As will be pointed out later in the thesis, although the pool of mineral N extracted by 2 M KCl is usually small, it is extremely dynamic. There are large inflows and outflows of N over short time periods. A simple measurement of the size of the mineral N pool, at one point in time is often therefore, not a good indication of the actual N fertility of the soil.

In an attempt to overcome some of these problems, an *in situ* N measuring method by ion exchange resin membrane spikes was developed. The possible utility of the technique was assessed in preliminary field studies and by using simulation modelling.

The overall objectives of this thesis were therefore to examine the fate of sheep urine in hill country pastures, using a range of established and novel measurement techniques. The information so gathered is then used to improve the quantitative modelling of N cycle in hill country pastures.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This literature review aims to familiarise the reader with the objectives of the series of experiments described in this thesis, and how the objectives were developed to fill the information gaps in the available literature. However, coverage of the relevant literature in this chapter is brief, with the main aim being to illustrate the broader concepts inherent in New Zealand hill country pastoral farming, and in particular variations in the above-ground nitrogen balances between different topographic units. More detailed reviews of the literature relevant to each experiment are contained within the introductions of individual chapters.

2.2 New Zealand hill country

New Zealand " hill country" is defined as steep non-arable hills below 1000 m, which cover about 5 million ha (40% of farmland) in the North Island and 4.9 million ha (51% of farmland) in the South Island (Joblin, 1983; White, 1990). Land is defined as moderately steep when the ground slope is between 21° and 25°, steep between 26° and 35° and very steep when the ground slope is >35° (NZLRI, 1979).

Campbell (1951) classified New Zealand hill country into three different types: i.e., wet hill country, dry hill country and tussock hill country. In the North Island, dry hill country extends the entire length of the east coast in a narrow strip 64 km wide in the Wellington province, narrowing to 16 km in the direction of East Cape (Campbell, 1951). This region has lower rainfall than wet hill country, with hot dry summers and occasional rains from the north-east.

At present this land resource carries 35% of the total sheep in New Zealand and 20% of the total cattle. These animals are on 6800 farm holdings, representing 30% of New Zealand sheep and beef farms (Mackay *et al.*, 1993). Sheep breeds vary widely but

Romney and Romney crosses predominate. Aberdeen Angus is the predominant beef breed although Herefords, Friesians, and various crosses of these breeds are popular.

2.2.1 Topography

Hill country topography varies from rolling to steep although most farms have at least a small area of relatively flat land. Hill country slopes may be moderate or steep and they differ in aspect and micro-topography. Contrasting aspects give distinctly different microenvironments. Variation in the amount of direct solar radiation received by sloping surfaces is one of the main reasons for the existence of microclimate differences in hill country. Seasonal temperature and moisture regimes vary markedly between warmer (north–facing) and cooler (south–facing) slopes.

Lambert (1973) investigated the differences in climate, soil and pasture between aspects in hill country. He observed different soil nutrient levels on various aspects, arising through nutrient transfer by grazing animals and the differential action of climate during soil formation. Furthermore, he noted different moisture levels on the various aspects, resulting from differential evapotranspiration (ET) rates and leading to different degrees of moisture stress, especially during the summer/autumn period. Lambert (1973) agreed with Suckling (1966), that hill country should, where practicable, be fenced with regard to aspect and where large scale variation due to aspect exists, fertiliser could be spread at varying rates as indicated by soil nutrient status. Gillingham *et al.* (1998, 1999) suggested adoption of differential fertiliser application to hill country farms using the information on pasture productivity from contrasting topographic land units and precise aerial fertiliser application with the use of Global Positioning Systems (GPS) and (GIS) Geographic Information Systems.

2.2.2 Soil

Gillingham (1978) described hill country soils as follows. "North Island hill soils range from Yellow-grey earths in parts of Hawkes Bay and Wairarapa to Northern Yellow-brown earths in Northland. The central North Island was originally covered by various ash showers. Rhyolitic ash blanketed the central and eastern North Island producing "Bush sick" or cobalt-deficient pumice soils while mainly andesitic ash formed Yellow–

brown loams in the remainder of the ash-covered area. Ash was lost from steep slopes and so steep land soils are derived almost entirely from underlying mudstone, siltstone, and sandstone parent materials (Steep land yellow-grey earths and Central yellow-brown earths)"

The nutrient status of hill soils is generally poorer than that of intensively farmed lowland soils (Mauger, 1979). Most North Island hill soils have low nutrient availability, especially N and P and sometimes S, K and Mo (Lambert *et al.*, 1982a). Many top soils in the moist hill country of the lower North Island contain very large quantities of nitrogen, rendered largely unavailable by the relatively wide carbon: nitrogen (C/N) ratio of the soil organic matter present (Ball *et al.*, 1982).

2.2.3 Pasture composition

Pasture botanical composition is one of the most suitable biophysical indicators of sustainability of North Island hill pastures (Lambert *et al.*, 1996). Machado (1994) observed high variability of pasture composition in his experiment conducted at seven different sites at the Ballantrae AgResearch hill country research station. The sites varied from undeveloped, unfertilised hill pasture containing only low-fertility adapted grasses and weeds to a highly productive sward with a high proportion of high fertility responsive grasses and white clover. The differences in plant species composition and production are a product of soil and environmental factors as influenced by topography and animal grazing and treading effects (Gillingham and During, 1973; Grant and Brock, 1974). Grant and Brock (1974) indicated that differences in pasture composition due to soil properties were not great, except where they appeared to be related to differences in soil-moisture characteristics. They observed that *Lolium perenne* (Perennial ryegrass) and *Trifolium repens* (White clover) were most frequent on flat to low slope areas, *Notodanthonia* common on steeper, drier sites and *Holcus lanatus* (Yorkshire fog), *Lotus pedunculatus* (Lotus), rushes and sedges on wetter sites.

Macfarlane and Sheath (1984) outlined the importance of flexibility in legumes on dry hill country, in terms of a wider range of flowering dates and high seed production, so that they can persist and produce under the variable soil moisture conditions. Ledgard *et al.* (1987) observed marked seasonal differences in legume growth. They observed

high growth of subterranean clover in spring, white clover in summer and autumn in campsites, and lotus in winter. The optimum content of legumes in hill pasture should be up to 20-25% of the sward (Suckling, 1959).

2.2.4 Nitrogen use in hill country

Until recently, most New Zealand hill country pastures have relied completely on legumes (mostly clover) to supply N by atmospheric N fixation. Phosphorus fertilisers are applied to pastures to produce satisfactory clover growth. Nitrogen fixed by clover is initially used in the growth of the clover and most of the fixed N is then recycled back to the soil, either through breakdown of plant litter, roots and nodules or by urine and faecal return from grazing animals (Tillman, 1993). Sears (1953) indicated that ingestion by stock with subsequent return in animal excreta is the major pathway of transfer of N from legumes to associated grasses. However, N supply from this low cost source is often limited in hill country by inadequate moisture for vigorous clover growth and persistence, especially during spring and summer. In summer-dry climates, white clover does not persist, and annual clovers form the basis of pasture legume content (Gillingham *et al.*, 1998). These annual clovers make a small contribution to annual pasture production and associated N fixation (Brock, 1973). Consequently, direct alleviation of N deficiency by fertiliser application has been suggested.

Several studies have observed large N fertiliser responses in hill country pastures; 43 kg DM/kg N (Gillingham *et al.*, 1998), 37.8 kg DM/kg N (Ball *et al.*, 1976), 28 kg DM/kg N (Lambert and Clark, 1986), 5-25 kg DM/kg N (Luscombe, 1980). Morton *et al.* (1993) reported that many Wairarapa hill country sheep and beef farmers apply N fertilisers at a mean rate of 20 kg N/ha/yr. This appears to be a strategy that is increasingly popular, though driven by product prices.

Gillingham *et al.* (1998) suggested adoption of a differential fertiliser application policy on hill country pastures. They suggested application of P and S to south aspects and moist north slopes, which have adequate clover content in the pasture. In contrast, steep, north-facing slopes should receive N fertiliser, and only very limited P, because of low legume contents. Furthermore, as mentioned in Section 2.2.1, use of GPS and

GIS for precise aerial fertiliser application on hill country was proposed. They highlighted from their desktop study that greater pasture and animal production can be achieved in this way than from the same amount of fertiliser applied uniformly over a block of typical hill land. However to adopt this type of advanced fertiliser policy there needs to be detailed information on N fertility in each micro-topographic unit of hill country.

2.3 Nitrogen balances in different topographic units of hill country

Farming is a profession that needs a detailed understanding of the interactions between plants, climate and soil as well as the influence of biotic factors above ground (man and grazing animals) and the soil fauna and flora (worms, bacteria, fungi etc.) below ground. The main challenge the hill country farmer faces is to provide adequate nutrients to match pasture demands whilst maintaining the soil fertility for future growth. No ecosystem, whether natural or managed is completely 'leak-free' but the opportunities for loss increase with increasing input, especially of N (in its various forms) where animal production is involved (Jarvis, 1999).

A nutrient balance provides detailed information on the inputs, outputs and internal recycling of the nutrient. The cycle usually includes a number of compartments, e.g. soil, crop, animal, and depending upon the level of detail required, these may be further subdivided into different pools. At the simplest level, a budget/balance is a nutrient accounting process that sums all the inputs and outputs to a given defined system. The need for detail and accuracy in budget compilation depends solely on the purpose of the balance (Jarvis, 1999).

The aim of this section is to develop simple above ground N balances for the main topographic units in summer-dry hill country (north aspect-easy, north aspect-steep, south aspect- easy, south aspect-steep and flat campsite) as a way of integrating available data in the literature (Fig. 2.1 and 2.2). These N balances are developed for a notional 1 ha hill country paddock with the same slope distribution as that studied by Gillingham (1978); 12.2% campsites, 45.5% easy slopes (25° slope) and 42.3 % steep slopes (45° slope). The same division of slopes was considered for notional 1 ha north and south facing paddocks. The paddocks were assumed to be located on summer dry hill country in Hawkes Bay at the AgResearch Waipawa research station.

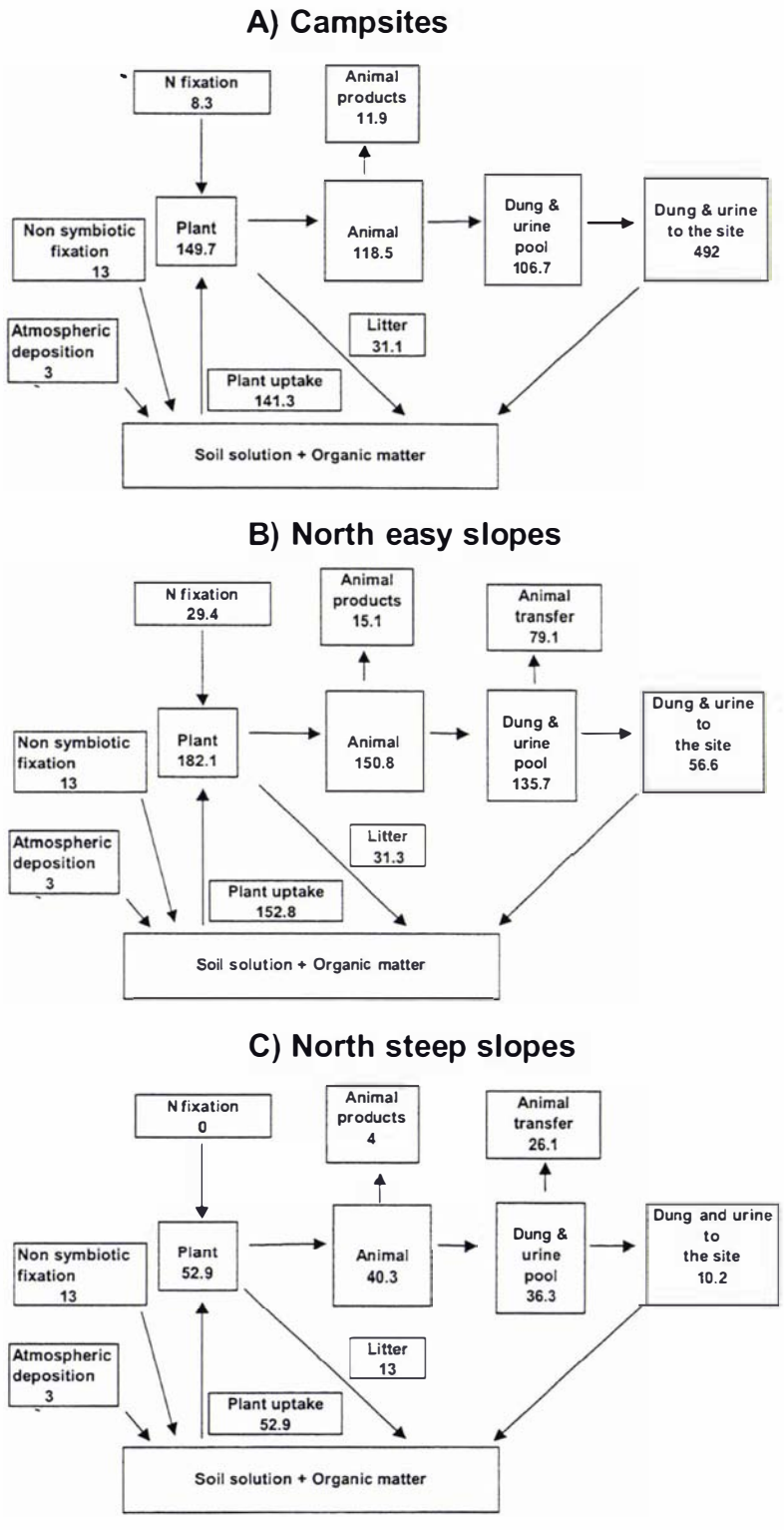


Fig. 2.1 Above-ground N balances for a sheep grazed hill country paddock with a north facing aspect. All values are kg N/ha/yr.

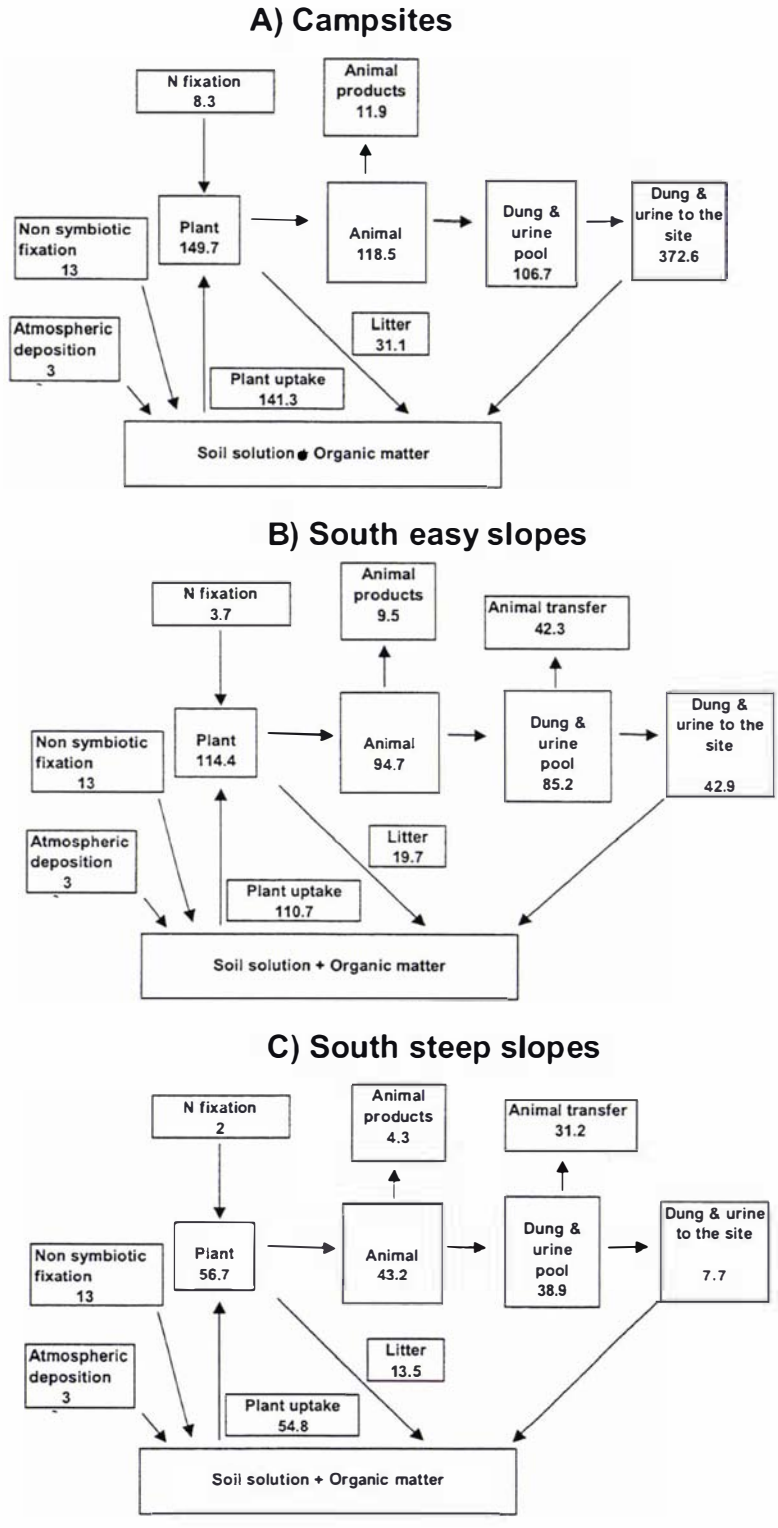


Fig. 2.2 Above-ground N balances for a sheep grazed hill country paddock with a south facing aspect. All values are kg N/ha/yr.

2.3.1 Pasture N uptake

The values for the pasture N uptake at each site were estimated from measured pasture production and pasture N concentration (N%) data of Blennerhassett (2002) at the Waipawa AgResearch research station. The values were taken from the control plots of low P fertility farmlets, which received sufficient superphosphate to maintain the original Olsen P status of 9 μg/g soil. The measured DM production by Blennerhassett (2002) consisted of both grass and clover DM. Hence to estimate the N uptake from soil the amount of fixed N (see Section 2.3.2) was deducted from the estimated total plant N uptake calculated by multiplying DM production and pasture N concentration.

On both the north and south aspects, N uptake was less on steep slopes than easy slopes and campsites. This reflects the differences in pasture production between steep slopes and campsites. Previous studies have also shown that flatter campsites produced higher DM production than steep slopes (Suckling *et al.*, 1959; Gillingham, 1978; Ledgard *et al.*, 1987).

Ledgard *et al.* (1982b) observed greater pasture growth on warmer, north–facing slopes than on colder, south-facing aspects. This was in agreement with Blennerhassett's (2002) data for easy slopes. However, Gillingham (1974) reported that slope accounted for more of the variability in pasture growth than did aspect.

2.3.2 N fixation

Symbiotic fixation of atmospheric nitrogen by *Rhizobia* in nodules on the roots of clovers is a key factor in the grassland systems of New Zealand. No country is more dependent upon the grass/clover association than New Zealand (Lee, 1971). The level of biological N fixation by pasture legumes can vary greatly. Annual N fixation in developed lowland pastures is around 184 (range 107-392) kg N/ha (Hoglund *et al.*, 1979) and N fixation through symbiotic fixation in unimproved North Island hill country was around 13 kg N/ha (Grant and Lambert, 1979). Seasonal correlations observed by Hoglund *et al.* (1979) indicated temperature to be the most influential component (negative in summer and positive in winter) of climate on N fixation.

Factors affecting N fixation have been extensively reviewed by Ledgard and Steel (1992).

Nitrogen fixation (kg N/ha/yr) by legumes was assumed to be proportional to clover growth. The proportionality constants varied between campsites and sloping sites (Ledgard *et al.*, 1987). The N fixation in the current N balances (Fig. 2.1 and 2.2) was estimated by multiplying legume dry matter production by the factors (0.040 for steep slopes and 0.030 for camp sites) suggested by Ledgard *et al.* (1987). The multiplication factors were developed by Ledgard *et al.* (1987) based on legume N concentration (mean 4.9%) and the proportion of legume N fixed from the atmosphere (P_N) (82% for steep and 62% for campsite). Lower P_N values in campsites were associated with high inorganic N levels, which were largely a result of transfer of dung and urine by grazing sheep to these sites.

The data on annual legume DM production (kg/ha) in control plots of low P farmlets of Blennerhassett (2002) were used in the current N balance. Interestingly, Blennerhassett (2002) did not observe any legume production on dry North-steep slopes. However, the highest legume production was observed in the North-easy slopes. Similarly, on the southerly aspect, more legume production was observed on campsites than slopes (Table 7.1 of Chapter 7).

The annual values for N fixation estimated in the current N balance (Fig. 2.1 and 2.2) were much less than the estimations (54-85 kg N/ha/yr) by Ledgard *et al.* (1987). In their experiment, they observed high legume DM production as the experimental area had received 350 kg/ha of superphosphate annually since development into pasture, about 20 years previously. In addition, the experimental site of Ledgard *et al.* (1987) was in moist hill country.

In a recent review Ledgard (2001) reported annual legume N fixation values of 15, 55 and 30 kg N/ha/yr for steep (>20° slope), easy (10-20° slope) and campsites (0-10°) respectively within hill country.

2.3.3 Non-symbiotic N fixation and atmospheric deposition

Grant and Lambert (1979) suggested that in a poorly developed hill country pasture, N fixation by non-symbiotic organisms and N in rainfall are together as important as clover N fixation. They estimated about 21 kg N/ha/yr for non-symbiotic N fixation and atmospheric deposition using the intercept of a regression between N fixation and legume DM production. Values for non-symbiotic fixation (13 kg N/ha/yr) and atmospheric deposition (3 kg N/ha/yr) in the current N balance, were obtained from the N balance reported for unimproved hill pasture by Lambert *et al.* (1982a).

2.3.4 Pasture utilisation

Under sheep grazing systems, poor pasture utilisation can occur because sheep tend to preferentially graze pasture on tracks or easy slopes rather than on banks or steep land zones (Gillingham, 1982; Clark *et al.*, 1984).

Clark *et al.* (1984) found in their study that ryegrass tillers on slopes < 12° were grazed more frequently (number of grazing events of a marked grass tiller during a given period) and severely (leaf length grazed per tiller) by sheep than those on slopes >25°. Under New Zealand conditions, the utilisation or consumption of the pasture that is produced can range from 40% to 90% depending on the stocking rate and method of grazing (Quin, 1982).

The pasture utilisation (%) for the current N balance was taken from Gillingham (1978). He estimated the annual pasture utilisation as 79.2%, 82.8%, and 76.2% for campsites, easy slopes and steep slopes respectively. This pasture utilisation was measured in a paddock that had a topography of 12.2% campsites, 45.5% easy slopes and 42.3% steep slopes. Pasture utilisation in a second paddock, that had 20.1% campsites, 55.7% easy slopes and 24.1% steep slope was 77.2%, 86.5% and 80.8% respectively (Gillingham, 1978).

2.3.5 N remaining in pasture litter

Gillingham (1978) defined litter as dead plant material present in the pasture below grazing level at the end of grazing. This included both loose and attached material. It also included any whole plants that had been uprooted during grazing, then rejected.

Nitrogen remaining in the litter was estimated for the current N balance by deducting the animal utilisation from the pasture N uptake. Radcliffe (1982) pointed out that herbage on flatter areas and wetter southerly aspects tended to decay faster than on north and steep slopes. Thus, accumulation of pasture litter was greater on northern steep slopes than on wetter, flatter areas. This would again lead to grazing discrimination between micro-sites as animals choose green herbage.

2.3.6 N in animal products

The N removed in animal products was estimated using the proportion of animal ingestion (41 kg N/ha/yr) that was removed in animal products (4 kg N/ha/yr) reported by Lambert *et al.* (1982). They calculated the N removal in animal products using the average N (2.5%) content of products (meat and wool). Gillingham (1978) also assumed that 10% of P intake by animals was lost from the grazing area in animal products.

2.3.7 Dung and urine N

As noted in the previous section, only about 10% of the pasture N ingested by grazing animals is retained in animal products. The reminder is returned in excreta to the paddock. The total amount of excretal N returned to the notional 1 ha paddock is calculated in Table 2.1 for the north-facing paddock.

Table 2.1 Calculation of amount of dung and urine N derived from on each slope category in the notional 1 ha paddock.

Site (% area)	Ingested N (kg/ha)	N retained in animal products (kg N/ha)	N in dung & urine pool (kg N/ha)	Dung & urine N derived from each slope category within the whole paddock
Campsites (12.2%)	118.5	11.9	106.6	106.6 x 0.122 = 13.0 kg N
Easy (45.5%)	150.8	15.1	135.7	135.7 x 0.455 = 61.7 kg N
Steep (42.3%)	40.3	4.0	36.3	36.3 x 0.423 = 15.4 kg N
Total dung & urine N deposited to 1 ha paddock				90.1 kg N

In hill country pastures the stock tend to camp on flat areas of land and significant quantities of nutrients are transported to these areas through dung and urine from the steeper slopes where the sheep graze (Rumble and Esler, 1968; Gillingham and During, 1973; Rowarth and Gillingham, 1990). Gillingham (1978) measured the dung P distribution in two hill country paddocks (Section 2.3.4). His data were used to estimate the proportion of the total excreta deposited on the whole paddock that were deposited on each slope category.

As noted earlier, the present N balance was developed for a notional 1 ha paddock, that had 12.2% campsites, 45.5% easy slopes, 42.3% steep slopes. This was the same topography as the paddock studied by Gillingham (1978). The measured proportions of total excreta deposited on each of the slope categories in the paddock of Gillingham (1978) were 66.6%, 28.6% and 4.8% for campsites, easy slopes and steep slopes respectively. These same proportions were assumed for the present study.

Using these data for excretal return, the quantities of dung and urine N returned to each slope category within the notional 1 ha paddock were calculated as follows.

Quantity of dung & urine N deposited on campsite =(66.6/100) (90.1) kg N
Quantity of dung & urine N per ha of campsite = ((66.6/100) (90.1)) / 0.122
=491.8 kg N/ha on campsites

Quantity of dung & urine N deposited on easy slope= (28.6/100) (90.1) kg N
Quantity of dung & urine N per ha of easy slope = ((28.6/100) (90.1))/0.455
=56.6 kg N/ha on easy slopes

Quantity of dung & urine N deposit to steep slope =(4.8/100) (90.1) kg N
Quantity of dung & urine N per ha of steep slope =((4.8/100) (90.1))/0.423)
=10.2 kg N/ha on steep slopes

2.3.8 Above ground N balance in hill country

The above ground N balance (Fig. 2.1 and 2.2) developed in this section indicates that N cycling in hill country is more controlled by slope than aspect. However, seasonal variations were not considered in this balance. In winter more pasture growth can be expected on north aspects due to better sunlight while in summer more pasture growth can be expect on southerly aspects due to less moisture stress.

Table 2.2 N balance on different land slopes within a notional sheep-grazed hill pasture. (Values are based on Fig. 2.1 and Fig. 2.2).

	North aspect			South aspect		
	Campsite	Easy slope	Steep slope	Campsite	Easy slope	Steep slope
Inputs (kg/ha/yr)						
Legume N fixation	8	29	0	8	4	2
Non-symbiotic N fixation	13	13	13	13	13	13
Atmospheric. deposition	3	3	3	3	3	3
Total Input	24	45	16	24	20	18
Outputs (kg/ha/yr)						
Animal products	12	15	4	12	10	4
Animal transfer	-385	79	26	-266	42	31
Total output	-373	94	30	-254	52	35
N surplus (kg/ha/yr)	+397	-49	-14	+ 278	-32	-17

Estimates of N inputs, removal by grazing, and transfer in excreta reveal the existence of two extreme topographic units in hill country pasture. They are net N-gaining flat campsites and net N-losing sloped sites. Ledgard (2001) reported a N balance for a hill country sheep-grazed pasture system with 45% of the area as steep slopes (>20°), 40% as easy slopes (10-20°) and 15% as campsites. He reported that steep slopes have a negative N balance (- 25 kg N/ha/yr) while easy slopes (+15 kg N/ha/yr) and campsites (+190 kg N/ha/yr) have a net gain of N. These results will be discussed in detail in Chapter 7.

When the N balances for each slope category are adjusted for the proportion of the paddock they occupy, and are then summed to give an overall N balance for the notional 1 ha paddock as a whole (Table 2.3), it appears that about 60-70% of the N input accumulates in the paddock (Table 2.3) and this accumulation is in the flat sheep campsites.

Table 2.3 N inputs and N surplus in the notional 1 ha hill country paddock. Data on N inputs per ha and N surplus per ha are from Table 2.2 and proportions of land in each slope category are from Table 2.1 and Gillingham (1978)

Site	N inputs kg N/slope category/yr	N surplus kg N/slope category/yr
North aspect paddock		
Campsite	24 x 0.122=03	+ 397 x 0.122 = + 48
Easy slope	45 x 0.455=21	- 49 x 0.455 = - 22
Steep slope	16 x 0.423=07	- 14 x 0.423 = - 06
Total/1 ha paddock/yr	31	+ 20
South aspect paddock		
Campsite	24 x 0.122=03	+ 278 x 0.122 = + 34
Easy slope	20 x 0.455=09	- 32 x 0.455 = - 15
Steep slope	18 x 0.423=08	- 17 x 0.423 = - 07
Total/1 ha paddock/yr	20	+ 12

The data presented above demonstrate importance o f the spatial distribution of excreta within the paddock in determining the above ground N balance. Excretal N can also influence the overall N balance through the leaching losses from urine patches (Carran *et al*., 1982; Ball and Keeney, 1983). However, although such leaching losses are well recognised in intensive, flat land pasture systems, Sakadevan *et al*. (1993) indicated that N appeared to be conserved in urine patches of hill country pastures in New Zealand. Lambert *et al*. (1982a) also pointed out that hill soils are strongly N retentive because of their high C/N ratios (14.5 average, but 12-17 depending on micro topography). Thus, whether the apparent N surplus observed from the above ground N balance (Table 2.3) actually eventuates will depend on the fate of excretal N. Research on the fate of urine N deposited in these landscapes will provide important information on the N cycle in hill country pastures.

2.4 Summary of literature review

Hill pastures have highly variable micro-topographic units with associated variation in pasture production and pasture composition. The physiographic factors of aspect and slope are major determinants of this variation through their influence on microclimate, stock grazing behaviour and soil fertility.

Most studies suggest that N cycling in hill country pasture is very inefficient. Recently, some scientists have suggested improving hill country N efficiency by differential N fertiliser application. In order to optimise this approach, there is a requirement for detailed information on N cycling in soil-plant-animal systems within the micro-topographic units of hill country.

Estimated above-ground N balances for different topographic units (Section 2.3) revealed the existence of two major units in hill country pasture in terms of N cycling. They are flat stock campsites and steep slopes. Significant quantities of N are transported to campsites from the sloped sites resulting in net N accumulation in campsites and net N loss from slopes. However, when the total paddock is considered, the above ground N balance revealed an apparent surplus of 60-65% of the N input per year. The actual extent of this apparent N surplus will depend on the fate of excretal N. The traditional assumption has been that New Zealand hill pastures are N conservative

systems, unlike intensive dairy farms that lose much of the N input. However, little experimental evidence is available on the fate of urine N in hill country pasture to justify this assumption.

The aim of the subsequent experimental chapters of this thesis is to study the fate of urine N in these hill pastures and to investigate the sustainability of the N cycle. Thus, in Chapter 4 a new technique for measuring soil mineral N using ion exchange resin is developed and evaluated.

In Chapter 3 and 5 the fate of urine N applied to hill country pastures is measured at contrasting locations.

In Chapter 6 a glasshouse incubation study is conducted to assess the effect of differences in soil organic matter on the transformations of urine.

Finally in Chapter 7, the information derived in earlier chapters is incorporated in a quantitative model of the N cycle in sheep-grazed hill country pastures.

CHAPTER 3

FIELD INVESTIGATION OF THE FATE OF URINE NITROGEN ON A SUMMER-DRY HILL COUNTRY PASTURE

3.1 Introduction

The literature review presented in Chapter 2 revealed that North Island hill pasture systems are characterised by steep slopes with marked aspect and micro-topographical variation. These topographical variations complicate studies of nutrient cycling in hill country pasture. However, most studies emphasised the dominant effect of grazing animals on the movement of nutrients through the soil-plant-animal system. Variations in land slope influence animal grazing and camping behaviour and lead to net accumulation of N in campsites and net N depletion in steep slopes. However, there are questions with respect to the efficiency of N cycling through the excreta of animals. Though there are some studies on the fate of urine, they are mainly confined to lowland dairy-based systems and very little research has been done on hill country sheep-based systems.

In recent years, Gillingham *et al.* (1998, 1999) have questioned the cost effectiveness of large additions of P fertilisers to sunny aspects of hill country pasture where legume growth is restricted severely by moisture stress. Instead, these workers have suggested that application of nitrogen fertiliser to these areas may be beneficial. It is however necessary to understand completely, the nitrogen cycle operating in the system to recommend such idea. The fate of urine N will be a vital component of this cycle. The aim of the experiment described in this chapter is to investigate the fate of urine N in hill country pastures.

3.2 Literature review

3.2.1 Nitrogen cycling through animals

The grazing animal affects N balances in pasture by first consuming much of the herbage produced. Then the N contained in the consumed herbage is either retained within the animal, transferred to non-productive areas, or returned to the soil in a spatially non-uniform fashion in dung and urine. For sheep grazing grass/clover pastures in New Zealand, 70-75% of the excreted N occurred in the urine (Sears, 1950). Barrow and Lambourne (1962) found that for sheep ingesting herbage containing more than 4% N, 80% of the N was excreted as urine whereas with herbage containing 0.8% N, the proportion of the excreted N present in the urine was only 43%.

3.2.2 Urine N

Urine is a concentrated aqueous solution containing N, sodium (Na), potassium (K) and sulfur (S) as the dominant inorganic elements and typically has a pH value of 8 to 9 (Haynes and Williams, 1992). Haynes and Williams (1993) comprehensively reviewed the information about urine N. They reported that sheep urinate 18-20 times per day. A single urination is normally 0.1 to 0.18 litres and the area covered by single urination is approximately 0.03-0.05 m^2. They further indicated that the N concentration in urine is around 10 g/litre and the equivalent application rate is 500 kg N/ha. Doak (1952) described the constituents of urine N as outlined in Table 3.1.

Table 3.1 The partition of urinary nitrogen (Doak, 1952).

Constituents	% Total urine N
Urea N	76.4
Allantoin N	4.1
Hippuric acid N	2.6
Creatine and Creatinine N	1.5
Amino N	12.4
Ammonia N	0.7

3.2.3 N transformations in the urine patch

Urine affected areas are characterised by large inputs of biologically labile N, with transformations and transport processes operating at high rates (Carran *et al.*, 1982). Nitrogen transformations that occur in urine patches cause large fluctuations in the pH, ionic composition and ionic strength of the soil solution in the urine patch (Carran, 1988; Haynes and Williams, 1992). Early work stressed the positive effects of urine N return to pasture herbage yield (Sears, 1956). This increase in herbage yield results from a speeding up of the N cycle through the conversion by the animal of organic nitrogen in plant material into readily available N in urine.

More recently, the potential for large losses of N from pasture via animals has been reported (Ball *et al.*, 1979; Carran *et al.*, 1982; Ball and Ryden, 1984). In New Zealand, Ball *et al.* (1979) at Palmerston North in the North Island and Carran *et al.* (1982) at Gore in the South Island attempted to construct a N balance in a urine patch. Fig. 3.1 illustrates the urine N recovery (%) up to 32 days after urine application (DAUA), using data extracted from Ball *et al.* (1979) and Carran *et al.* (1982).

In the Palmerston North experiment, Ball *et al.* (1979) had two urine treatments (300 and 600 kg urine N/ha) and in Gore, Carran *et al.* (1982) used one urine treatment (300 kg urine N/ha) under two moisture regimes. In Fig. 3.1, data from the 300 kg urine N/ha treatment from Ball *et al.* (1979) and the 300 kg urine N/ha treatment on dry plots by Carran *et al.* (1982) were considered.

Constructing a mass balance for N is not easy, as it is difficult to measure all the possible N pools in the soil and all the possible pathways of N loss. In the work of Ball *et al.* (1979) and Carran *et al.* (1982) measurements were made of N taken up by pasture and lost by volatilisation. Within the soil, mineral N in the forms of NH_4^+ and NO_3^- were measured by both groups and Carran *et al.* (1982) also measured the clay-fixed NH_4^+-N.

Because the pool of organic N in the soil is so large, changes in its size through immobilisation of urine N cannot be detected in the short term. Thus, in these studies

urine N that could not be accounted for would include N immobilised in soil organic matter as well as N lost by processes such as leaching and denitrification.

In Palmerston North, Ball *et al.* (1979) observed an initial steady N recovery of 70-80% which then decreased to about 50% 32 DAUA. In contrast Carran *et al.* (1982) observed an initial increasing N recovery from 55% to >90% 18 DAUA, followed by a decrease in recovery to 85% of that added 32 DAUA.

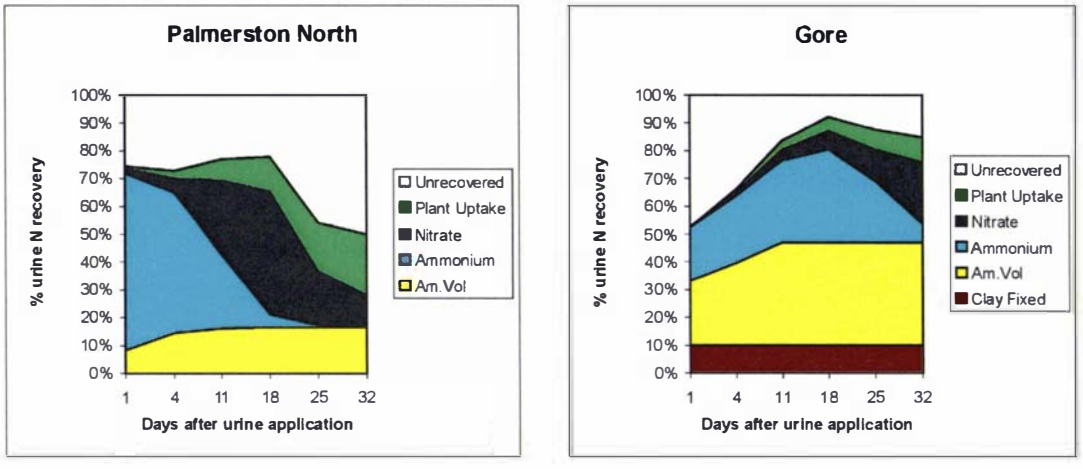


Fig. 3.1 Percentage urine N recovery in urine patches. Data extracted from Ball *et al.*, 1979 (Palmerston North) and Carran *et al.*, 1982 (Gore).

Surprisingly, 1 DAUA neither Ball *et al.* (1979) nor Carran *et al.* (1982) observed full recovery. In Palmerston North, urine N recovery at 1 DAUA was approximately 70% while at Gore it was approximately 50%. Both groups commented that this initial unrecovered urine N might have been immobilised into microbial biomass.

This view is supported by the progressive increase in recovery of urine N in Gore (Fig. 3.1). This increase in urine N recovery over time could be due to remineralisation of immobilised urine N. However, this was not apparent in the Palmerston North experiment (Fig. 3.1).

The volatilisation losses varied between the two sites. In Palmerston North, 15% of added urine N was lost as NH_3 and at Gore it was 40%.

Mineral N changes over time were very different in the two experiments. At Gore, NH_4^+-N was the dominant mineral N form until about 25 DAUA and nitrification wasn't a major N transformation process. However at Palmerston North, by 11 DAUA NO_3^--N was the dominant mineral N form. Thus, urine N losses through leaching and denitrification could be possible N loss mechanisms in the Palmerston North experiment (Fig. 3.1). During that experiment Ball *et al.* (1979) observed that all of the NO_3^--N had disappeared by day 46.

The urine N recovery by herbage was also different at the two sites (Fig. 3.1). In the Palmerston North experiment, Ball *et al.* (1979) observed that urine N recovery in herbage was 37% while at Gore, Carran et al. (1982) observed only 15%.

Inspection of Fig. 3.1 makes clear that the fates of urine N added in similar amounts in two experiments at two different sites were different. The differences observed in N transformation processes at the two sites (e.g. plant uptake, volatilisation, nitrification) are due to the differences in soil and environmental conditions prevailing at the two experimental sites. This demonstrates why it is difficult to directly apply research work done on fate of urine N in flat dairy soils to extensively-managed sheep-based hill country pastures.

3.2.3.1 Urea hydrolysis

Urea accounts for about 76% of urine N (Table 3.1). After urine deposition to the soil, the urea is rapidly hydrolysed to NH_4^+-N (Haynes and Williams, 1993).

$$(NH_2)_2CO + 2\,H_2O \longrightarrow (NH_4)_2CO_3 \longrightarrow NH_4^+ + CO_3^{2-} \quad (3.1)$$

$$CO_3^{2-} + OH^- \longrightarrow HCO_3^- + OH^- \quad (3.2)$$

The rate of hydrolysis of urea N in urine patches varies, mainly with soil temperature and to a lesser extent with soil moisture (Quin, 1977). However, even under unfavourable conditions urea hydrolysis is complete within a few days. Quin (1977) reported that under warm moist conditions, complete conversion to NH_4^+ took place

within 24 hours. Sherlock and Goh (1984) calculated half-lives of urine urea as 3 and 4.7 hours, under summer and autumn conditions respectively. Haynes and Williams (1993) indicated that urea in animal urine hydrolyses extremely rapidly after release from the animal.

The urea in urine is hydrolysed by urease, a microbial enzyme that is widespread in soil (Bremner and Mulvaney, 1978) and on plants and plant litter (Freney and Black, 1988). Due to urea hydrolysis, rapid rises in pH in the surface soil of up to two pH units occur within 48 hours of urination (Holland and During, 1977).

Whitehead et al., 1989 reported that hydrolysis of urine urea is more rapid than that of pure urea. The major reason for this is that hippuric acid, a minor nitrogenous constituent of animal urine, has a stimulatory effect on urea hydrolysis.

3.2.3.2 Ammonia volatilisation

Volatilisation of NH_3 is favoured by the presence of large quantities of NH_4^+-N and a high soil pH, according to the following equation.

$$NH_4^+ + OH^- \leftrightarrows NH_3 + H_2O \qquad (3.3)$$

As noted above, under suitable conditions, enzymatic urea hydrolysis will be rapid in urine spots, creating high pH conditions, and large volatilisation losses could therefore occur shortly after urine deposition (Doak, 1952; Carran *et al.*, 1982; Ball and Keeney, 1983). Carran *et al.* (1982) observed that 80% of total volatilisation occurs over the first 3 days. However, a wide variation in the extent of NH_3 volatilisation can be expected as many soil and environmental factors are involved.

Soil pH is a major factor affecting volatilisation. Higher pH (increase in hydroxyl ion concentration) tends to increase production of NH_3.

NH_3 volatilisation tends to increase with increasing temperature (Lyster *et al.*, 1980). Maximum loss can be expected in high temperatures where evaporation is prominent.

Lowest losses would occur when it is cool. Ball and Keeney (1983) found losses of NH_3 from urine patches that averaged 5, 16, and 66% of added urine N under cool moist, warm moist, and warm dry conditions, respectively.

Haynes and Sherlock (1986) pointed out that increasing wind speed should tend to increase NH_3 volatilisation rate by promoting more rapid transport of NH_3 away from the air-soil interface. Thus, in hill country the effect of wind speed could play a vital role.

Soil moisture content has an important influence on the rate of NH_3 volatilisation since it affects the concentration of NH_4^+ and therefore NH_3 in soil solution. Vallis *et al.* (1982) observed relatively low NH_3 loss from dry soil and speculated that the lack of water for evaporation would have restricted volatilisation. Haynes and Sherlock (1986) pointed out that in dry soils, dissolved NH_4^+ may be adsorbed onto soil colloids while in initially wet soils, NH_4^+ might tend to remain in macropores. Then convection to the soil surface would tend to proceed through macropores, thus transporting more NH_4^+ to the surface of initially wet soils. However, the data of Carran *et al.* (1982) indicated the reverse, with 20% volatilisation loss from wet plots and 40% loss from dry plots.

Haynes and Sherlock (1986) cited the results of several workers suggesting that increasing soil cation exchange capacity (CEC) has a negative effect on NH_3 volatilisation.

Haynes and Williams (1993) cited a range of field measurements of NH_3 volatilisation losses (9% - 46%) from urine patches. Among them, under New Zealand conditions, volatilisation losses were 15-18% (Ball *et al.*, 1979), 17-36% (Carran *et al.*, 1982) and 12-25% (Sherlock and Goh, 1984). However, for hill country there are no field measurements for NH_3 volatilisation losses. This is mainly because of the technical obstacles associated with hill country research.

It can be seen in Plate 3.1 that the instruments used by Ball *et al.* (1979) for volatilisation measurement were highly complex. This NH_3 trapping system consisted of a steel frame (40 cm x 25 cm) embedded 10 cm into the soil immediately after urine application. Then a plastic chamber was attached to the frame. Ambient air was drawn

Plate 3.1: Ammonia volatilisation measurement using chamber methods (Ball *et al.*, 1979; Theobald, 1983).

Thus it is difficult to set up these instruments under hill country conditions. Carran *et al.* (2000) developed a passive sampler (Plate 3.2) for assessing NH_3 volatilisation from difficult sites, which is quite useful in hill country studies.

Plate 3.2: Ammonia volatilisation measurement using passive samplers (Carran *et al.*, 2000).

through the chamber from polyethylene tubing with the inlet on a 1.5 cm mast placed outside the plot area. The air was drawn through a high capacity vacuum pump. The air flow from chamber was passed through acid traps containing 100 mL of 0.2 N H_2SO_4.

In the absence of measured values, Lambert *et al.* (1982) assumed 5% of excretal N for volatilisation losses from hill country. He explained that the low value was used because he believed that the hill country environment he studied was unlikely to be conducive to volatilisation.

3.2.3.3 Nitrification

After the hydrolysis of urea, the NH_4^+ produced can be converted to NO_3^-. This process is called nitrification and is defined as the process whereby NH_4^+ is oxidised via NO_2^- to NO_3^-. These reactions are carried out by chemoautotrophic nitrifying bacteria. In soil, five genera of autotrophs are known to be able to oxidize NH_4^+ to NO_2^-: *Nitrosomonas, Nitrosococcus, Nitrosospira, Nitrosolobus*, and *Nitrosovibrio.* And one genus: *Nitrobacter* is known to oxidise NO_2^- to NO_3^- (Haynes and Williams, 1993). However, Haynes (1986a) also put emphasis on the significance of heterotrophic nitrification mainly by fungi. In addition, he pointed out evidence from several workers for nonmicrobial chemical nitrification in soil.

Oxidation of NH_4^+ to NO_2^- by *Nitrosomonas* occurs as follows (Norton, 1999).

$$NH_3 + O_2 + 2H^+ + 2e^- \rightarrow NH_2OH + H_2O \rightarrow NO_2 + 5H^+ + 4e^- \quad (3.4)$$

Oxidation of NO_2^- to NO_3^- by *Nitrobactor* occurs as follows (Norton, 1999).

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \quad (3.5)$$

Wrage *et al.* (2001) described the enzymes involved in nitrification. The oxidation of NH_3 to NH_2OH is catalysed by ammonia monooxygenase. This enzyme has a broad range of substrates for catalytic oxidations. Thus these substrates can inhibit the NH_3

oxidation function of the enzyme. Conversion of NH_2OH to NO_2^- is catalysed by hydroxylamine oxidoreductase. Production of NO_3^- from NO_2^- is catalysed by nitrite oxidoreductase.

Where nitrification is high, pasture growth could be limited by loss of N through leaching and denitrification, which would not occur in a soil of low nitrification activity. Consequently, nitrification is an important process to consider in a urine patch, because large quantities of NH_4^+ are available to act as a substrate for nitrifying bacteria. Nitrification is heavily dependent on soil and environmental factors. This is clearly exemplified in Fig. 3.1 where two different soils received the same amount of urine N. Nitrification is primarily affected by the NH_4^+ substrate supply, soil temperature, moisture, and soil pH (Gilmour, 1984; Paul and Clark, 1988).

The autotrophic nitrifiers are dependent on either NH_4^+ or NO_2^- as specific energy sources so substrate concentration can be a very important factor influencing nitrifier activity. Several studies have shown that addition of NH_4^+ (McLaren, 1971; Ardakani *et al.*, 1974) can increase the population of *Nitrosomonas* and addition of NO_2^- (Ardakani *et al.*, 1973) can increase *Nitrobacter*.

Malhi and McGill (1982) studied nitrification in three Alberta soils following the addition of NH_4^+ at concentrations of 50, 100, 200 and 300 μg NH_4^+-N/g soil. They observed that nitrification increased up to 200 μg NH_4^+-N/g soil but was inhibited at 300 μg NH_4^+-N/g soil. The depression at 300 μg NH_4^+-N/g soil was thought to be due to the combined effect of lowered pH, due to the NH_4SO_4 addition, and an increase in salt content.

Application of urine can increase the soil NH_4^+-N content up to 390-440 μg NH_4^+-N/g soil (Williams and Haynes, 2000). These large amounts of NH_4^+-N are surplus to plant requirements and therefore nitrifiers do not have to compete with other organisms for NH_4^+substrate.

The time taken to completely oxidise the NH_4^+-N in a urine patch varies - 35 days in dry conditions and 21 days in moist conditions (Carran *et al.*, 1982), 21 days (Ball *et al.*, 1979), 14 days (Vallis *et al.*, 1982), and 40 days (Williams and Haynes, 2000).

Temperature is an important factor regulating nitrification (Gilmour, 1984; Haynes, 1986a; Bramley and White, 1990). The optimum temperature for nitrification is usually between 25° and 35° C (Haynes, 1986a), but nitrification can occur over a wide temperature range. Selvarajah (1996) reported NO_3^--N production in moist soils stored under refrigerated conditions. Haynes (1986a) cited some evidence that indigenous nitrifiers have temperature optima adapted to their climatic regions.

Under warm temperate conditions NO_3^- is often the major form of mineral N present in a urine patch after 3-5 weeks (Holland and During, 1977; Ball *et al.*, 1979; Carran *et al.*, 1982). In contrast, low levels of nitrate have been observed after urine application in cooler conditions (Thomas *et al.*, 1988).

Soil moisture content and degree of aeration are fundamentally important to nitrification as autotrophic nitrifiers are strictly aerobic organisms (Bramley, 1989). Under very high soil moisture contents, water logging limits the diffusion of O_2 and nitrification is suppressed. Similarly, nitrification can be suppressed by insufficiency of water by retarding the bacterial proliferation (Paul and Clark, 1988). Haynes (1986a) mentioned that the maximum rate of nitrification occurs at soil moisture potentials in the range of -10 to -33 kPa.

There have been number of studies on the effect of pH on nitrification. Paul and Clark (1988) suggested that optimum pH values might vary between 6.6 to 8. In agreement with this, Sarathchandra (1978) reported much greater nitrification in a Wharekohe silt loam at a pH of 7.5 than in the same soil at a pH of 5.5.

Bramley and White (1990) carried out some interesting work in which they showed that across a range of soils the optimum pH for nitrification was generally close to the pre-existing soil pH, suggesting that the indigenous nitrifier populations adjusted to the prevailing soil pH. Haynes and Williams (1992) studied urine transformations in urine patches and observed that nitrification was occurring across a range of pH values down to a pH of at least 5.

Monaghan and Barraclough (1992) reviewed the effect of urinary Cl^-, osmotic potential and N content on the rate and dynamics of nitrification in urine-affected soil. They

concluded that in most temperate grassland soils at near neutral pH, urinary Cl^- and N are unlikely to reduce nitrification rates, except where urine N concentrations exceed 16 g N/litre.

There is some evidence of an effect of clay minerals on nitrification. Soils containing high amounts of allophanic minerals have been found to enhance the nitrification process (Baber, 1978; Sarathchandra, 1978). Although the exact reason for this is unclear, Selvarajah (1996) regarded this as an important observation and indicated that Waikato soils have a greater potential for generating NO_3^- than other soils in New Zealand.

Nitrification activity and the number of nitrifying bacteria were measured in nine New Zealand soils by Sarathchandra (1978) as Short Term Nitrification Activities (SNA). This was the mean rate of nitrification between 1 and 17 hours, from 5 g of oven-dry soil perfused with 50 mL of $(NH_4)_2SO_4$ (14 mg/l). The nitrification activities of nine soils were widely different ranging from 0.25 to 3.31 μg NO_3^--N produced/g soil/hour.

Steel *et al.* (1980) investigated the nitrification activity of soils from sixty-eight sites in New Zealand grassland. Nitrification activity was measured as Initial Nitrification Activity (INA), which was the mean rate of nitrification between 1 and 17 hours, in 10 g of oven dry soil mixed with 20 g of acid washed, autoclaved quartz sand, perfused with 100 mL 0.005M $(NH_4)_2SO_4$ previously adjusted to the pH of the soil measured in a 1:2.5 soil: water suspension after 16 hours equilibration.

Similar to Sarathchandra (1978), Steel *et al.* (1980) also observed considerable variation (<0.02 to 5.7 μg N oxidised/g soil/hour) of INA among the studied soils. They observed four general patterns of nitrification (Fig. 3.2)

In Type 1, NH_4^+-N rapidly oxidised to NO_3^--N and the rate of oxidation was linear. Type 1 nitrification was observed in soils with high INA values, which were yellow brown and red and brown loams. In Type 2, nitrification was linear but at a very much slower rate compared to Type 1. Type 2 nitrification, occurred in four yellow brown earths, one of the yellow grey earths, and one of the yellow brown pumice soils. In Type 3 soils, NH_4^+-N was oxidised slowly to NO_3^--N at a rate that increased

exponentially with time after an initial lag phase. Most soils exhibited Type 3 nitrification. In Type 4 soils, nitrification occurred with a temporary accumulation of NO_2^- at the start. This pattern was observed only in soils of high pH.

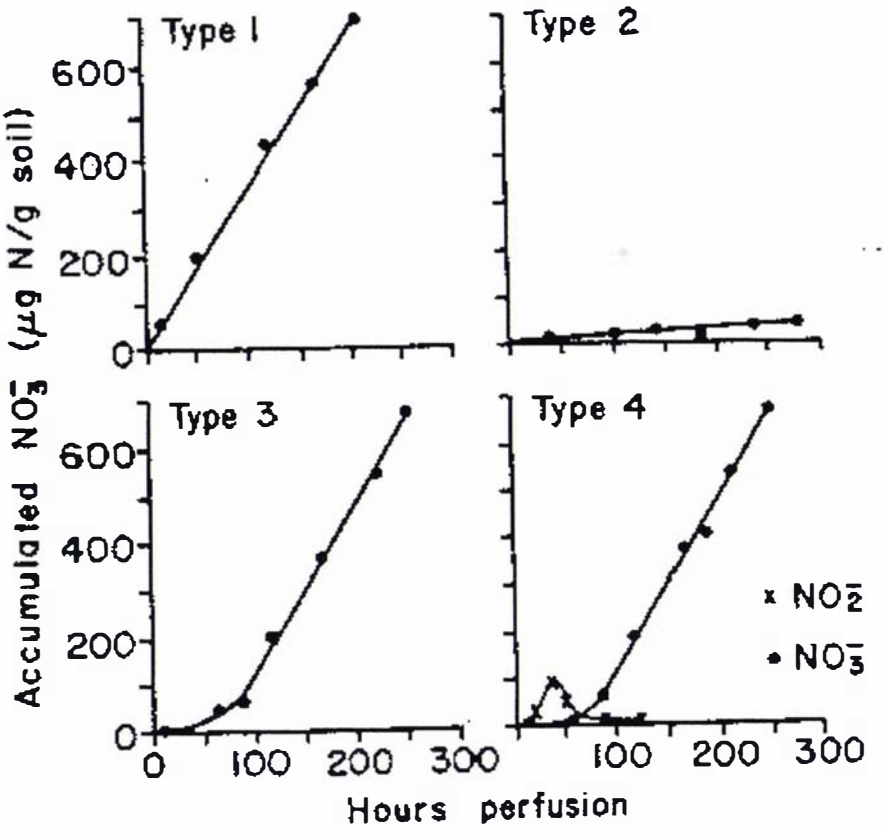


Fig. 3.2 Four general patterns of nitrification observed by Steel *et al.* (1980) when soils are perfused with .005M $(NH_4)_2SO_4$.

Fig. 3.3 and 3.4 illustrate the relationships of INA to total N (%) and C/N ratio developed from the data presented in Steel *et al.* (1980). When soils exhibiting Type 1 and Type 2 nitrification behaviour are considered alone (Fig. 3.3) it appears that soil total N (%) and C/N ratio have strong relationships with nitrification. However, when all the data presented in Steel *et al.* (1980) are considered, the general pattern of the graphs is similar though the relationships are not very strong (Fig. 3.4).

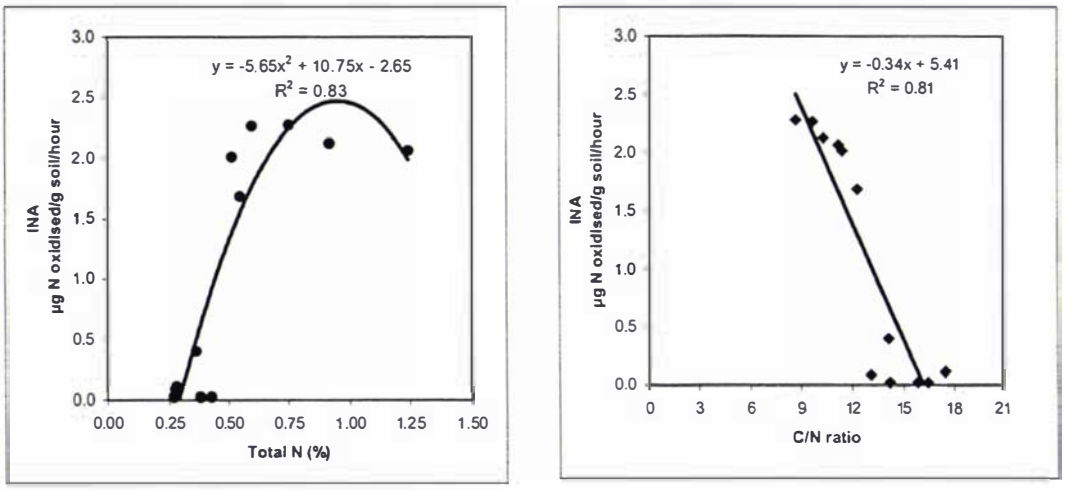


Fig. 3.3 Relationships between INA (Initial Nitrification Activity) and total N (%) and C/N ratio of soil. The data are extracted from soils that showed the Type 1 and Type 2 nitrification patterns of Steel *et al.* (1980).

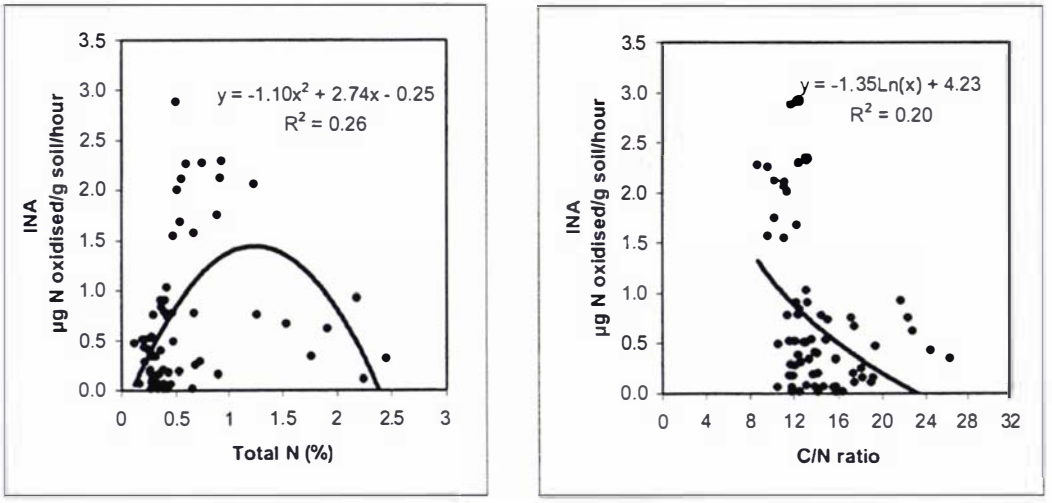


Fig. 3.4 Relationships between INA (Initial Nitrification Activity) and total N (%) and C/N ratio of soil. All the data presented in Steel *et al.* (1980) were used for the relationships.

According to the graphs, nitrification activity increased up to total N contents of about 1% and then decreased. Soils with total N contents beyond this level are mostly peaty soils. Although they have a high N content, the N is unavailable to microbes due to a high C/N ratio. This may retard the nitrifier population. Hence, substrate quality is a major determinant of nitrification.

Lambert *et al.* (1982a) pointed out that hill country soils have high C/N ratios ranging from 12-17. Also, in Chapter 2, N depletion in steep hill soils due to animal transfer was discussed. In steep soils, the main C source is from decomposing plant materials and roots. Root materials have a relatively high C/N ratio. Thus, with low N levels plus a high C/N ratio in steep hill soils, it can be anticipated that there will be relatively low nitrification. This might be the reason that Sakadevan *et al.* (1993) didn't observe any accelerated leaching of NO_3^--N in urine patches on hill country soil.

3.2.3.4 Leaching

Mineral N concentrations occurring in urine patches are often in the range of 100-440 μg N/g soil (Ball and Ryden, 1984; Thomas *et al.*, 1988; Haynes and Williams, 1992; Williams and Haynes, 2000). Once most of this mineral N has nitrified, leaching of NO_3^--N will occur when water moves down through the soil after excess rainfall. Thus, leaching could be a major N loss mechanism responsible for the unaccounted-for urine N discussed in Fig. 3.1. Both Ball *et al.* (1979) and Carran *et al.* (1982) commented that leaching of NO_3^--N could be one of the probable loss mechanisms.

The movement of NO_3^--N in soil is affected by a large number of physical, chemical, and microbiological processes. Hence, a range of experimental, mathematical and physical sciences are required to study and describe solute transport in soil. Transport of a dissolved substance (solute) depends on the magnitude and direction of the solvent (water) flux. Cameron and Haynes (1986) reviewed the principles of solute movement in relation to the process of NO_3^- leaching. They summarised the main transport processes as being convection (solute transport due to mass flow of water alone), diffusion (solute movement from areas of high concentration to areas of low concentration) and dispersion (mechanical action of a solution flowing through soil that

causes mixing and equalises the solute distribution). In addition, they paid attention to anion exclusion, anion adsorption, and transformations and plant uptake of nitrogen. The combined effects of convection-diffusion, dispersion and the rate of N production and disappearance can described by

$$\frac{\partial c}{\partial t} = E\frac{\partial^2 c}{\partial x^2} - U\frac{\partial c}{\partial x} + S \qquad (3.6)$$

where

c = concentration of NO_3^- (μg/mL)

t = time (days)

U = average pore velocity (cm/day)

x = linear distance in direction of flow (cm)

E = dispersion coefficient (D_s+ mU)

D_s = effective diffusion coefficient in soil (cm^2/day)

m = dispersivity

S = index for rate of NO_3^- production or disappearance (μg/mL /day)

Burns (1975) developed an equation to predict the leaching of surface applied nitrate. Scotter *et al.* (1993) identified the usefulness of the Burns equation and also the problems associated with it. They modified the equation for use in a wider range of conditions as follows.

$$X = \exp(-z\theta / I) \qquad (3.7)$$

X = fraction of solute leached below depth z

z = depth

θ = volumetric water content at field capacity

I = net rainfall

Season and climate play a major role in leaching. Summer rainfall is generally used to satisfy the evapotranspiration deficit and leaching is therefore usually minimal. Winter rainfall readily leaches any nitrate present in the soil profile since there is excess of

rainfall over evapotranspiration and low plant N uptake. Also, a dry summer can result in the accumulation of soil nitrate due to poor pasture N uptake and significantly higher than average leaching losses then occur over the subsequent winter (Cameron and Haynes, 1986).

Steel and Judd (1984) estimated that leaching losses from an intensively grazed pasture over one year were 88 and 193 kg/ha for a no N fertiliser treatment (control) and a plus N treatment (3 applications of 57.5 kg N/ha as urea) respectively.

The direct impact of the grazing animal on NO_3^- leaching was demonstrated by Ryden *et al.* (1984). They observed an annual loss of NO_3^--N of 29 and 162 kg N/ha/yr from cut swards and grazed grass swards (both receiving 420 kg N/ha/yr) respectively. Thus, the leaching losses from the grazed sward were 5.6 times greater than from the cut sward. They pointed out that the enhanced loss of NO_3^--N below the grazed sward was mainly due to return in urine and dung which accounted for as much as 90% of the N in the herbage consumed by cattle.

Grazing animals deposit dung and urine in localised patches at average rates equivalent to 500 and 1000 kg N/ha/yr for sheep and cattle respectively (Haynes and Williams 1993). These rates are in excess of plant demands and can lead to significant N leaching as Ryden *et al.* (1984) pointed out. Quin (1979) demonstrated that 80% of the urine urea-N was eventually leached as NO_3^--N from a typical urine patch under surface irrigation. Ball *et al.* (1979) observed considerable amounts of applied urine N lost from the 0-45 cm soil profile after 53 days and indicated that leaching of NO_3^--N was the probable loss mechanism. In contrast, Fraser *et al.* (1994) in a lysimeter study observed only 8% of the applied urine ^{15}N leached below 1200mm after 1 year, although the experiment was conducted under intense rainfall and irrigation conditions. This may be due to the presence of a low hydraulic conductivity layer in the monolith at 20-30 cm depth. This could have led to anaerobic conditions leading to high denitrification losses which they have identified as a probable loss mechanism of 28% of the added urine N.

There are few quantitative estimations in the literature of leaching losses from hill country. This is mainly because of the technical obstacles associated with hill country

measurement. However, scientists generally believe that the leaching loss from hill country is minimal because the soils are strongly N retentive (Lambert *et al.*, 1982a). This view was confirmed by Sakadevan *et al.* (1993) who did not observe any accelerated leaching of N from urine-affected soil in hill country pasture.

3.2.3.5 Denitrification

Microbial reduction of NO_3^- to NO_2^- and then to gaseous N_2O and N_2, which are commonly lost to atmosphere, is known as denitrification. Ryden (1986) pointed out that denitrification also can occur in urine patches. Theoretically the potential for denitrification from pastures would appear to be high due to high amounts of organic C in the surface soil and high concentrations of NO_3^--N present in the soil under urine and dung patches (Haynes and Williams, 1993). Sherlock and Goh (1983) suggested that any attempt to quantify global N_2O production should recognize the possibility of enhanced N_2O production from urine patches in grazed grassland. In contrast, Carran *et al.* (1995) reported that nitrification or other transformations of urine derived N do not contribute to overall emissions of N_2O in an important way. In the same way, Luo *et al.* (2000) reported an annual nitrogen loss of only 4.5 kg N/ha through denitrification from a legume based intensive dairy pasture in New Zealand.

3.2.3.6 Mineralisation and immobilisation

Mineralisation is the general term for the conversion of organic N to inorganic N as either NH_4^+ or NO_3^-. Immobilisation is the conversion of inorganic N to organic N. This can be mediated by microorganisms or by chemical interactions with complex carbon compounds.

Direct immobilisation of N in the soil organic matter provides a mechanism whereby urine N is retained to be again recycled. The rate of incorporation of N into the microbial biomass and other soil organic fractions will depend on factors influencing the mineralisation/immobilisation turnover. These factors include the C:N ratio of organic residues and environmental conditions.

The incorporation of N into microbial biomass and organic N occurs through numerous enzymatic and abiotic pathways. Norton (1999) reviewed the microbial N immobilisation process extensively. The preferred inorganic N source for assimilation by bacteria and fungi is NH_3/NH_4^+ although NO_3^- is also used under appropriate conditions. Ammonia enters microbial cells by rapid diffusion across cytoplasmic membranes. Biological NH_4^+ immobilisation by soil microorganisms is mainly accomplished by two enzymatic pathways. They are the Glutamate dehydrogenase (GDH) system and the Glutamine synthatase (GS) – Glutamate synthase (GOGAT) system. In soils with low NH_4^+-concentrations the GS-GOGAT system is operative and the GDH pathway immobilizes N at relatively high concentrations. The two systems are shown below as described by Moat and Foster (1999).

GDH system

$$\alpha\text{- ketoglutarate} + NH_4^+ + NADH + H^+ \leftrightarrow \text{L-glutamate} + NAD^+ \quad (3.8)$$

$$\alpha\text{- ketoglutarate} + NH_4^+ + NADPH + H^+ \leftrightarrow \text{L-glutamate} + NADP^+ \quad (3.9)$$

GS-GOGAT system

$$\text{L-glutamate} + NH_4^+ + ATP \xrightarrow{GS} \text{L-glutamine} + ADP + Pi \quad (3.10)$$

$$\alpha\text{- ketoglutarate} + \text{L-glutamine} + NADPH + H^+ \xrightarrow{GOGAT} 2\ \text{L-glutamate} + NADP^+ \quad (3.11)$$

Nitrate may be immobilised directly by assimilatory nitrate reduction by both bacteria and fungi (Paul and Clark, 1988).

$$NO_3^- + NO_2^- \rightarrow NH_2OH \rightarrow NH_4^+ \rightarrow R\text{-}NH_2 \quad (3.12)$$

The enzymes responsible for reduction are assimilatory nitrate reductase and assimilatory nitrite reductase. Broadbent and Tyler (1962) observed nitrate immobilisation when NO_3^- was the only form of N available. Rice and Tiedje (1989) also observed nitrate assimilation when there was a demand for N (excess C) and low concentrations of NH_4^+. They also observed the inhibition of NO_3^- assimilation by NH_4^+. Ammonium inhibited the NO_3^- assimilation immediately (< 1 min) and when present in very low concentrations (0.1 μg N/g soil).

Urine patches in a soil with high nitrification activity normally contain both NH_4^+ and NO_3^- ions. Thus, N assimilation by microbes could take place by uptake of either NH_4^+ or NO_3^-. As NH_4^+-N is the preferred source, immobilisation in urine patches would normally occur in the initial days after urine application because NH_4^+-N is the dominant N form at that time. Keeney and MacGregor (1978) observed that apparent ^{15}N immobilisation was more rapid in urea and $(NH_4)SO_4$ treated plots compared to KNO_3 treated plots.

Soils with very high nitrification rates could produce high amounts of NO_3^- ions within a day or two after urine application. Assimilation of this NO_3^--N by microbes could be inhibited by the presence of NH_4^+-N. Once most of the NH_4^+-N has been nitrified, the NO_3^--N could be assimilated by microbes.

Broadbent (1965) observed an increased rate of soil organic N mineralisation with higher initial concentrations of added ^{15}N-$(NH_4)_2SO_4$. This is called a "Priming effect" or added nitrogen interaction (Molina *et al.*, 1990). Several studies have observed the priming effect due to added fertiliser or salts. (Agrawal *et al.*, 1971; Jenkinson *et al.*, 1985; Molina *et al.*, 1990; Leon *et al.*, 1995). However, the actual cause for this so called priming effect is not clear.

Broadbent and Nakashima (1971) postulated that osmotic effects contributed to the salt-stimulated mineralisation of soil organic N, partially due to the extraction of organic N by the salt solution. The organic N thus rendered soluble would constitute a pool of easily mineralisable N. Another possible contributing factor could be that the high salt concentrations result in the death and breakdown of microbial cells with the release of readily available N, for subsequent mineralisation by the remaining microbial population (Haynes, 1986b).

Ball and Tillman (1994) suggested stripping of resident organic N from urine patches. They pooled the data from several studies, and viewed different seasonal runs as replications over time and observed a significant decline in total N in topsoil, which had received urine. They commented that urine had imparted some "priming effect", thereby stripping some of the resident organic N from the soil, during the period when its benefit to plant growth was being perceived aboveground.

3.2.3.7 Plant uptake

Plant uptake is another critical mechanism whereby urine N is recycled through the system. The two major forms of nitrogen taken up by plants are NO_3^- and NH_4^+. Although the most common form of N adsorbed by most plants is NO_3^-, in acidic soils NH_4^+ predominates because nitrification is largely inhibited (Pilbeam and Kirkby, 1992).

Haynes (1986c) pointed out that the majority of plant species produce the greatest growth when the soil has a mixture of NO_3^- and NH_4^+. Pilbeam and Kirkby (1992) also cited similar evidence of increased growth rate when both forms of nitrogen are supplied simultaneously. Reisenauer *et al.* (1982) observed maximum yield of ryegrass by supplying low levels of NH_4^+ (36 μM) with adequate NO_3^- (72 μM).

The reason for the stimulating effect of NH_4^+ on the growth of plants supplied with NO_3^- is not clear. However, the total energy requirement for N uptake is less when both forms are taken up than when NO_3^- is taken up alone because NO_3^- uptake needs extra energy to be reduced to NH_4^+ after uptake (Pilbeam and Kirkby, 1992). There is some evidence of restriction of NO_3^- uptake by the presence of NH_4^+ (Youngdahl *et al.*, 1982; Pilbeam and Kirkby, 1992).

In a urine patch, the abundance of NH_4^+ and NO_3^- varies with time. Ammonium is predominant immediately after urine application and later NO_3^- become prominent in soils with high nitrification activity. In high nitrification activity soils, both forms of mineral N can be found up to about four weeks after application. In low nitrification soils, NH_4^+-N is the dominant form in a urine patch for a longer period. These variable combinations of mineral N forms existing in a urine patch could be the reason for the resulting highly variable urine N recoveries by pasture herbage in previous studies. It has been observed that the urine N recovery by herbage ranges from 8-55% (Holland and During, 1977; Ball *et al.*, 1979; Carran *et al.*, 1982; Ledgard et al., 1982a; Ball and Keeney, 1983; Thomas *et al.*, 1988)

Many workers in New Zealand have observed increased pasture growth in urine patches (Ball *et al.*, 1979; Carran *et al.*, 1982; Sakadevan *et al.*, 1993; Williams and Haynes,

2000; Theobald and Carran, 2000). Dale (1961) noted that response is greatest in spring and autumn. The responses to urine N in midsummer and winter are generally restricted by environmental conditions (i.e., low soil moisture and low temperature, respectively) that are not conducive to rapid pasture growth.

Many workers have observed that N fixation by the clover component of the sward is markedly depressed in urine patches (Ball *et al.*, 1979; Ledgard *et al.*, 1982a). This is due to the inhibitory effects of high soil mineral N on N_2 fixation by the *Rhizobium* bacteria (Haynes and Williams, 1993).

3.2.3.8 Fixation to clay minerals

NH_4^+-N is generally held in soils as an exchangeable cation, but in soils that contain 2:1 clay minerals (e.g., illites, vermiculites, and montmorillonites) it can also be held in a non-exchangeable "fixed" form. In a Waimumu (Southland) soil, Carran *et al.* (1982) (Fig. 3.1) reported that fixed NH_4^+-N concentrations increased from 42 to 85 mg/kg in plots treated with urine. They regarded NH_4^+ fixation as environmentally desirable, as the NH_4^+ ions were quickly removed from soil solution, thereby inhibiting losses, and were then released slowly. Crush and Evans (1988) measured fixed NH_4^+-N in artificial urine patches in four Manawatu soils containing high quantities of 2:1 minerals. They found that less than 8% of urine N applied in spring and less than 3% in summer were fixed to clay minerals.

3.3 Materials and methods

3.3.1 Field site

This experiment was carried out at the AgResearch hill country research site near Waipawa, North Island, New Zealand. Waipawa is approximately 300 m above mean sea level and receives an annual average rainfall of about 800 mm, most regularly falling in winter and early spring. Warm, dry summers and much cooler winters are typical of the site. The major soil type at the experimental site is Waipawa Stony Silt Loam (Pallic Soil) which has a low water holding capacity. The soil is low in P, S, and

N (Gillingham *et al.*, 1998). The pastures of the steep northerly facing slopes contain low proportions of clover due to the regularly dry summer conditions.

3.3.2 Field trial design

The experiment was carried out at a site within an ongoing AgResearch trial. The AgResearch trial occupies 48 ha divided into 4 farmlets of 12 one-hectare paddocks each receiving contrasting P and N fertilizer treatments. This experiment was carried in a north-facing paddock receiving high phosphorus and no nitrogen (Paddock # HP25). Two experimental sites; a steep sloping site (15-25°) and a lower flatter sheep campsite (0-15 °) were selected from the paddock for this experiment. Some soil fertility indices of the two sites are listed in section 3.5.7 (Table 3.9).

The whole paddock was grazed by sheep before the plots were selected. The locations of recent urine patches were checked in the experimental plot area by a field pH meter as increased pH values could be observed immediately after urine deposition due to urea hydrolysis (Section 3.2.3.1). These patches were avoided in selecting the experimental plots. In each experimental site, twelve (0.5m x 1m) plots were established and arranged into 4 blocks of 3 plots. Three treatments were assigned at random within each of the 4 blocks to give a randomized complete block design. The plots were established with enough space around the edges to prevent interference from other treatments by runoff etc.

3.3.3 Treatments

A synthetic urine solution (Table 3.2) was used in the experiment and was made according to Muller (1995). The N application rate in urine patches greatly varies depending on diet and animal. Therefore a range of application rates has been found in previous experiments; 300 and 600 kg N/ha (Ball *et al.*, 1979), 300 kg N/ha (Carran *et al.*, 1982), 280 kg N/ha (Sakadevan *et al.*, 1993). Hence, in this preliminary experiment three N rates (0, 200 and 400 kg N/ha) were used as treatments (Table 3.3) to represent the wide range of application rates found in the literature. However, these application rates were further reviewed in next experiment (Section 5.2.3). The 200 and 400 kg

N/ha treatments were applied as 2 liters of 0.5%N and 1% N urine solution respectively. The 2 liters of urine solution (0.5%N or 1%N) was added evenly by a small watering can to the appropriate plots. The application rate was such that there was no visible surface runoff.

In natural conditions, urination adds both water and nutrients to the soil. In the current experiment the application rate of water was broadly comparable to that supplied by urine. Some consideration was therefore given as to whether the control plots should have 2 liters of water added- so as to isolate the effect of adding N. In the end however, it was decided that the control plots would receive nothing.

Table 3.2 Constituents of the synthetic urine solution (pH= 7.8).

Constituent	0.5% N solution (g/l)	1% N solution (g/l)
Urea	9.8	19.6
Glycine	2.7	5.4
KCl	2.6	5.2
K_2SO_4	1.0	2.0
$KHCO_3$	7.5	15.0

Table 3.3. Treatments used in the experiment.

Rate N kg/ha	Treatment	
	Flat	Steep
0	F0	S0
200*	F200	S200
400**	F400	S400

* Applied as 2 liters of 0.5%N artificial urine solution

** Applied as 2 liters of a 1%N artificial urine solution

3.3.4 Soil and plant sampling

Soil samples were collected 1, 6, 27, 100, and 142 days after urine application (DAUA). At each sampling, five soil cores (25 mm diameter) were taken from each plot and bulked into a polythene bag to provide a plot sample. Samples were taken from 0-75 mm and 75-150 mm depths. Soil samples were taken from a 0.25 m^2 area in the down-slope half of the plot and the rest of the area was kept undisturbed for pasture yield

measurements. The first soil core samples were collected from near the bottom of the slope and the next sampling taken from further up slope to minimize the effect of early samplings on subsequent measurements. All soil samples were kept in a refrigerator at 4°C to minimize microbial action, and samples were analysed within a day. A sub-sample of soil was used to determine soil moisture content by drying at 105^0C for 16 hours.

Soil cores in each plot sample were crumbled and well mixed, then 4 grams of field moist soil was weighed into a 50 mL centrifuge tube. Thirty mL of 2 M KCl was then added and the tubes shaken for 1 hour. The mixture was centrifuged at 9000 rpm for 2 minutes, then the solution was decanted off and filtered through Whatman No. 41 filter paper. Extracts were analysed NH_4^+-N and NO_3^--N contents colorimetrically by a Technicon auto-analyser (Searle, 1975; Blakemore *et al.*, 1987).

Herbage yields were taken from an area of each plot undisturbed by soil sampling. Herbage cuts were made using a hand cutter at 27 and 103 DAUA. Dry matter yield was measured by drying at 60°C and weighing. The total N content of herbage was determined by a semi-micro kjeldahl method. A herbage sample (0.1g) was digested with 4 mL of kjeldahl digest acid (McKenzie and Wallace, 1954) in a 100 mL test tube in a drilled aluminium block (350 °C) for 7 hours. The digested solution was allowed to cool down, diluted to 50 mL with distilled water, and mixed using a vortex mixer. The NH_4^+-N content of the solution was analysed colorimetrically by a Technicon auto analyser (Searle, 1975; Blakemore *et al.*, 1987) and expressed as the total herbage N.

Soil potentially mineralisable N content was measured using an anaerobic incubation (Sparling and Schipper, 1999) from soil samples collected at 27, 100, and 142 DAUA. The incubation carried out was similar to the method used by Blennerhassett (2002). Five g of field moist soil was weighed into a 50 mL centrifuge tube, 20 mL of distilled water was added, tubes were sealed and incubated for 4 weeks at 30°C. After the incubation period, N was extracted by adding 10 mL of 3M KCl solution and shaking for 1 hour. Extracts were centrifuged at 9000 rpm then filtered (Whatman 41) and the NH_4^+-N contents of the extracts were analysed colorimetrically by a Technicon auto

analyser (Searle, 1975; Blakemore *et al.*, 1987). The difference between NH_4^+-N content before and after the incubation was considered as soil mineralisable N.

Total C and N contents of control soils were determined by combustion using a Leco FP-2000 CNS analyser.

3.3.5 Ammonia volatilisation

Ammonia volatilisation after urine application was estimated using the method described by Carran *et al.* (2000). Two cylindrical polycarbonate vials with internal dimensions 21 x 90 mm (Plate 3.1) were placed in the middle of each plot to assess the effect of urine on ammonia volatilisation. Inside the polycarbonate vials three layers of stainless steel mesh (0.5 mm) were secured against the bottom of the tubes. The mesh was loaded with oxalic acid by dipping in a solution of 10% oxalic acid in acetone and drying. The each vial can trap a maximum of 2.6 mg NH_3-N (Carran, Personal communication). After exposure in the field for 6 days, tubes were recapped until analysis. Analysis involved adding 10 mL distilled water and 0.1 mL of 10M NaOH to each tube and determining the NH_3-N concentration with an NH_3 gas-sensing electrode.

Carran (Personal communication) has developed the following relationship between ammonia volatilisation values obtained from the method used in this experiment and the amount of ammonia volatilised on a per hectare basis.

$$NH_3\text{-N Volatilised (kg N/ha)} = (0.8)\ (\mu g\ NH_3\text{-N/sampler}) \quad (R^2 = 0.6) \qquad (3.13)$$

To develop this relationship, the current method and a quantitative method (Schojerring *et al.*, 1992) were used to measure ammonia volatilisation from a range of urine application rates on a Manawatu silt loam. These measurements were made over a period of months from late summer to winter. The above-mentioned relationship was used to estimate the amount of ammonia volatilised on a per hectare basis from this experiment in the absence of any more directly relevant information.

3.3.6 Statistical analysis

Analysis of variance was carried out using SAS for Windows (Version 8). The 2 M KCl extracted NH_4^+-N, NO_3^--N (0-15 cm soil depths), total mineral N (0-15 cm depth) and mineralisable N data were analyzed using a repeated measures model in mixed procedure (Little *et al.*, 1998) to examine and compare response trends over time. Autoregressive co-variance structure was used in the model. Means were compared using the Least Mean Square Multiple Comparison method at 5% significant level.

Analysis of variance for data on NH_3 volatilisation, herbage DM, and herbage N accumulation was carried out using the General Linear Model (GLM) procedure. Mean comparisons were done using Fishers Least Significant Difference (LSD) at 5% significance.

3.4 Results

3.4.1 Rainfall

The rainfall data was obtained from the Waipawa AgResearch research site. The total amount of rainfall during the experimental period was 181 mm (Fig. 3.5).

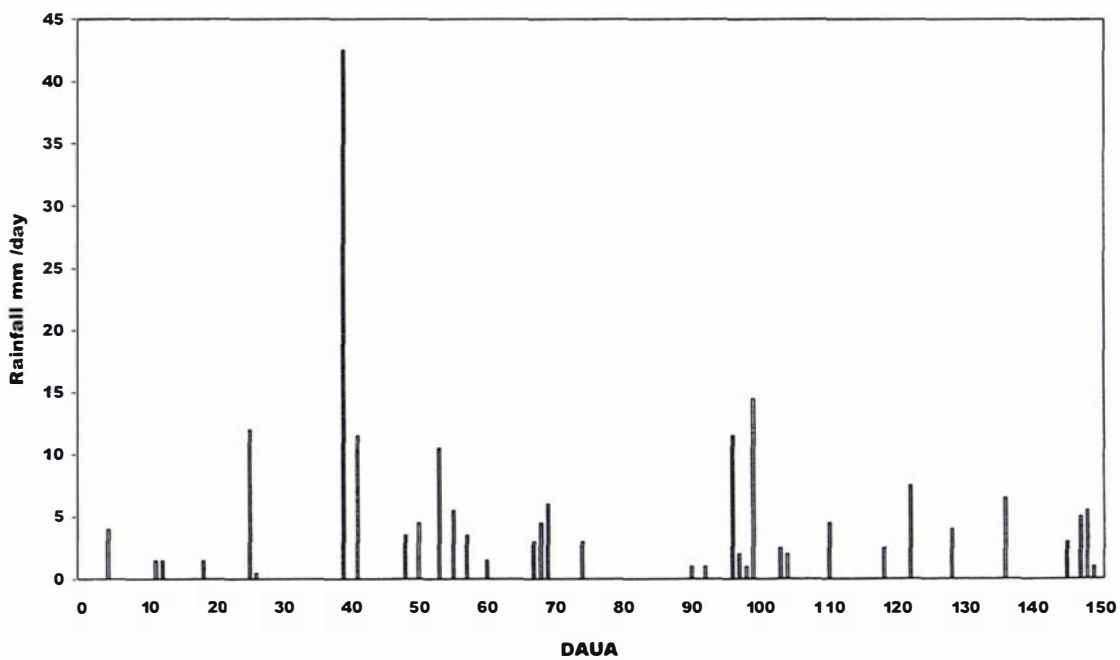


Fig. 3.5 Daily rainfall during the experimental period.

There was little rainfall during the first 30 days. At 39 DAUA heavy rainfall (42.5 mm) occurred. During the period of 27 to 100 DAUA, frequent and substantial amounts of rainfall (130 mm) were received.

3.4.2 Statistical data interpretation

The repeated measures model in a mixed procedure made it possible to compare the treatment means at a particular sampling time as well as treatment means between sampling times within a site. No comparisons were made between sites, as the site locations were not replicated appropriately. The least squares mean procedure for mean comparison supplied mean comparisons for all possible comparisons. This caused some difficulties in tabulating the statistical data. Thus, the existence of statistically significant differences at specific sampling times are pointed out in Fig. 3.6, Fig. 3.7 and Fig. 3.8. When there is at least one statistically significant difference between treatments at a particular sampling time it is indicated by " * " and " NS " is used when no significant treatment differences were observed. However, there was no convenient way of indicating exactly which treatments were significantly different from which at each sampling time. This detailed information is tabulated in Appendix 1. When necessary, any important statistically significant differences within and between samplings are identified and discussed in the text.

3.4.3 Mineral nitrogen

Mineral N comprises NH_4^+-N and NO_3^--N. These two components are discussed separately in Sections 3.4.4 and 3.4.5. This section provides general comments on the combined quantities of NH_4^+-N and NO_3^--N extractable by 2 M KCl in the soils.

Mineral N in soil, to a depth of 15 cm, was significantly increased (Table 1 of Appendix 1) at both sites, after urine application. Unsurprisingly, these increases were higher when urine was applied at 400 kg N/ha than applied at half the rate, 200 kg N/ha, at both the sites (Fig. 3.6). For example, the soil (0-15 cm) mineral N levels were increased 8, and 11-fold relative to control at 1 DAUA for the S200 and F200

treatments while the mineral N levels in the S400 and F400 treatments increased 15 and 33-fold respectively.

The elevated mineral N levels in urine treated plots decreased with time. As a result, only 36-53% of mineral N found at 1DAUA was present in the soil by 27 DAUA. By 100 DAUA, the mineral N levels in urine treated plots were not statistically different from the controls. This pattern of mineral N change after urine application was similar at both flat and steep sites.

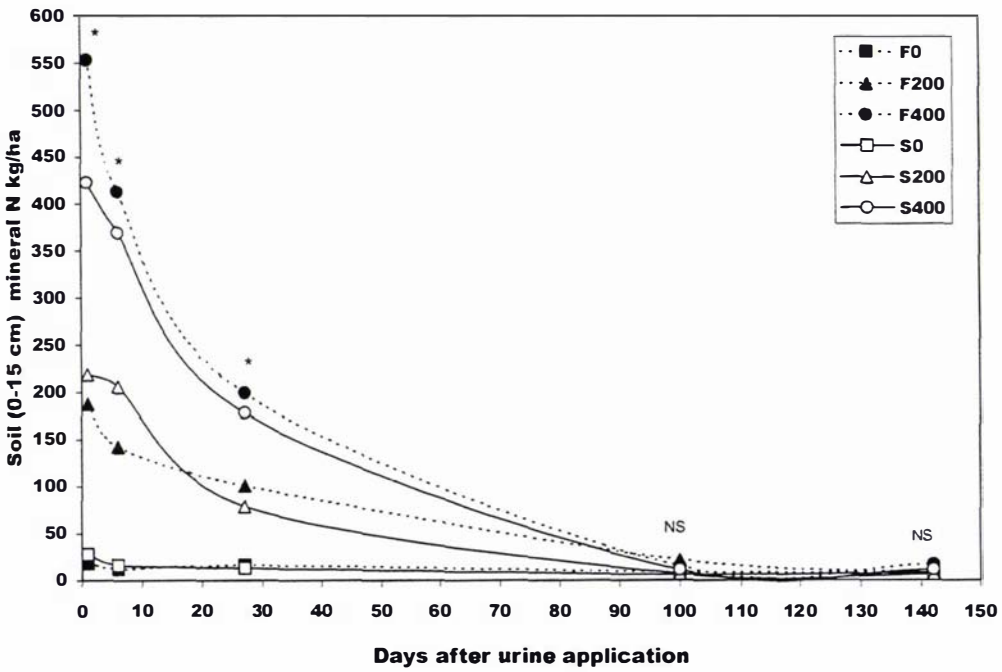


Fig. 3.6 Effect of urine application on soil (0-15 cm) mineral N level. * = significant treatment differences were observed within a sampling at the same site. NS = no significant treatment differences were observed within a sampling at the same site.

At 1 DAUA in the F400 urine treatment, the urine N recovery as mineral N was greater than 100% (Table 3.4) suggesting a possible priming effect. The mineral N recoveries in the other urine treatments were also close to 100% (Table 3.4).

Soon after the urine application, movement of urine N to the 7.5-15 cm-soil depth was evident (Table 3.4). This is discussed in more detail in Section 3.4.4.

Table 3.4 Apparent recovery of urine N as mineral N and mineralisable N after urine application (kg N/ha/7.5 cm depth) in the soil profile (0-15 cm) i.e. all values are treatment minus control. * = did not measure

Treatment	DAUA	Soil depth						% recovery in soil
		0-7.5 cm			7.5-15 cm			
		NH_4^+-N	NO_3^--N	Mineralisable N	NH_4^+-N	NO_3^--N	Mineralisable N	
S200	1	139	1	*	51	1	*	96
	6	171	2	*	16	0	*	95
	27	50	2	0	4	9	34	50
	100	1	0	0	0	0	5	3
	142	0	0	0	0	0	3.5	2
S400	1	348	1	*	45	1	*	99
	6	328	2	*	21	0	*	88
	27	139	2	51	22	2	7	56
	100	2	1	19	2	0	29	13
	142	2	0	12	1	0	14	7
F200	1	156	1	*	14	0	*	86
	6	117	1	*	11	0	*	65
	27	76	4	44	6	0	0	65
	100	6	0	35	6	1	16	32
	142	0	0	9	1	0	4	7
F400	1	462	2	*	72	1	*	134
	6	359	3	*	39	1	*	101
	27	140	24	59	18	3	0	61
	100	2	1	39	2	1	28	18
	142	8	1	17	1	0	22	12

At the last two samplings (100 and 142 DAUA), very little urine N was recovered as mineral N but reasonable amounts were recovered as mineralisable N (Table 3.4 and Section 3.4.6).

3.4.4 Ammonium

The amount of 2 M KCl -extractable soil NH_4^+-N (μg NH_4^+-N/g soil) to a depth of 15 cm followed a similar pattern to the mineral N changes after urine application (discussed in the previous section). This was because NH_4^+-N was the dominant form of mineral N in both treatments at both sites over the whole experimental period (Table 3.4).

Soil (0-15 cm) NH_4^+-N contents were significantly increased (Table 2 of Appendix 1) by urine treatments in both sites (Fig. 3.7).

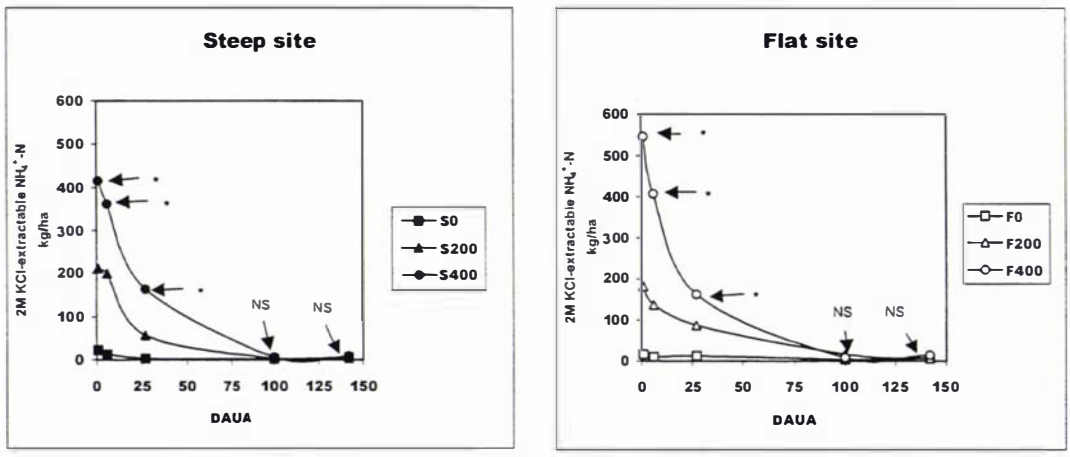


Fig. 3.7 Effect of urine treatments on soil (0-15 cm) NH_4^+-N. * = significant treatment differences were observed within the sampling time. NS = no significant treatment differences were observed within the sampling time.

At 1 DAUA, 190, 393, 170, and 534 kg N/ha were recovered as NH_4^+-N in soil (0-15 cm) (Table 3.4) from the S200, S400, F200 and F400 treatments respectively. These amounts were 95%, 98%, 85% and 133% of added urine N for the S200, S400, F200 and F400 treatments respectively.

The large amount of NH_4^+-N observed 1 DAUA indicates rapid urea hydrolysis after urine application. In addition, the >100% recovery in the F400 treatment suggests again a possible priming effect.

The elevated NH_4^+-N levels in urine treatments then declined with time. Within the period of 1-27 DAUA, 254 and 390 kg NH_4^+-N/ha disappeared from the S400 and F400 treatments respectively. These amounts were 61 and 71% of soil NH_4^+-N present at 1 DAUA in the S400 and F400 treatments respectively. Thus, the rate of soil NH_4^+-N disappearance was faster in the flat site than the steep site in the 400 kg urine N/ha treatment.

In contrast, in the 200 kg urine N/ha treatment, the rate of soil NH_4^+-N disappearance was faster in the steep site than the flat site. From 1-27 DAUA, 161 and 102 kg soil NH_4^+-N/ha disappeared from the S200 and F200 treatments respectively. These amounts were 74 and 54% of soil NH_4^+-N present at 1 DAUA in S200 and F200 treatments respectively

At 100 DAUA, the soil (0-15 cm) NH_4^+-N levels in urine treatments had reached the levels of the controls.

Downward movement of NH_4^+-N occurred immediately after urine application. By 1 DAUA, 26%, 12%, 7% and 18% of the added urine N in the S200, S400, F200 and F400 treatments respectively, was recovered as NH_4^+-N in the 7.5-15 cm soil depth (Table 3.4). This is probably due to preferential flow through soil macro-pores, as there had been no rainfall on the first day (Fig. 3.5).

3.4.5 Nitrate

After urine application, the 2 M KCl -extractable NO_3^--N (μg NO_3^--N/g soil) levels in the soil to a depth of 15 cm showed a different pattern to the soil ammonium (discussed in the previous section). At both sites, urine treatments did not significantly affect the soil (0-15 cm) NO_3^--N levels at 1 and 6 DAUA (Table 3 of Appendix 1). Then soil NO_3^--N levels began to increase due to nitrification. Though there was a trend of increasing NO_3^--N content over the first 4 weeks, the increase was small relative to the total quantities of N added. For example, by 27 DAUA, only 2 to 7 % of added urine N was recovered as NO_3^--N in soil (0-15 cm) at both sites (Table 3.4). In addition, there was a lack of quantitative agreement between the decrease of NH_4^+-N and the NO_3^--N production in the soil. The increases in NO_3^--N levels in soil by 27 DAUA were only 8,

7, 9 and 3% of the amounts of soil NH_4^+-N that had disappeared between 1 and 27 DAUA from the F200, F400, S200 and S400 treatments respectively.

However, whether further increases in NO_3^--N occurred shortly after 27 DAUA could not be determined as there were no sampling times between 27 and 100 DAUA.

No statistically significant differences in NO_3^--N levels were observed between control and urine treatments at 100 and 142 DAUA at both sites.

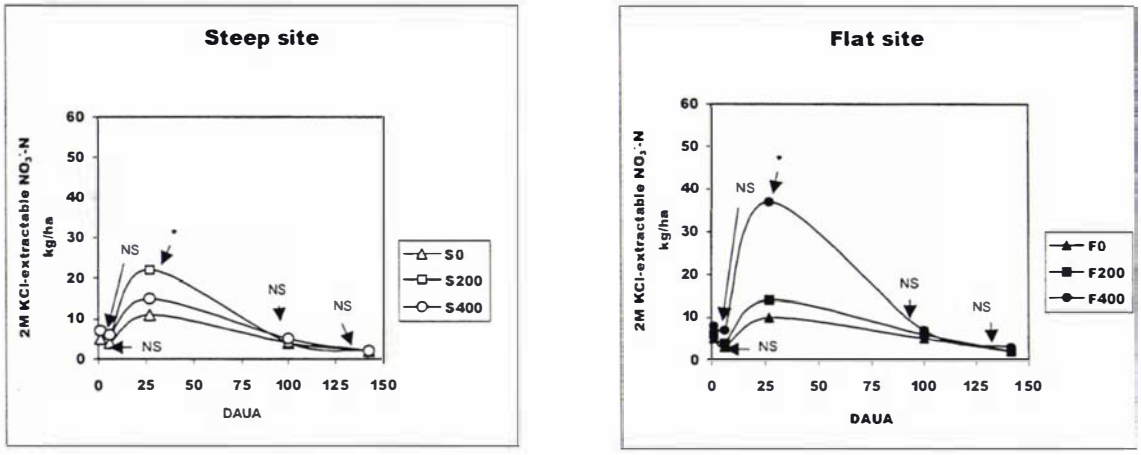


Fig. 3.8 Effect of urine treatments on soil (0-15 cm) NO_3^--N. * = significant treatment differences were observed within the sampling time. NS = no significant treatment differences were observed within the sampling time.

These results appear to indicate that although some nitrification occurred during the experiment it was relatively small compared to the total amount of NH_4^+-N in the urine treated plots.

3.4.6 Mineralisable N

The urine N recovered as soil mineral N was less than 50% of that added by 27 DAUA in all the urine treatments. To investigate whether this unaccounted-for-N had been converted into readily mineralisable organic N, an anaerobic incubation was conducted to investigate any changes in soil mineralisable N levels in soils sampled 27 DAUA. Thereafter anaerobic incubation was also conducted on soils from samplings at 100 and 142 DAUA.

At both sites, in all treatments, higher mineralisable N levels were observed in the 0-7.5 cm soil depth than the 7.5 –15 cm soil depth (Table 3.5).

At both sites, mineralisable N in the 7.5-15 cm soil depth, was not significantly affected by urine treatments. Therefore, only changes in mineralisable N in the 0-7.5 cm soil depth are discussed (Fig. 3.9).

Table 3.5 Mineralisable N levels (kg N/ha) in control soils at different depths. Values are the average of soils sampled 27, 100 and 142 DAUA.

Soil Depth	Flat site	Steep site
0-7.5 cm	107.7	84.5
7.5-15 cm	51.3	45.9
Total (0-15cm)	159	130.4

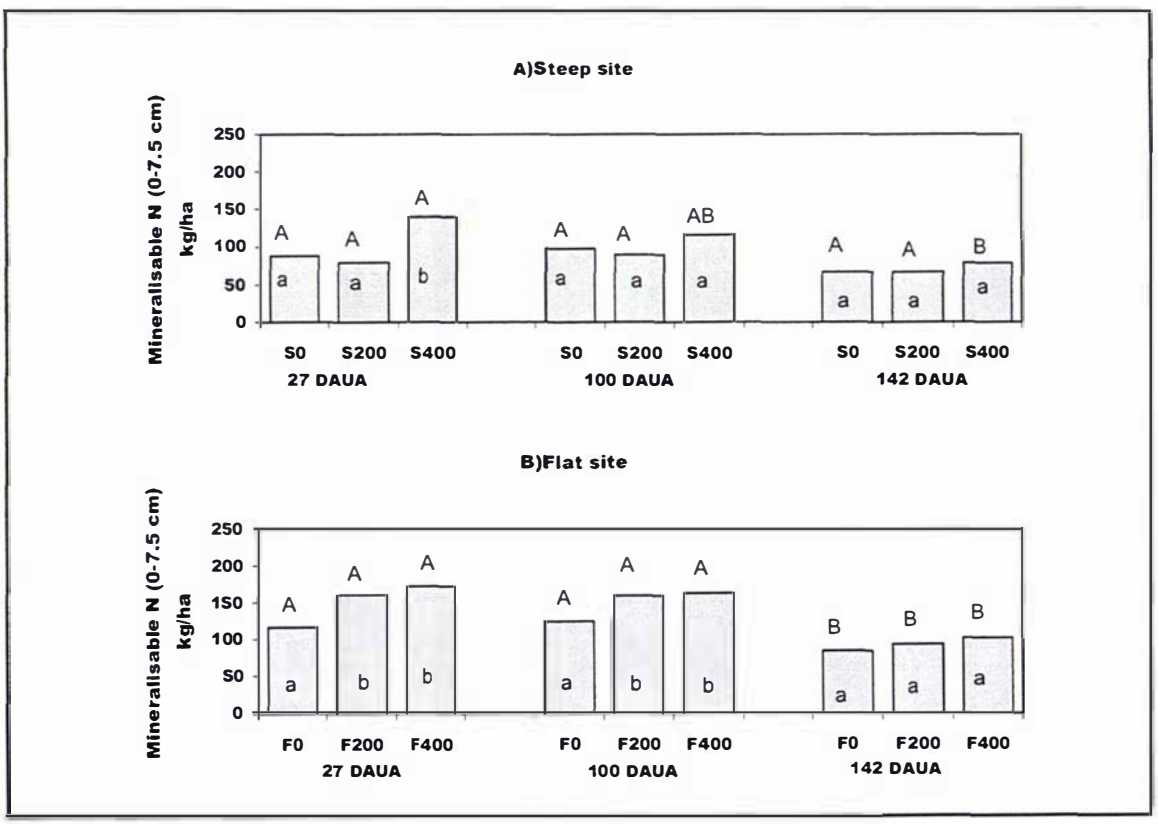


Fig. 3.9 Effects of urine treatments on soil (0-7.5 cm) mineralisable N levels at 27, 100, 142 DAUA. Treatments with common lower case letters do not differ (P<0.05) within a sampling day at the same site. Treatments at the same site with common upper case letters do not differ at (P<0.05) between sampling days.

Urine treatments significantly increased the soil (0-7.5 cm) mineralisable N levels. At the steep site this was observed only in the S400 treatment at 27 DAUA. In contrast, at the flat site, mineralisable N levels significantly increased in both treatments at 27 and 100 DAUA.

It is interesting to note that at the flat site, in all treatments including controls, the mineralisable N levels were similar from 27 to 100 DAUA but then decreased by 142 DAUA. This was also observed in the S400 treatment (Fig.3.9).

At 27 DAUA, mineralisable N had increased by more than 56 and 51 kg/ha, compared to controls, in the F400 and S400 treatments respectively. During the period 1-27 DAUA, the decrease in soil (0-7.5 cm) NH_4^+-N was 327 and 218 kg/ha in the F400 and S400 treatments respectively (data not presented). Therefore, the increases in mineralisable N levels accounted for 17 and 23% of the loss of NH_4^+-N in the F400 and S400 treatments respectively.

3.4.7 Pasture response

Pasture yields were measured on two occasions, at 27 DAUA on 06 July1999 (Cut 1) and at 100 DAUA on 17 August 1999 (Cut 2). At the completion of the trial, 142 DAUA, on 29 October 1999 there had been no measurable pasture regrowth in any of the plots after the cut at 100 DAUA.

Over the two pasture growth periods, urine treatments significantly increased the combined (27 DAUA + 100 DAUA) pasture dry matter accumulation (Fig 3.10). The total pasture dry matter accumulation on the S200, S400 and F200 treatments increased by 2 fold, and on the F400 treatments 3 fold, compared to the control treatments.

At the first cut (27 DAUA), no statistically significant increases in DM accumulation were observed at either site. This could be due to poor pasture growth because of cold winter conditions. As a result of this, a low uptake of urine N was observed, although the pasture N concentration was markedly increased by urine addition. At the first harvest, the lower dry matter production and lower pasture N uptake on the 400 kg urine

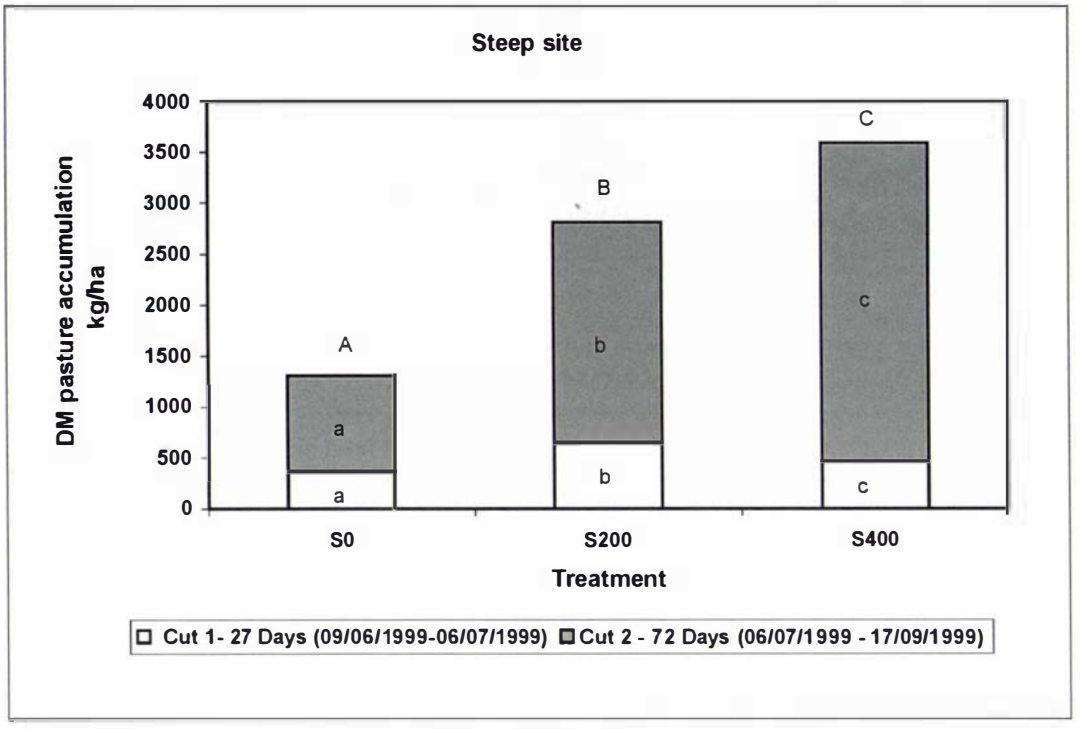
N/ha treatment compared to the 200 kg urine N/ha treatment, could be due to pasture burn and other indirect effects.

At the second cut, urine treatments significantly increased ($P<0.05$) the DM accumulation at both sites. This may be a combined result of better environmental conditions for pasture growth in spring and the extended growing period. At both sites DM accumulation during the second pasture growth period was 2 times higher in the 200 kg urine N/ha treatment and 3 times higher in the 400 kg urine N/ha treatment, compared to the control.

The N uptake by pasture was significantly increased by the urine application (Fig. 3.11 and Table 3.6). Total pasture N uptake was increased 2 - 4 fold compared to controls. At 27 DAUA, pasture N uptake at the higher urine N rates at both sites was lower than at the lower urine N rate treatment. As noted previously this could be due to pasture burn.

Total urine N recoveries in pasture were 26%, 24%, 22% and 18% in the S200, S400, F200 and F400 treatments respectively.

Urine N recovered as soil mineral N at 27 DAUA had declined by 64 (S200), 160 (S400), 73 (F200) and 179 (F400) kg N/ha by 100 DAUA (Table 3.4). The urine N uptake by pasture from 27-100 DAUA was 36, 86, 34 and 69 kg/ha from S200, S400, F200 and F400 treatments respectively (Table 3.6). These amounts of pasture N uptake accounted for 55%, 54%, 47% and 39% of the decrease in soil mineral N from 27-100 DAUA.



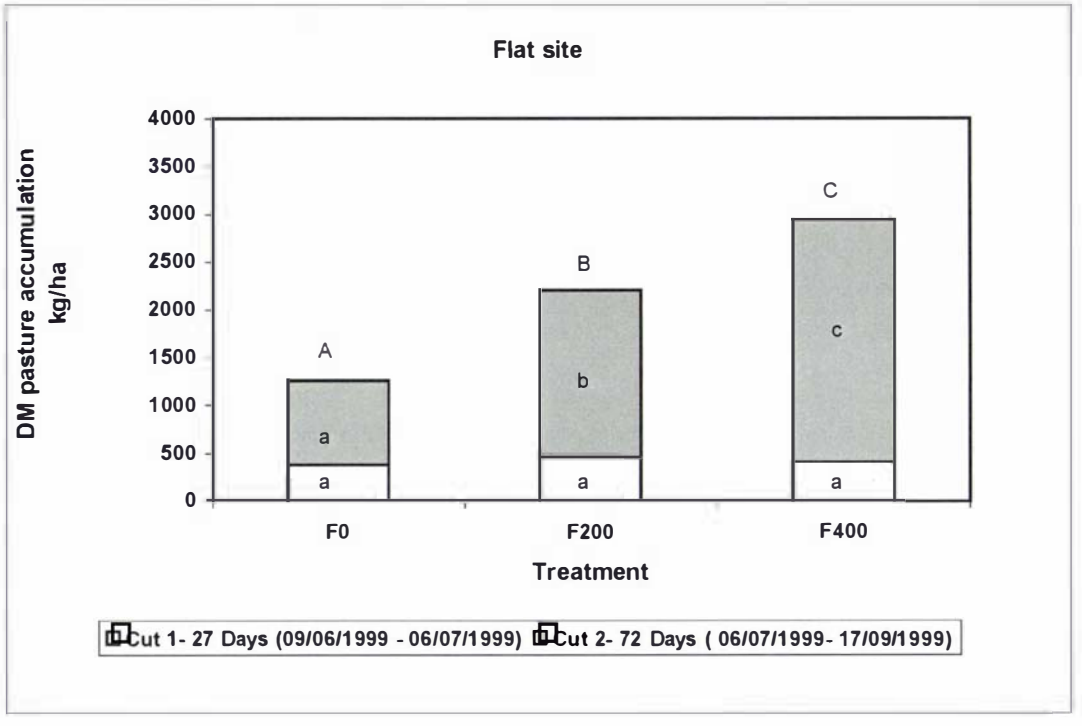
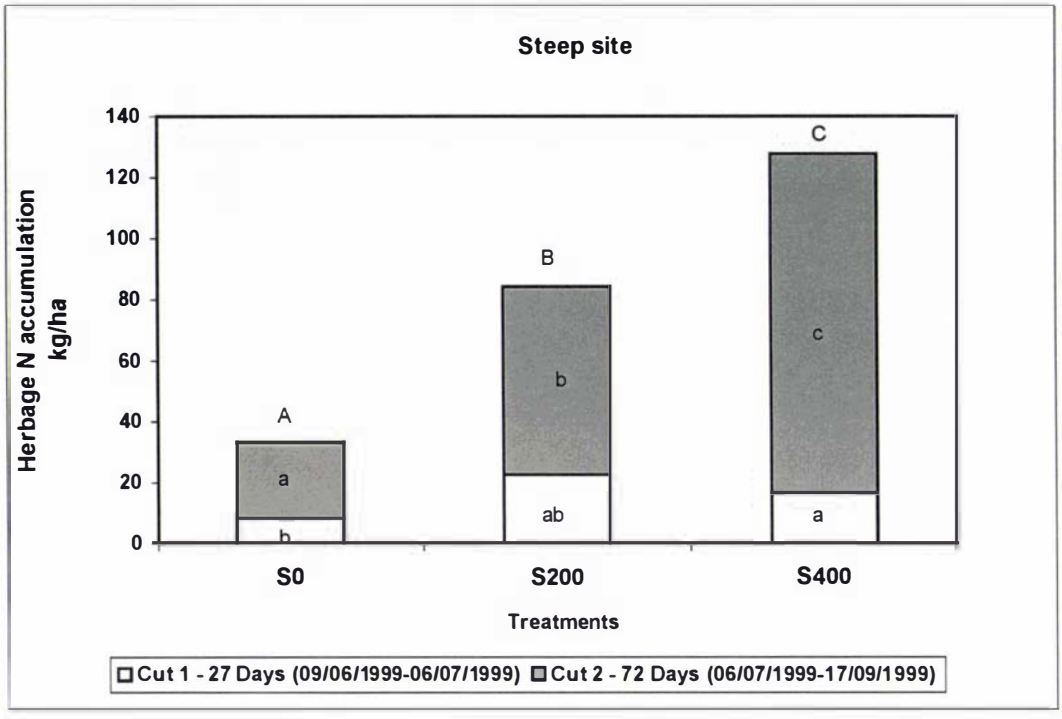


Fig. 3.10 Effect of urine treatments on pasture DM accumulation. Total DM accumulations at the same site with common upper case letters do not differ at the $P<0.05$ level. Treatments at the same site and at the same harvest with common lower case letters do not differ at the $P<0.05$ level.



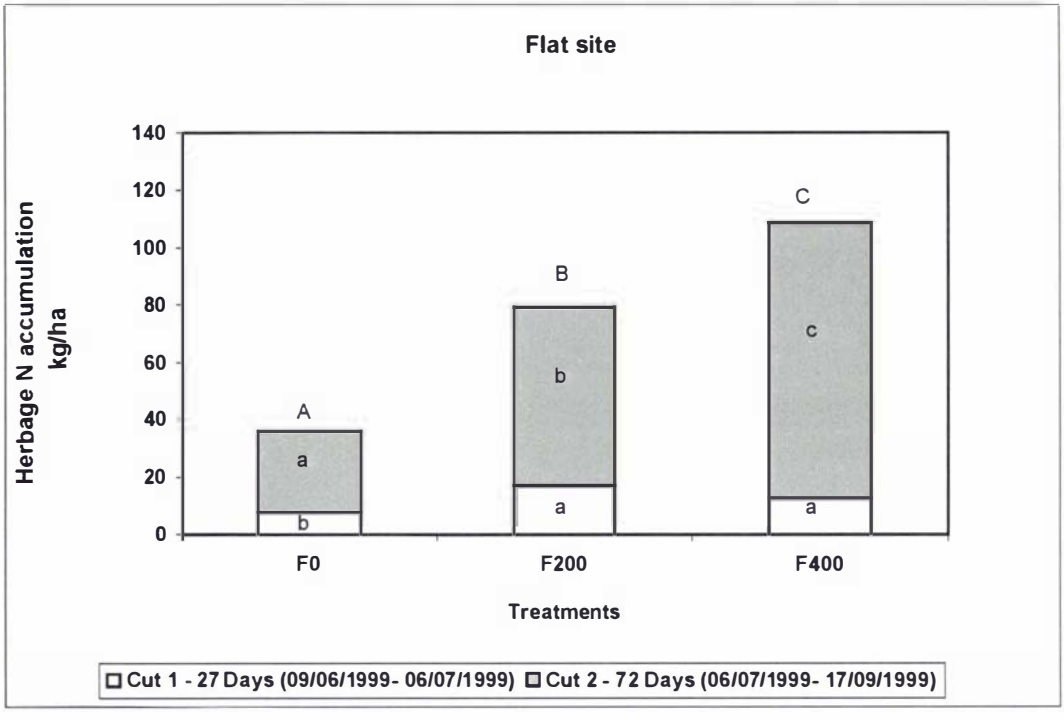


Fig. 3.11 Effect of urine treatments on pasture N accumulation. Total pasture N accumulations at the same site with common upper case letters do not differ at the $P<0.05$ level. Treatments at the same site and at the same harvest with common lower case letters do not differ at $P<0.05$ level.

Table 3.6 Pasture DM production and N uptake as effected by urine application.

Treatment	Cut 1			Cut 2		
	DM kg/ha	N %	N Uptake kg/ha	DM kg/ha	N %	N Uptake kg/ha
F0	380	2.0	8	883	3.1	28
F200	451	3.7	17	1759	3.5	62
F400	406	3.0	12	2533	3.9	97
S0	361	2.2	6	943	2.6	25
S200	643	3.6	23	2172	2.8	61
S400	464	3.6	17	3129	3.5	111

3.4.8 Ammonia volatilisation

At both sites, urine treatments significantly increased ($P<0.05$) the ammonia volatilisation (Fig. 3.12). The ammonia N trapped by the samplers was more than 7, 18, 11 and 33 times greater than the controls for the S200, S400, F200 and F400 urine treatments respectively. Not surprisingly, the ammonia loss through volatilisation was higher in the 400 kg urine N/ha treatment than the 200 kg urine N/ha treatment.

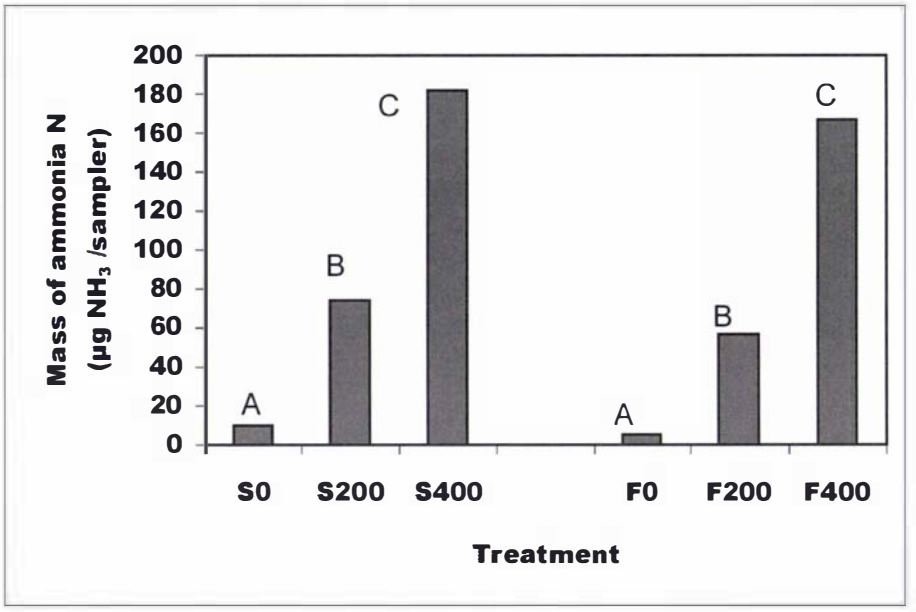


Fig. 3.12 Effect of urine treatments on ammonia volatilisation. Treatments with common letters within a site do not differ at the $P<0.05$ level.

The relationship described in Section 3.3.5 was used to estimate the quantities of urine N lost through ammonia volatilisation per hectare. The resulting estimates of urine N loss were very large, ranging from 21% to 34% of that added (Table 3.7).

Table 3.7 Effect of urine treatments on ammonia volatilization.

Treatment	μg NH_3-N/sampler	kg NH_3-N/ha	% of added urine N
S0	10.1	8.1	-
S200	74.0	59.2	25.6
S400	182.0	145.6	34.4
F0	5.2	4.16	-
F200	56.7	45.4	20.6
F400	166.6	133.3	32.3

3.5 Discussion

3.5.1 Urine N recovery

During the experiment the apparent recovery of added urine N as soil mineral N and mineralisable N was assessed by comparing the appropriate soil analyses in control and treated plots. In a similar way, uptake of urine N by pasture, and loss of N through ammonia volatilisation, were assessed by comparing measurements on control and treated plots.

The total urine N recovery (%), calculated from the sum of urine N in the mineral and mineralisable soil N pools plus urine N lost from the soil through plant uptake and volatilisation, is illustrated in Fig. 3.13.

Soon after urine application in all the treatments, the quantity of urine N accounted for was either greater than or close to 100% of that added. This suggests a priming effect

after urine application (Fig. 3.13 and 3.14). This is discussed in more detail in Section 3.5.6.

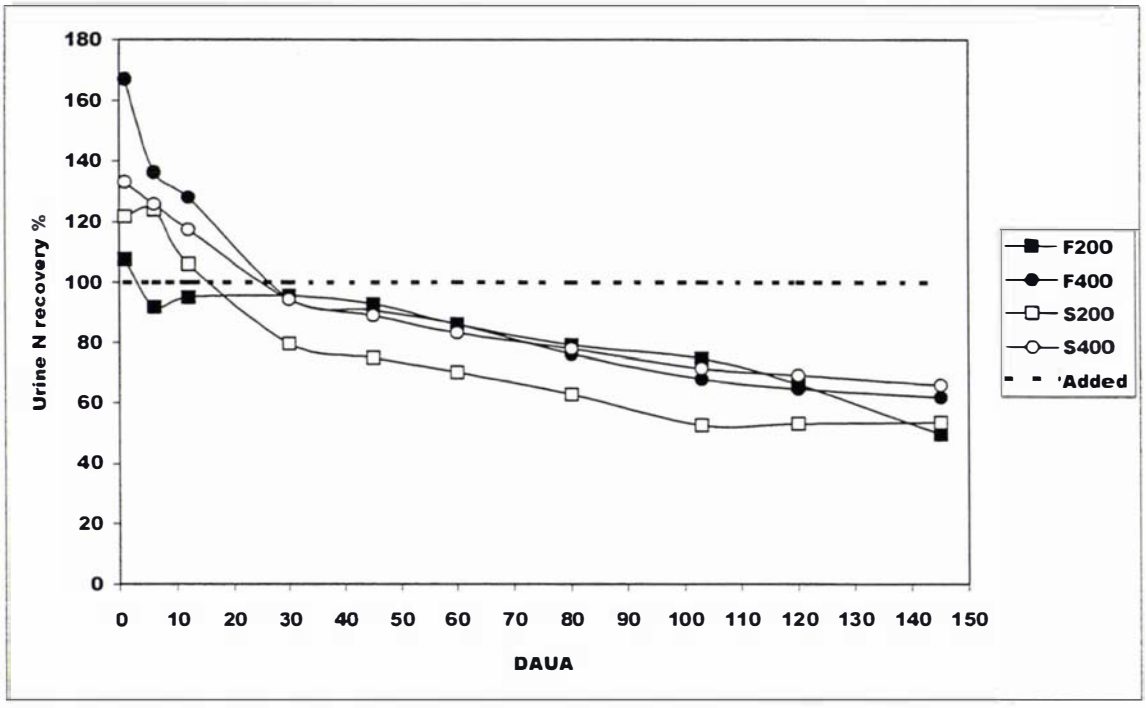


Fig. 3.13 Total urine N recovery (%) during the experiment.

The proportion of urine N accounted for at the beginning of the current experiment was high compared to other studies discussed earlier in Section 3.2.3. In an experiment conducted at a flat land site in Palmerston North (Ball *et al.*, 1979), 30-35% of the added urine N could not be accounted for 1 day after the experiment began. Carran *et al.*, (1982) at a flat site in Gore, also found that about 50 and 30% of the applied urine N could not be accounted for in dry and wet plots respectively, a day after application. Both these sites in Palmerston North and Gore were well developed as well as being relatively flat. They also had a history of high production and intensive use.

At the end of the experiment at 142 DAUA, 66% (S400), 62% (F400), 54% (S200) and 50% (F200) of added urine N was accounted for in the soil as mineral or mineralisable N, or lost by volatilisation or plant uptake (Fig. 3.13). It was assumed that urine N not accounted for in any of these pools during the experiment was immobilized to complex organic matter in soil and converted to non-mobile N.

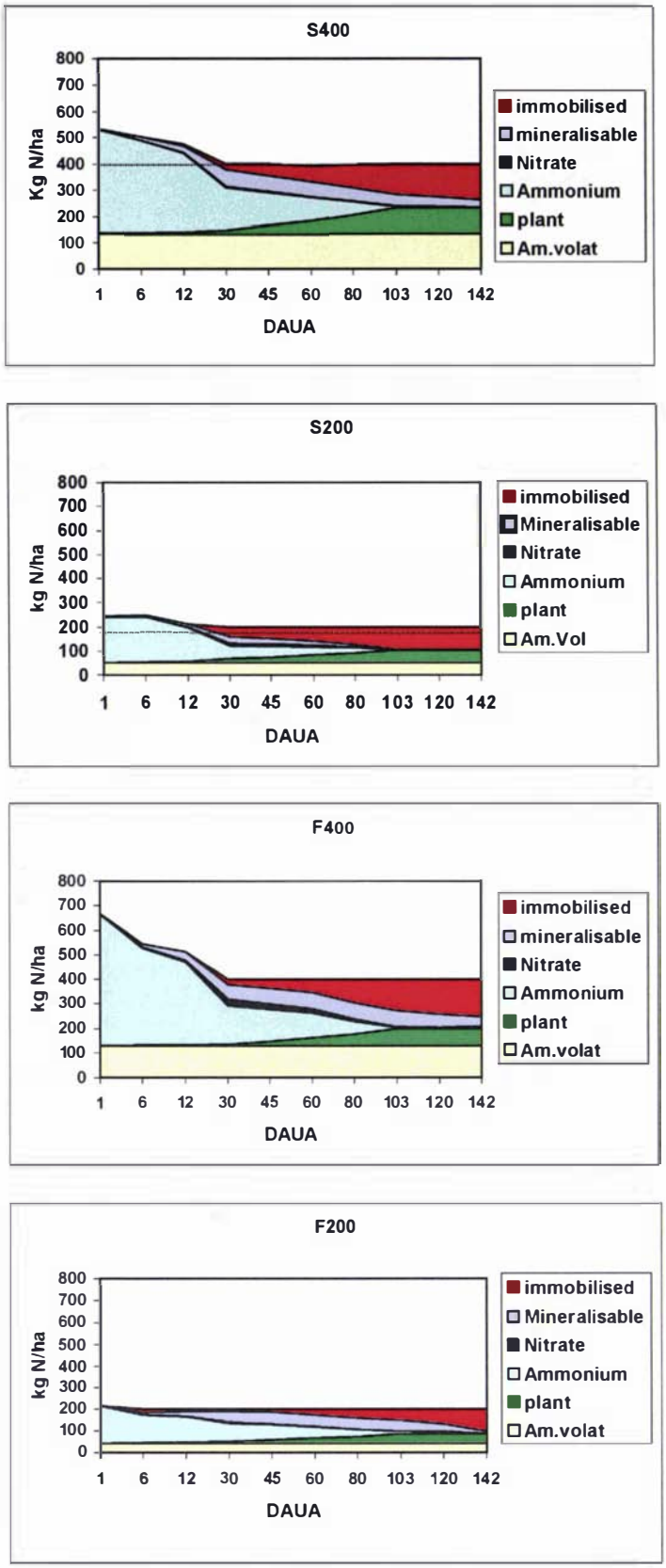


Fig. 3.14 Urine N recovery during the experiment.

The apparent distribution of urine N in the pools described earlier is illustrated in Fig. 3.14.

The urine N in the mineral N pool was mainly in the form of NH_4^+-N throughout the experiment. This suggested that nitrification rates were low and that leaching losses of NO_3^--N would therefore be low.

Only 18-27% of the added urine N was recovered in the plant. The urine N loss by ammonia volatilisation was large, ranging from 21-34% of added N. At the end of the experiment (142 DAUA), 34 -50% of added urine N was assumed to be immobilized into complex organic matter. Urine N transformations in these various pools are discussed separately in the following sections.

3.5.2 Mineral N

This experiment demonstrated that increased soil mineral N levels could occur during the first 2-3 months after urine application (Fig. 3.14). Large amounts of NH_4^+-N were observed at 1 DAUA in both urine treatments at both sites (Fig. 3.7). This observation agrees with other reports of rapid urea hydrolysis after urine application (Section 3.2.3.1).

As noted earlier, NH_4^+-N was the dominant mineral N form found in urine-treated plots throughout the experiment. This is in contrast to many other studies that have found that NO_3^--N is often the major form of N present in the urine patch 2-5 weeks after application (Ball *et al.*, 1979; Carran *et al.*, 1982; Haynes and Williams, 1992).

Although NH_4^+-N was the dominant form of mineral N throughout the trial, the large quantities of soil NH_4^+-N that were present at 1 DAUA in the urine-treated plots, declined rapidly with time. Between 88 and 376 kg/ha of the NH_4^+-N present 1 DAUA had disappeared by 27 DAUA (Table 3.4 and 3.8). The NH_4^+-N levels in urine treated plots then continued to decline after 27 DAUA to reach levels similar to the controls by 100 DAUA.

In most treatments except F400, the urine NH_4^+-N (0-15 cm) that had disappeared within the first 27 DAUA could be substantially accounted for by ammonia volatilisation, the increase in mineralisable N and plant uptake (Table 3.8).

Of these three pathways of loss during the first 27 DAUA, ammonia volatilisation appeared to be the greatest, ranging from 34-59% of the decrease in NH_4^+-N. However, the quantities of urine N lost through volatilisation were measured from the day of urine application (Day 0) to 6 DAUA and the decrease in urine N in the form of NH_4^+-N (0-15 cm) in Table 3.8A was calculated from 1 to 27 DAUA. Therefore, not all the measured amount of ammonia volatilisation would have contributed to the decrease in urine NH_4^+-N observed between 1 and 27 DAUA, i.e. some volatilisation would have occurred between 0-1 DAUA.

In the F400 treatment, the disappearance of urine NH_4^+-N could not be accounted for by ammonia volatilisation, plant uptake, the increase in mineralisable N and nitrification. Approximately 160 kg N/ha remained unaccounted for.

From 27-100 DAUA, although urine NH_4^+-N in soil continued to decline, plant uptake could only account for approximately half of the apparent N loss in all treatments.

It is commonly observed (see Chapter 6 of this thesis) that decreases in soil NH_4^+-N are mirrored by corresponding increases in soil NO_3^--N, through the process of nitrification. The lack of quantitative agreement between the rates of NH_4^+-N decline (Fig. 3.7) and NO_3^--N accumulation (Fig. 3.8) during this experiment can be explained by one of two scenarios.

The first possibility is that nitrification rates were indeed low during the experiment, and as noted above, significant amounts of NH_4^+-N were lost through NH_3 volatilisation (Section 3.4.8), by preferential downward movement (Section 3.4.4), by uptake of NH_4^+-N by plants and by immobilisation of NH_4^+-N into the soil organic matter.

The second possible scenario is that large amounts of nitrification did take place in the long interval between samplings at 27 and 100 DAUA, but the resulting NO_3^--N was then leached (see later Section 3.5.3).

Table 3.8 Apparent fate of urine NH_4^+-N from 1-27 DAUA (A) and 27-100 DAUA (B). All quantities are expressed as kg N/ha.

A) 1-27 DAUA

Treatment	Decrease in urine NH_4^+-N from 1-27 DAUA	Apparent fate of urine NH_4^+-N				Quantity of N unaccounted for
		Plant uptake	NH_3 volatilisation	Increase in mineralisable N	Increase in urine NO_3^--N	
S200	136	17	51	34	9	25
S400	232	11	138	58	2	23
F200	88	9	41	44	3	-9
F400	376	4	129	59	24	160

B) 27-100 DAUA

Treatment	Dccrease in urine NH_4^+-N from 27-100 DAUA	Apparent fate of urine NH_4^+-N				Quantity of N unaccounted for
		Plant uptake	NH_3 volatilisation	Increase in mineralisable N	Increase in urine NO_3^--N	
S200	53	36	-	-29	0	46
S400	157	86	-	-10	-3	84
F200	70	34	-	7	-3	32
F400	154	69	-	8	-25	102

3.5.3 Nitrification and leaching

The results of this experiment appear to suggest that little nitrification occurred following urine N application. However, as noted above, there was a possibility that further nitrification was occurring, but the NO_3^--N so formed had then been leached from the profile before it could be detected.

The results of this experiment show some similarities to the work of Ball *et al.* (1979) conducted at a lowland site at Palmerston North. Ball *et al.* (1979) however had more frequent sampling times and observed marked nitrification followed by leaching to end up with low NO_3^--N values in the 7.5-15 cm depth, 53 days after urine application. This final outcome at 53 DAUA was similar to that observed in the current experiment. It was therefore possible that the infrequent sampling carried out in the current experiment might not have detected the nitrification and leaching loss.

This possibility was explored in more detail as follows. Leached NO_3^--N could not be observed in the 7.5-15 cm soil depth, 100 DAUA. So if leaching had occurred, the NO_3^--N must have moved beyond 15 cm depth.

A simple water balance calculated for the experimental period suggested that by 100 DAUA only 52 mm of drainage would have occurred. The field capacity in the 0-150 mm soil depth considered for the water balance was 53 mm. Therefore, even if all the NH_4^+-N that had disappeared was assumed to be nitrified; large amounts of NO_3^--N should still be in the 75- 150 mm soil depth 100 DAUA. The apparent absence of any such NO_3^--N therefore suggests that the nitrification rates at these sites were indeed low and there had been little leaching of NO_3^--N.

The current experiment agrees with the previous work of Sakadevan *et al.* (1993), who observed no accelerated leaching of N from urine-affected soil in grazed hill pasture in New Zealand. However, although Sakadevan *et al.* (1993) measured leaching using *in situ* mini lysimeters with ion exchange resin traps, they did not measure soil NO_3^--N with time after urine application. Therefore, it is not clear whether or not the lack of leaching was due to low rates of nitrification, as was thought to be the case in the current experiment.

3.5.4 Pasture response

Urine treatments markedly increased the pasture dry matter production, pasture N concentration and pasture N accumulation (see Section 3.4.7), highlighting the value of urine N to hill country pasture production. These responses lasted only up to 100 DAUA. Haynes and Williams (1993) also indicated that pasture response to added

urine N normally lasts for 2 to 3 months. However, Theobald and Carran (2000) reported that responses in herbage production to urine application, persisted for periods exceeding 12 months in an experiment conducted in flatland in Palmerston North.

Pasture DM response to urine was higher at the steep site than at the flat campsite. This could be due to higher sunlight on the north facing steep site than the flat campsite, which was in a valley bottom.

The urine N recoveries by pasture, ranging from 18-27%, are within the range cited in literature (Section 3.2.3.7).

Although the low nitrification that appeared to occur in this soil may have decreased N losses through preventing leaching, it could also reduce N uptake by pasture. This is because plants prefer to take up a mixture of N forms or NO_3^--N (Section 3.2.3.7). In addition, microbes prefer NH_4^+-N for N assimilation (Section 3.2.3.6). This would lead to competition between plants and microbes for N.

3.5.5 Ammonia volatilisation

Estimation of NH_3 volatilisation after urine addition in this experiment indicated this to be a substantial loss of N from the system. In this experiment, 21- 34% of added urine N was lost as ammonia. Many other workers have also recorded considerable N losses by NH_3 volatilisation in urine patches (Ball *et al.*, 1979; Carran *et al.*, 1982; Vallis *et al.*, 1982). The technique used to estimate NH_3 volatilisation in this experiment (Carran *et al.*, 2000) greatly overcomes the technical difficulties associated with hill country volatilisation measurements and the technique is simple to use. The present experiment clearly showed the potential for high NH_3 volatilisation in hill country pasture, even during the wet, cooler winter period.

3.5.6 Mineralisation and immobilization

At both sites, the quantities of NH_4^+-N at 1 and 6 DAUA remained high (Fig. 3.7), although it appeared that a substantial amount of NH_3 volatilisation occurred during this period. This resulted in an apparent recovery of urine N of greater than 100% as

described earlier. This suggests that additional NH_4^+-N may have been produced by mineralisation of organic matter in some sort of priming effect. Ball and Tillman (1994) have also commented on recoveries of urine N in excess of 100%.

The exact cause of the priming effect is not clear. High salt concentrations in urine could dissolve some organic matter resulting in release of N, or cause the death of microbes (Section 3.2.3.6).

The F400 treatment showed a larger priming effect than did the S400 treatment. This could be due to differences in the mineralisation potential of the two soils as shown in Section 3.4.6; flat site soils had slightly higher mineralisable N (159 μg N/g soil in 0-15 cm) than soil from the steep site (130 μg N/g soil in 0-15 cm).

If N mineralisation is a common process when urine is added to the soil, the N loss from urine patches will include losses of N from the original organic matter as well as urine N.

As noted in Section 3.4.1, it was assumed that urine N not accounted for by soil mineral N or mineralisable N, or urine N lost from the soil through plant uptake, and volatilisation during the experiment was immobilized into complex organic matter in the soil and converted to non-mobile N. The increase in mineralisable N in urine treatments was a hint that immobilization of urine N was occurring. However, the exact source of the increased mineralisable N is not clear, as some of the N released by the priming effect could also be reimmobilized.

The estimated amount of immobilization at the end of the experiment was large. Values were 46% (S200), 50% (F200), 34% (S400) and 38% (F400) of added urine N. Ball *et al.* (1982) reported that many top soils in the summer wet hill country of the lower North Island contain very large quantities of N, rendered largely unavailable by the relatively wide C:N ratio of the soil organic matter present. Sakadevan *et al.* (1993) also indicated, from an experiment conducted at Ballantrae AgResearch hill country research station, that the majority of added urine N was immobilized in hill country soil.

3.5.7 Comparison of urine N transformations at two sites

The review of literature (Chapter 2) indicated that in hill country the N cycle is complex due to the existence of contrasting landscapes. This experiment was carried out on two contrasting landscapes, a flat site that showed some evidence of sheep camping and a steep slope.

Surprisingly, the general patterns of urine N transformations over time in the two sites were quite similar (Fig. 3.14). However, when compared using a number of soil fertility indices the two sites in fact, did not appear greatly different (Table 3.9).

Table 3.9 Soil fertility indices of the two sites.

Soil fertility index	Flat site	Steep site
Total N 0-7.5 cm (%)	0.34	0.37
Total C 0-7.5 cm (%)	4.7	4.9
C/N (0-7.5 cm)	14	14
Olsen P (0-7.5 cm) (μg/g soil)	44	83
pH	5.3	5.3

This may explain the similar behaviour between the sites that topographically were very different.

3.6 Conclusions

Urine application markedly increased the soil mineral N availability. A priming effect after urine application was indicated in both experimental sites. Increased mineral N could be found about 2-3 months after urine application.

NH_4^+-N was the dominant mineral N form throughout the experiment indicating that a low level of nitrification existed in the experimental soils. Therefore, the potential for leaching of added urine N was low in the experimental sites.

Pasture responses to the added urine were observed. Pasture dry matter production was increased 2-3 fold in the urine treated plots, compared to controls, during the experimental period. However, the estimated urine N recovery by pasture was only 18% to 27%.

Ammonia volatilisation after urine application was a major N loss mechanism, ranging from 21% to 34% of added urine N.

Immobilisation of urine N seems to be high in hill country pastures. During the first 27 DAUA 16% to 50% (mean 29%) of the loss of urine NH_4^+-N, could be accounted for by increased mineralisable N and at the end of the experiment, estimated immobilisation was 34% to 50% of added urine N.

CHAPTER 4

DEVELOPMENT OF ION EXCHANGE RESIN MEMBRANE SPIKES FOR CONTINUOUS MONITORING OF AVAILABLE SOIL NITROGEN IN HILL COUNTRY PASTURE

4.1 Introduction

The results of Chapter 3 revealed that more than 40-50% of added urine N could not be recovered as mineral N by 27 DAUA. Probable mechanisms of loss of urine N were assumed to be immobilization into microbial biomass and other complex organic carbon materials, and ammonia volatilisation. However, the widely spaced sampling times during the experiment resulted in a number of questions such as whether nitrification occurred or not, the detailed pattern of mineral N change with time, and exactly at what stage did most of the urine N start to disappear. Answers to these questions are extremely important in determining the fate of the unaccounted-for urine N.

The 2 M KCl -extractable N method, which was used in the experiment detailed in Chapter 3, has several disadvantages. First, the method is laborious. Five cores were taken from each plot, leading to 120 cores per sampling in what was a relatively small experiment. In hill country, taking this number of cores involves a lot of labour. In addition, soil samples needs to be extracted with 2 M KCl as soon as possible because mineral N does change due to microbial reactions. Hence, frequent sampling is not practicable using this technique.

In addition, the data obtained are only a measure of available mineral N at the time of sampling. The availability of N in the soil is regulated by numerous interacting processes including microbial mineralization and immobilization, diffusion, mass flow and plant uptake. Thus, the available N pool is highly variable over time and space. Over 90% of soil N is held in soil organic matter and its release by mineralisation and nitrification is dependent on a number of soil environmental factors. So the rate of

release of N is difficult to predict. In addition, nitrate which is produced from mineralisation is susceptible to leaching, denitrification and immobilization.

Consequently, soil tests for N availability have proved difficult to develop, and no single test has been universally adopted (McLaren and Cameron, 1996).

Methods involving the incubation of ion exchange resins in soils and their subsequent removal and extraction for nutrient ions have shown particular promise for providing integrative indices of available soil N. Anion exchange resins contain positively charged surface functional groups, that attract anions including phosphate, sulphate and nitrate by electrostatic attraction. Cation exchange resins contain negatively charged surface groups, that attract cations such as potassium and ammonium to their surfaces. Thus, ion exchange resins act as a sink for ions when placed in a suspension of soil and water.

The objective of this chapter is to develop a new method for N measurement using ion exchange resin membranes which may be suitable for use in hill country situations to enable continuous N measurements over time.

4.2 Literature review

4.2.1 Ion exchange resins

In recent years, interest in the use of ion exchange resins to study natural soil systems, has increased. The theoretical descriptions of ion exchange resins, discussed in this section, are based on the information in; BDH (1981), Harland (1994) and Skogley and Dobermann (1996).

Many specialty resin products have been developed. Macroporous ion exchange resins are the most common resins used in soil studies. They are generally uniform in external shape (spherical), with individual particles referred to as beads. Ion exchange resins in the form of sheets are called ion exchange resin membranes. During manufacture, membranes are extruded into sheets and combined with reinforcing material to provide dimensional stability and mechanical strength.

Most ion exchange resins are solid organic polymers with an electrostatic charge that is neutralized by a selected counterion of opposite charge. Hence, they function in a manner analogous to charged soil colloids. Most ion exchange resins are made from styrene polymerized with itself to form long chains. These chains are reacted with divinylbenzene to produce cross-linkages. Ion exchange membranes are made "cation permeable" or "anion permeable" by chemical treatment, whereby sulphonic acid (-SO3-) or quaternary ammonium ($-NR_3^+$) groups respectively are attached to the membranes (Fig. 4.1).

Cation exchange resins are classified as either strong acid or weak acid and anion exchange resins are either strong base or weak base. Strong acid cation exchange resins have active groups having a greater affinity for cations other than H^+ and weakly acidic cation exchange resins have a strong affinity to H^+. Resin studies involving the release of cations from soils and subsequent accumulation by resins, as a measure of cation mobility or bioavailability, should involve use of a strongly acidic type of cation exchanger. Strong or weak base anion exchange resins differ similarly by relative affinity of the active group for OH^-, compared with other anions.

Resins exhibit preferential selectivity for various ions. Knowing the relative affinity of the resin for each ion in the medium is critical to understanding the results of a particular study. When ion-exchange resins are equilibrated with a solution containing a mixture of ions, the proportions adsorbed by the resin will not be the same as the ionic proportions in the bulk solution. The following sequence (Harland, 1994) represents the order of adsorption usually found for dilute solutions of commonly encountered ions with standard resins.

Strong Acid Cation Resin (styrenic-sulfonate)

$Ag^+ > Cs^+ > K^+ > NH_4^+ > Na^+ > H^+ > Li^+$;
$Ba^2+ > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > Cs^+$

Strong Base Anion Resin (styrenic-quaternary ammonium)
$SO_4^{2-} > HSO_4^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > HSiO_3^- > F^- > OH^-$

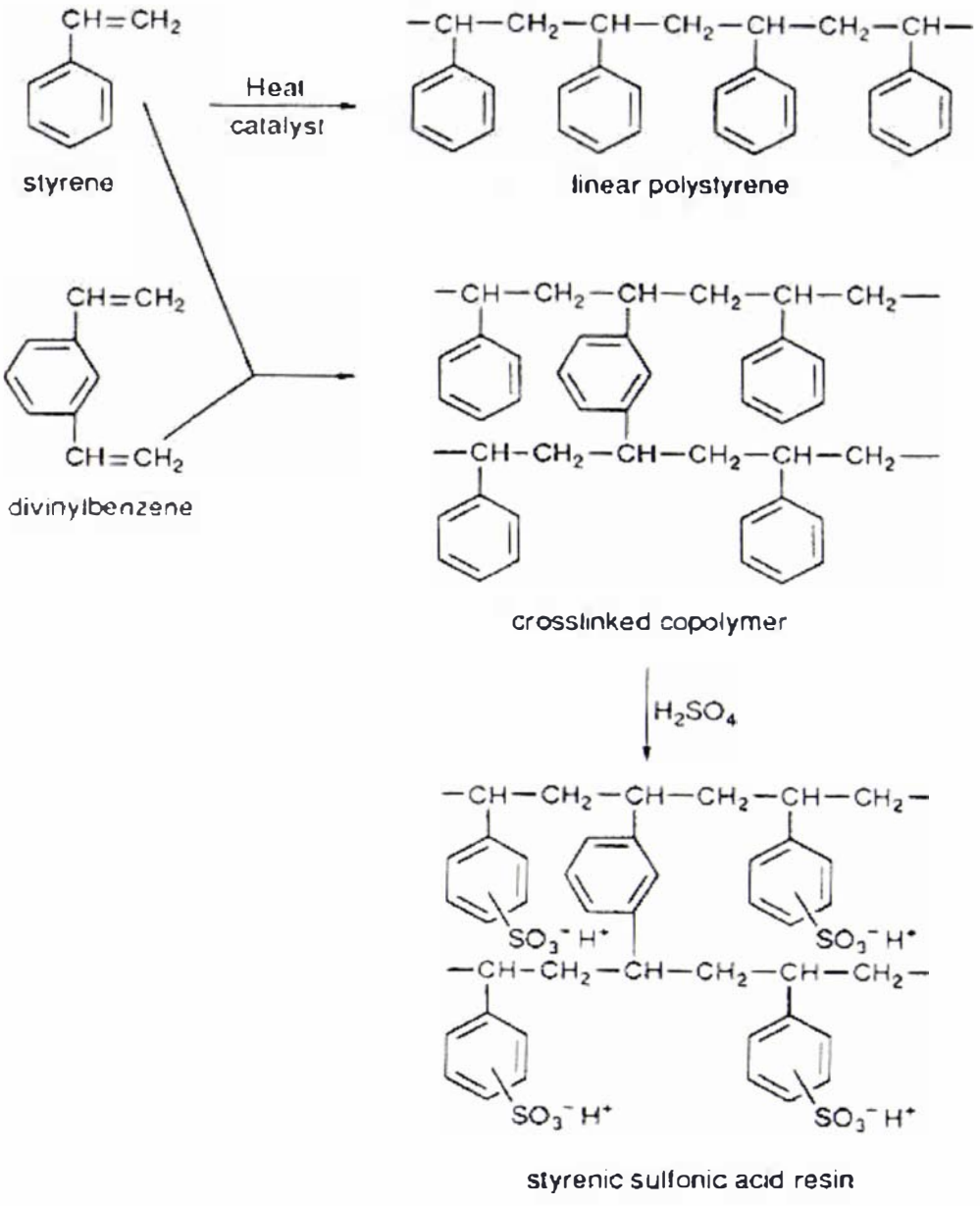


Fig. 4.1 Polymerization synthesis of a styrene sulfonic acid cation exchange resin (Harland, 1994).

Characteristics of commercially available BDH ion exchange resin membranes are described as:

- High permselectivity: This describes their ability to allow, for example, a cation to pass through much more easily than an anion.
- Low electrical resistance

- High mechanical strength : The polymeric fibre cloth used in these membranes give them adequate strength for any normal application.
- Resistance to chemical attack: These membranes are stable in alkalis and acids and in inorganic salt solutions.
- High thermal resistance: Generally suitable for temperatures up to 60 °C, but for continuous use a maximum working temperature of 40 °C is recommended.

4.2.2 Diffusion

Ion exchange involves the redistribution of ions from the solution to the resin. This redistribution occurs through diffusion. Diffusion means 'spreading out', and is caused by random thermal motion, as is the Brownian movement of colloidal particles observable under the microscope (Wild, 1981). In unstirred liquids, all the molecules and ions of the solvent and solute have this random movement. As a result of this spontaneous molecular motion, diffusion intermingles the ions and molecules in gases, liquids and solids without the participation of external forces.

The motion of individual ions or molecules is irregular, and at equal concentrations, no net movement occurs. However, if concentrations are different, substances move from regions of higher to those of lower concentration. The driving force is the existence of a concentration gradient. Diffusion is the processes by which nutrients migrate to the depletion zone near roots to maintain soil solution equilibrium levels (Wild, 1981; Jungk and Claassen, 1997). Tinker and Nye (2000) extensively reviewed the subject of solute flux through soil. The following formula was used to calculate the diffusion flux.

$$F = - D_l \theta f \, dC/dx + F_E \qquad (4.1)$$

where

F = flux density of solute (kg/m^2/s)

D_l = the diffusion coefficient of the solute in free solution (m^2/s)

θ = the fraction of the soil volume occupied by solution; and gives the cross section for diffusion through solution (m^3/m^3)

f = an impedance factor (dimensionless)

dC/dx = the concentration gradient of solute in the soil solution (kg/m^4)

F_E = the excess flux created by the possibility of surface diffusion ($kg/m^2/s$)

The impedance factor needs to be measured indirectly. It varies with the moisture content of the soil because, as soil becomes drier the diffusive pathway becomes more tortuous. The relationship between the impedance factor and soil moisture for chloride ion in a sandy loam is shown in Tinker and Nye (2000). The same data were used to draw the logistic curve fit (Fig. 4.2) for the relationship between impedance factor and moisture. It can be seen that under very dry conditions the impedance factor (f) is very low.

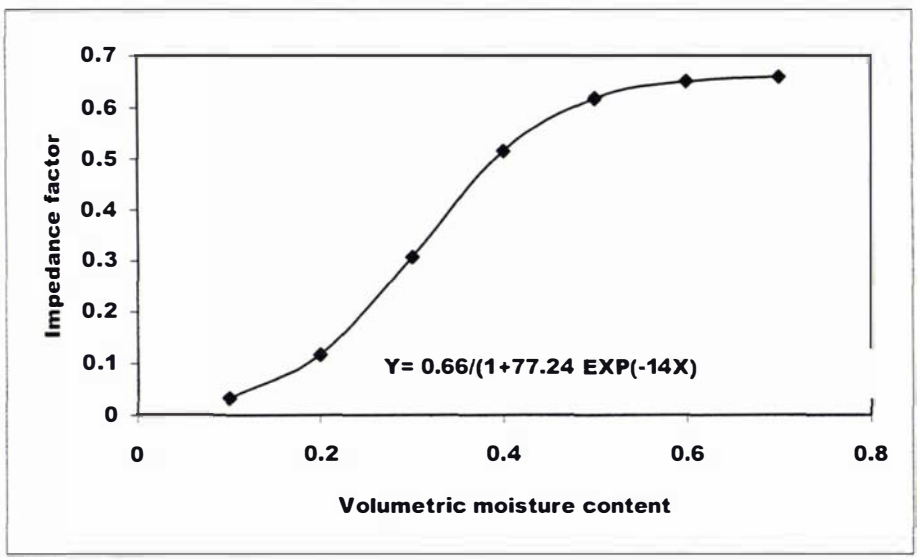


Fig. 4.2 Relationship between diffusion impedance factor and moisture content. (Logistic curve fit for the data in Fig. 4.1 of Tinker and Nye (2000).)

4.2.3 Ion exchange resin use in recent soil research

Recently, ion exchange resins have been used in a number of ways in soil analysis. Sibbesen (1978) used resin bead-water-soil suspensions to extract soil phosphate. The suspensions were shaken and transferred to a sieve (mesh size 0.355 mm), which retained the resin and allowed the soil suspension to pass through. Then the resin was washed to remove adhering soil and resin-adsorbed P was extracted with 1 M HCl.

However, Sibbesen (1977) had earlier suggested a better method to separate soil and resin after shaking. In that method, the resin was placed in a nylon netting bag which was immersed in a soil suspension and shaken. Compared to the method (Sibbesen (1978) where the resin beads are freely suspended in the soil-water mixture, the bag procedure allowed quicker separation of resin from the soil suspension.

Subsequently, researchers used these resin-filled bags directly in the field to assess N availability in soil (Binkley and Matson, 1983; Binkley, 1984; Carlyle and Malcom, 1986), to measure N mineralisation and nitrification (Distefano and Gholz, 1986; Hubner *et al.*, 1991), nitrate movement (Schnabel *et al.*, 1993) and as a phytoavailability soil test (Skogley *et al.*, 1990).

A major disadvantage of the buried resin bag technique is the shape of the resin bags. The three dimensional nature of the resin bags means that the results are likely to be highly dependent upon the placement methods because of differences in the flow of water and nutrients through or around the bags and surrounding soil. Saggar *et al.* (1990) suggested that when used in pasture soil, the resin bags trap fine root material and soil particles. If not removed by washing, these entrapped materials interfere with further analysis. Furthermore, with normal wear and tear the sealed edges of the bags may rupture resulting in the loss of resin beads to the soil suspension during shaking. Sakadeven *et al.* (1994) used mixed resins in an *in situ* mini lysimeter for measuring nutrient losses by leaching from grazed pastures.

Saggar *et al.* (1990) introduced the use of an ion exchange resin membrane technique for extracting phosphorus from soil. Strips of anion and cation exchange membrane were shaken with suspensions of soil in deionised water for 16-17 hours. Then phosphate retained on the anion exchange resin strip was determined by shaking the strip directly with a colorimetric reagent (Murphy and Riley, 1962). Subsequently, some studies did simultaneous extraction from soil of N, S, Ca, Mg, K, Mn, Al and P by shaking soil with a resin membrane in distilled water (Qian *et al.*, 1992; Mclaughlin *et al.*, 1993). The resin was then separated from the soil and ions desorbed from the resin using an acid/salt solution.

Recently some work has been done on the use of ion exchange membranes for *in situ* measurement of soil nutrients (Cain *et al.*, 1999). Subler *et al.* (1995) and Qian and Schoenau (1995) directly inserted the membrane strip into soil that was incubated in containers. Cain *et al.* (1999) constructed a tool to place ion exchange resin membranes directly in the field. Cain *et al.* (1999) studied spatial and temporal variation in soil N availability in coastal dunes. Many of the disadvantages of the buried resin bags technique may be overcome by the *in situ* use of ion exchange resin impregnated membranes. Their essentially two dimensional structure ensures more surface area will be in contact with the soil. Compared to the resin bags, resin membranes can be inserted into the soil with minimal disturbance.

This technique could also offer additional advantages compared to their use in laboratory water-soil suspensions. Direct burial of resin strips in soil will more closely resemble a plant root in its natural environment. Subler *et al.* (1995) emphasized that *in situ* use of ion exchange membranes needed more work before reliable interpretations can be made under a wide variety of field and laboratory conditions. In New Zealand, use of ion exchange resin membranes in soil analysis has received much attention after the method was introduced by Saggar *et al.* (1990). However, there has been no attempt to use ion exchange membranes for *in situ* measurements of nutrients.

4.3 Development of the ion exchange resin membrane spike

For direct soil burial of resin membranes to be effective, a technique that allows rapid placement, removal and handling, needs to be developed. A series of studies were carried out to identify the most effective technique for direct burial of resin membranes.

4.3.1 Experiment 1: Preliminary assessment of the ability of resin strips to adsorb mineral N from Soil

At the first attempt, both anion and cation resin membranes were cut into 1 x 5 cm pieces and glued, using methacrylatebase epoxy glue (Cain *et al.*, 1999), to two sides of a rigid acrylic spike. These spikes were placed in saturated KCl solution for 24 hours, rinsed with deionised water and air-dried. The spikes were then buried into the soil of

two pasture plots, which were known from earlier studies to have contrasting levels of soil fertility and pasture growth. After 3 days, the resin spikes were removed from the soil, washed free of adhering soil with deionized water and then placed in centrifuge tubes containing 25 mL 2 M KCl and shaken for 1 hour. All nutrient ions adsorbed from the soil by the resin were then displaced into KCl eluent and the NH_4^+-N and NO_3^--N concentrations determined by Technicon Auto Analyzer (Searle, 1975; Blakemore *et al.*, 1987). Amounts of NH_4^+-N and NO_3^--N were expressed as μg-N/5 cm^2resin /3 days.

Table 4.1. Resin-adsorbed N (μg-N/5 cm^2/3 days) from two different pasture plots.

Spike	Plot 1:Poor Growth		Plot 2:Good Growth	
	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N
1	2.1	6.9	6.9	16.2
2	5.4	4.5	8.1	6.9
3	7.5	6.0	9.6	12.6
4	5.1	2.7	13.5	10.2
5	13.2	7.2	8.7	15.3
Average	**6.7**	**5.5**	**9.4**	**12.2**
CV%	62	34	27	31

The results (Table 4.1) show that the resin membranes successfully adsorb both NH_4^+-N and NO_3^--N when directly buried in the soil. This was the main conclusion to be drawn from this small experiment. An additional observation was that on average, resin adsorbed N values were higher in the fertile plot with good pasture growth than in the plots with poor pasture growth although there was considerable variation in N adsorption among the resin spikes. These results were sufficiently promising to move on to the next stage.

4.3.2 Experiment 2: Assessment of variability with resin spikes

Next, another simple experiment was carried out to find out whether the variation in resin-adsorbed N between spikes, observed in the previous experiment, was due to variability in the soil or variability between the spikes. Five resin spikes were placed in a large volume of a solution of NH_4NO_3 containing 10 μg NH_4^+-N/mL and 10 μg NO_3^--N/mL for a day, and the resin-adsorbed N analyzed (Table 4.2).

The results suggested that there was a considerable variation in N adsorption among the spikes (Table 4.2) even though they had been immersed in a uniform solution. Thus these resin spikes were thought to be not suitable for use in the field.

Table 4.2 Resin-adsorbed N (μg-N/5 cm^2/day) from NH_4NO_3 solution containing 10 μg/mL NH_4^+-N and 10 μg/mL NO_3^--N.

Spike	NH_4^+-N	NO_3^--N
1	56.8	203.8
2	71.3	119.5
3	52.0	326.0
4	129.3	162.8
5	135.3	323.3
Average	**88.9**	**227.1**
CV%	**45**	**41**

4.3.3 Experiment 3: Optimization of resin spike construction

The resin membranes used in the previous experiment were double sided-that is exchange resin was on both sides of the supporting fabric. It was suspected therefore that by gluing the membranes to the acrylic spikes, variable proportions of the cation /anion exchange sites were inactivated or rendered inaccessible by the glue. To test this, glued spikes and unglued pieces of resin membrane cut to the same size were immersed in separate 25 mL samples of NH_4NO_3 solution containing 10 μg NH_4^+-N/mL and 10 μg NO_3^--N/ mL for a day.

Table 4.3 Adsorption of N (μg-N/5 cm^2/day) by glued spikes and fresh resin membranes from 25 mL samples of NH_4NO_3 solution containing 10 μg NH_4^+-N/mL and 10 μg NO_3^--N/mL over a day.

Spike	Resin membranes (5 cm^2) glued to spikes		Fresh resin membranes (5 cm^2)	
	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N
1	34.8	86.3	122.8	211.3
2	124.0	182.0	135.3	228.3
3	75.5	158.0	116.3	174.3
4	81.8	108.8	121.8	222.5
5	38.3	95.8	116.8	220.5
Average	70.9	126.2	123.5	211.4
CV%	52	33	6	10

The results (Table 4.3) clearly suggest that the unglued portions of resin membranes adsorbed more NH_4^+-N and NO_3^--N and had greater uniformity than the resin membranes glued to spikes, therefore supporting the hypothesis that the variability in N adsorption of resin membrane spikes was due to the use of glue. This finding led to an alternative design of the resin membrane spikes.

4.3.4 Experiment 4: Optimization of resin spike construction II

The next experiment involved using a water-resistant adhesive tape instead of glue to attach the resin membranes to the acrylic spikes. Strips of cation and anion membranes (1x 6 cm) were taped to two sides of an acrylic spike (2 x 0.5 x 8 cm) using water resistant tape, leaving 5 cm^2 of membrane area for adsorption. Initially 16-resin membrane spikes were made and the variation among the spikes was again examined in NH_4NO_3 solution.

Table 4.4 N adsorption (μg-N/5 cm^2/day) to resin spikes immersed in NH_4NO_3 solution containing 10 μg/mL NH_4^+-N and 10 μg/mL NO_3^--N for a day.

Spike	Adsorbed NO_3^--N	Adsorbed NH_4^+-N
1	149.3	44.0
2	167.5	55.3
3	176.3	58.5
4	152.0	58.3
5	186.0	49.0
6	154.5	57.3
7	182.5	64.5
8	189.5	50.0
9	174.0	64.3
10	181.8	56.5
11	181.5	53.3
12	167.3	58.5
13	180.0	51.3
14	182.3	50.5
15	165.3	54.8
16	172.5	62.3
Average	**172.6**	**55.5**
CV%	**7**	**10**

The results (Table 4.4) indicated that there was relatively little variation in the amount of N adsorbed by resin membrane spikes when the membranes were attached to the spike using tapes. It was interesting to note that from a solution containing equal amount of NH_4^+-N and NO_3^--N, adsorption of NO_3^--N to resin spikes was greater and less variable than NH_4^+-N adsorption.

4.3.5 Experiment 5 : Evaluation of resin spike variability in soil

These resin spikes were also examined in a homogeneous soil to check suitability for field use. Soil (Manawatu Sandy Loam) was sieved (<2 mm) uniformly moistened (23.67%w/w) and placed in a container at a bulk density approximately similar to that in the field. Then eight KCl-saturated resin spikes were buried in the container of compacted soil. After seven days in the soil, spikes were removed and the resin-adsorbed NH_4^+-N and NO_3^--N were analyzed (Table 4.5). In addition in this experiment, after the standard single extraction with 2 M KCl , resin membranes were extracted a second time with another 25 mL of fresh 2 M KCl to check further recovery of N from the resin. In the second extract, only negligible amounts of N were detected. This suggests that one extraction is sufficient to recover a high proportion of adsorbed N from the resin membrane.

Table 4.5 N adsorption to resin spike from homogeneous soil (μg-N/5 cm^2/7 days).

Spike	Adsorbed NO_3^--N	Adsorbed NH_4^+-N
1	66.5	15.0
2	32.0	18.8
3	55.3	11.3
4	39.3	9.5
5	66.8	10.0
6	51.8	7.0
7	63.8	3.8
8	51.8	6.0
Average	**53.4**	**10.2**
CV%	**24**	**48**

The results in Table 4.5 indicated that the resin membranes attached to spikes with tape still showed some variation in the amounts of adsorbed N when inserted into relatively homogeneous soil. Adsorption of NO_3^--N showed lower variation than NH_4^+-N. From

this experiment, it was not clear whether the variation in N adsorption was due to soil variation or due to differences in the N adsorption capacity of each resin spike. Even though the soil used in the laboratory was relatively homogeneous there will inevitably be some variability remaining and this may account for some of the variation between resin spikes.

4.4 N adsorption to resin membranes

The N adsorption behaviour of the $5cm^2$ ion exchange membrane spikes was examined using different concentrations of NH_4NO_3 solutions. The KCl saturated resin spikes were kept for 24 hrs in 25 mL of NH_4NO_3 solutions containing 20, 40, 60, 80, 100, 150, 200, 250 and 300 μg/mL of NH_4^+-N and NO_3^--N.

Adsorbed N was then extracted by shaking the resin spikes for 1 hour with 25 mL of 2 M KCl . The concentrations of resin-adsorbed NH_4^+-N and NO_3^--N were analysed using a Technicon Auto analyser (Searle, 1975; Blakemore *et al.*, 1987).

Both NH_4^+-N and NO_3^--N adsorption to resin increased linearly with increasing initial solution N concentration up to 200 and 150 μg N/mL respectively. At these initial solution concentrations, the resin membranes (5 cm^2) adsorbed 1635 μg of NO_3^--N and 1111 μg of NH_4^+-N. Thereafter, N adsorption to resin was relatively constant indicating that these values were the maximum adsorption capacities of the resin spikes under these conditions. As previously noted, NH_4^+-N adsorption to resin membrane was less efficient than NO_3^--N adsorption.

The actual maximum N adsorption by resin spikes was determined by repeatedly placing the resin spike in fresh NH_4NO_3 solutions containing 300 μg/mL of NH_4^+-N and NO_3^--N until no further adsorption took place.

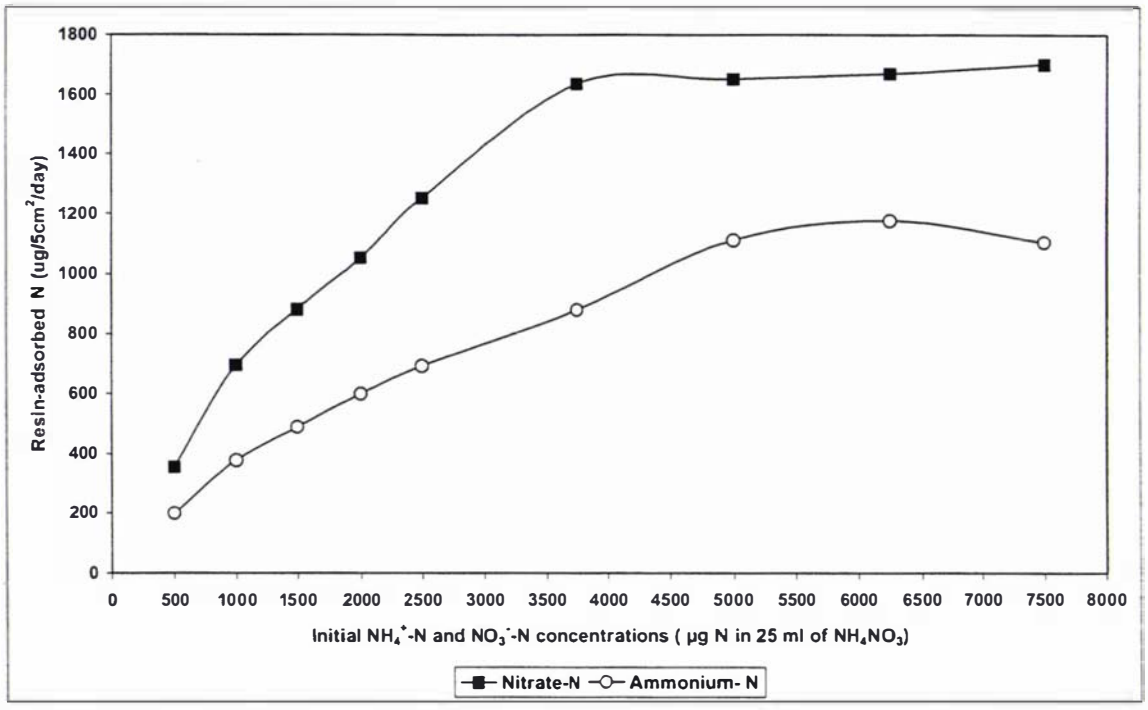


Fig. 4.3. N adsorption to resin spikes from different concentrations of NH_4NO_3 solution. Each point represents the average of three replicates.

Under these conditions, the maximum quantity of NH_4^+-N that was adsorbed to the resin spikes (5 cm^2 of cation membrane) was 2393 µg (171 µmoles) NH_4^+-N and the maximum quantity NO_3^--N adsorption to the resin spike was 2179 µg (156 µmoles) NO_3^--N.

In the previous experiments, NH_4^+-N adsorption to resin was much lower than the NO_3^--N adsorption to resin. Thus, it was surprising that in the results described in the previous paragraph, the maximum adsorption capacity of the 5 cm^2 cation membrane was higher than the 5 cm^2 anion membrane.

Simple arithmetic calculations were used to model the amount of N adsorption to KCl-saturated resins from 25 mL samples of NH_4NO_3 solutions of different concentrations.

Maximum capacity of 5 cm^2anion membrane = 156 µmoles

Maximum capacity of 5 cm^2cation membrane = 171 µmoles

It was assumed that Cl^- and NO_3^- do not show any differential selectivity in adsorbing to resin. Thus;

$$\frac{Cl^-(resin)}{Cl^-(solution)} = \frac{NO_3^-(resin)}{NO_3^-(solution)} \qquad (4.1A)$$

Example calculation of the amount of NO_3^--N adsorption to resin from the 25 mL sample of NH_4NO_3 solution containing 20 μg/mL of NH_4^+-N and NO_3^--N.

Initial amount of Cl^- on resin surface	= 156 μmoles
Amount of NO_3^--N in 25 mL sample of 20 μg/mL NH_4NO_3 solution	= 36 μmoles
Total amount of anions in the system	= 192 μmoles
Fraction of NO_3^- on the resin surface	= *a*
Fraction of Cl^- on the resin surface	= *a*

$$a\,(156) + a\,(36) = 156$$

$$a = 0.81$$

Thus, 81% of each anion will be adsorbed on the resin surface and 19 % will be in the solution.

Similar calculations were done using the other concentrations (Table 4.6) and the modelled values for resin-adsorbed N were plotted against the initial concentration of NO_3^--N in 25 mL of NH_4NO_3 solution in Fig. 4.3. It can be seen that the measured resin-adsorbed NO_3^--N and the estimated values were very close (Fig. 4.4), suggesting that the measured maximum sorption capacity of 5 cm^2 resin membrane was reasonable and the assumption of the resin's non-selectivity between NO_3^- and Cl^- was valid.

Similarly, the quantity of resin-adsorbed NH_4^+-N was estimated assuming the resin showed no selectivity between K^+ and NH_4^+ (Fig. 4.5). It can be seen that the measured resin–adsorbed values for NH_4^+-N were much lower than the estimated values. This suggests that resin is showing higher selectivity for K^+ than NH_4^+. Thus ,

$$\frac{NH_4^+(resin)}{NH_4^+(solution)} = n\frac{K^+(resin)}{K^+(solution)} \qquad (4.1B)$$

where n is the selectivity coefficient.

Table 4.6 Estimation of resin-adsorbed NO_3^--N from NH_4NO_3 solution containing different initial quantities of NO_3^--N.

μmoles of NO_3^--N in solution (x)	Total anions in system (x+ 156)	Proportion of anions adsorbed on resin a =(156/ (x+156))	Resin-adsorbed NO_3^--N (μg) (14) (x) (a)
36	192	0.81	407
71	227	0.68	686
107	263	0.59	889
143	299	0.52	1044
179	335	0.47	1166
268	424	0.37	1380
357	513	0.30	1520
446	602	0.26	1618
536	692	0.23	1691

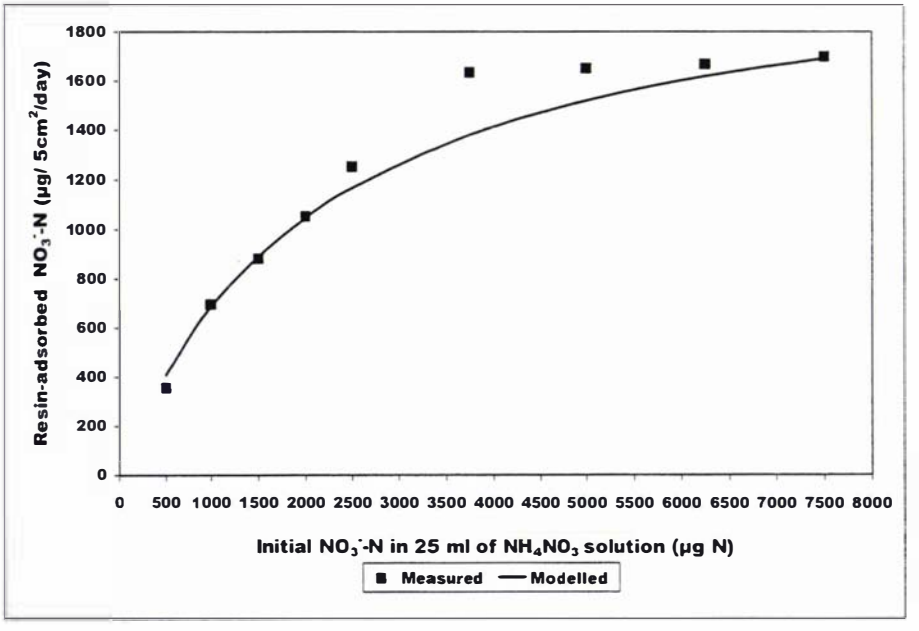


Fig. 4.4 Estimated and measured resin-adsorbed NO_3^--N from NH_4NO_3 solutions containing different initial quantities of NO_3^--N.

To estimate n and resin-adsorbed NH_4^+-N, the following simple arithmetic calculation was used.

Fraction of K^+ on resin surface	= b
Fraction of NH_4^+ on resin surface	= b/n
Maximum sorption capacity of 5 cm^2 resin membrane	= 171μmoles
Initial μmoles of NH_4^+ in solution	= y
$b\,(171) + b/n\,(y)$	= 171

An iterative approach was then used to estimate the value of n that best described the adsorption of NH_4^+-N illustrated in Fig. 4.3. The n value which gave the best fitted values to measured resin-adsorbed NH_4^+-N was chosen as the coefficient of selectivity for K^+. The estimated resin-adsorbed NH_4^+-N when n was assumed as 2.5 provided the best fit to the measured resin-adsorbed NH_4^+-N values (Table 4.7 and Fig. 4.5).

Table 4.7 Estimation of resin-adsorbed NH_4^+-N from NH_4NO_3 solutions containing different initial quantities of NH_4^+-N.

μmoles of NH_4^+-N in solution (y)	Proportion of K^+ on resin b=171/(171+(y/2.5))	Proportion of NH_4^+-N on resin (b/n)	Estimated resin-adsorbed μg NH_4^+-N (14) (y) (b/n)
36	0.92	0.37	185
71	0.86	0.34	343
107	0.80	0.32	480
143	0.75	0.30	600
179	0.71	0.28	705
268	0.61	0.25	922
357	0.54	0.22	1090
446	0.49	0.20	1223
536	0.44	0.18	1332

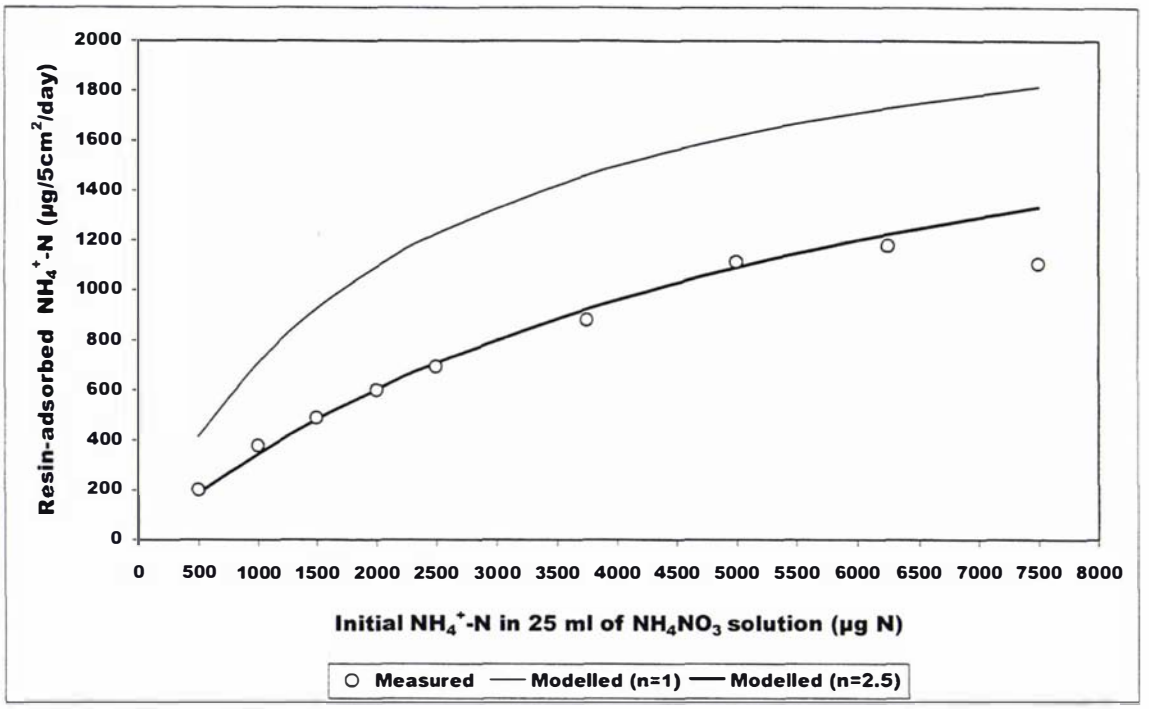


Fig. 4.5 Estimated and measured resin-adsorbed NH_4^+-N from NH_4NO_3 solutions containing different initial concentrations of NH_4^+-N. n = Selectivity coefficient of K^+

4.4.1 N adsorption to resin spikes over time

4.4.1.1 Experiment 1: N adsorption from solution

The rate of N adsorption by resin membrane spikes in soil depends on the kinetics of the adsorption process itself and also the rate of diffusion of NO_3^--N or NH_4^+-N through the soil to the resin membrane. In this simple preliminary experiment, the rate of adsorption of NO_3^--N and NH_4^+-N from a solution of NH_4NO_3 was investigated.

The KCl-saturated resin membrane spikes were put into centrifuge tubes containing 25 mL of solution of NH_4NO_3 containing 10 µg NH_4^+-N/mL and 10 µg NO_3^--N/mL . At 5, 10, 20 and 30 minutes and 1, 2, 6 and 12 hours after immersion in the NH_4NO_3 solution, 3 replicate spikes were removed and resin adsorbed NH_4^+-N and NO_3^--N contents were analysed (Fig. 4.6).

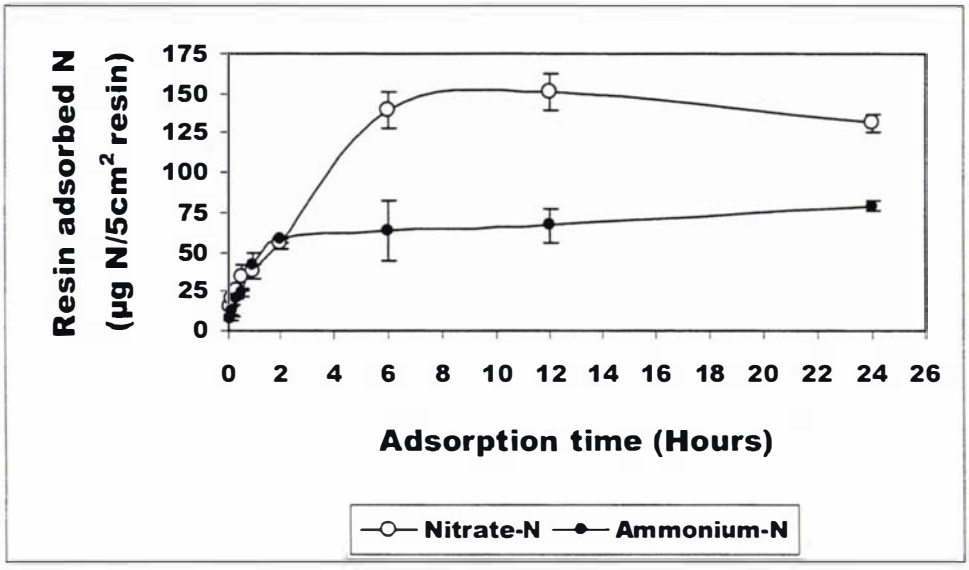


Fig. 4.6 N adsorption by resin spikes with time from NH_4NO_3 solution containing 10 µg NH_4^+-N/mL and 10 µg NO_3^--N/mL .

N adsorption by the resin membrane spikes was non linear with time. Initially rapid uptake was followed by a relatively slow rate of adsorption as the maximum adsorption was approached. It took 2-6 hours to achieve maximum adsorption. Up to 2 hours both NH_4^+-N and NO_3^--N were adsorbed at the same rate. From then on NH_4^+-N adsorption was much slower while NO_3^--N adsorption continued up to 6 hours. As seen previously, approximately twice as much NO_3^--N was adsorbed to resin membranes than NH_4^+-N at their maximum adsorption under these conditions.

4.4.1.2 Experiment 2: N adsorption from soil

To study the rate of N adsorption from soil the following experiment was conducted using air-dried, 2 mm sieved, homogeneously moistened Manawatu sandy loam. At the beginning of the experiment the moisture content (26.6% w/w) and 2 M KCl - extractable NH_4^+-N (15 µg/g soil) and NO_3^--N (131 µg/g soil) contents were analysed. Twenty-one plastic cups (143 cm^3) were filled with moist soil equivalent to 190 g air-dry soil. These cups were incubated at room temperature in the dark with the cups covered by a polythene sheet to minimise evaporation. From time to time, the polythene sheets were opened to maintain aerobic conditions. The soil 2 M KCl -

extractable NH_4^+-N and NO_3^--N contents were analysed in three cups at day 3 and in a further 3 cups at day 7.

A major difficulty in determining the rate of adsorption of soil nutrients to resins is ensuring that the nutrient level in the soil is constant with time. Any change in soil nutrient level over time will confound the apparent rate of sorption. In this experiment it was expected that any initial flush of mineralisation would have ceased after 7 days and the levels of NH_4^+-N and NO_3^--N in the soil would then be reasonably constant. The samples on day 3 and 7 were used to check that this was indeed the case.

At day 7, KCl-saturated resin spikes were inserted into the rest of the cups. On each of days 8, 9, 11, 15 and 22 (1, 2, 4, 7,and 14 days after resin spikes burial) three cups were taken and the resin adsorbed NH_4^+-N and NO_3^--N contents and 2 M KCl -extractable soil NH_4^+-N and NO_3^--N contents were analysed.

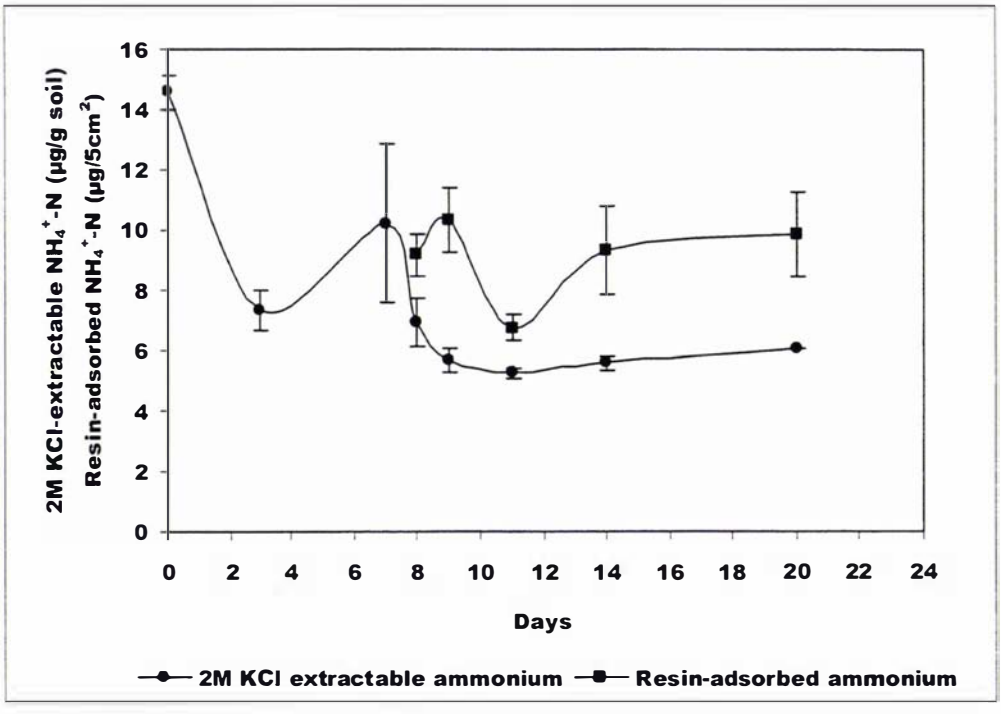


Fig. 4.7 NH_4^+-N levels during the incubation as measured by the 2 M KCl -extractable and Resin methods.

The 2 M KCl -extractable soil NH_4^+-N levels decreased over the first 8 days and thereafter stayed at steady levels. This could be due to nitrification, during the initial

period of the incubation. This decrease was also indicated by the resin spikes from 9 to 11 days. Once the soil NH_4^+-N levels achieved the steady levels, resin adsorbed NH_4^+-N started to increase and then stayed constant to the end of the experiment. It seemed that the resin spikes had achieved equilibrium within 2 days of insertion in the soil.

Relatively uniform 2 M KCl -extractable NO_3^--N levels were observed throughout the incubation. The NO_3^--N adsorption to resin spikes was non linear with time (Fig. 4.8). Initially NO_3^--N adsorption to resin was rapid. Thereafter, gradual changes in membrane bound NO_3^--N were observed.

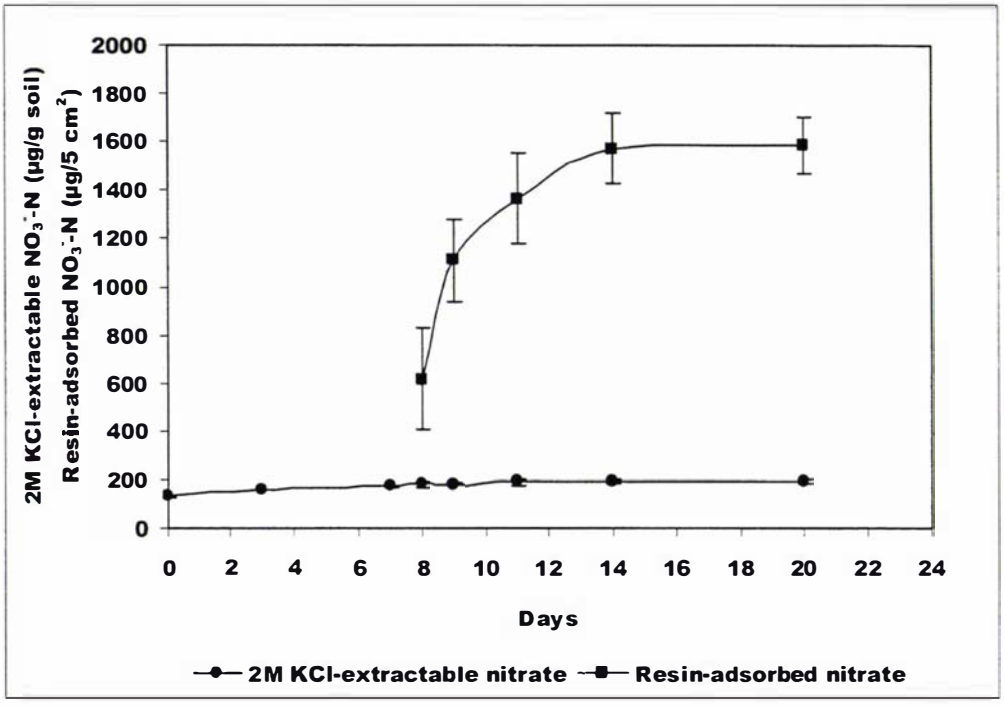


Fig. 4.8 NO_3^--N levels during the incubation as measured by 2 M KCl -extractable and Resin methods.

The key point of these results was that the resin spikes took a number of days before equilibrium of NO_3^--N was observed. Seven days after resin spike burial, resin-adsorbed NO_3^--N was constant indicating that a 1 week burial period in the soil may be appropriate for field measurements.

4.5 Resin spikes performance in field

Two simple field experiments were conducted to check the resin spikes performance in field conditions.

4.5.1 Field experiment 1

The resin spikes were used to assess the mineral N status at sites, where ongoing N trials were being conducted by AgResearch, Palmerston North. The same experiment was repeated at two different sites (Site 1 and Site 2). The soil types at the two sites were Manawatu sandy loam and Kairanga silt loam (both Fluvial Recent soils) for site 1 and site 2 respectively.

Each site contained control (C) plots that did not receive any N and treated plots that had received more than 400 kg N/ha/yr of fertilizer and 3 inputs of 1000 kg urine N over 4 years (U+N).

Each of the (C) and (U+N) treatments had four replicate plots. The procedure for resin spikes burial is detailed in Section 4.7. One resin spike was buried in each plot (1 x 2 m). Before resin spikes were buried, the pasture was mowed and soil cores (0-7.5 cm) were collected for NH_4^+-N and NO_3^--N analysis, using the standard 2 M KCl method. After 12 days in the soil the resin spikes were removed and extracted for adsorbed NH_4^+-N and NO_3^--N. Soil cores were also collected for 2 M KCl -extractable NH_4^+-N and NO_3^--N determination at day 12. Pasture was cut to determine dry matter production and then analyzed for total N to assess the N uptake on each plot over the 12-day period.

Analysis of variance of data was carried out using the GLM procedure in SAS for Windows (Version 8). Mean comparisons were done using Fishers LSD at 5% level of significance.

This first *in situ* resin spike experiment produced promising results (Table 4.8).

Table 4.8. Soil NH_4^+-N and NO_3^--N assessed by 2 M KCl extraction and resin adsorption, together with pasture N uptake over 12 days at 2 sites. Means with common letters are not significantly different ($P<0.05$) within a column at each site.

Site 1

Plot	2 M KCl NH_4^+-N µg/g soil DAY 1	2 M KCl NO_3^--N µg/g soil DAY 1	2 M KCl NH_4^+-N µg/g soil DAY 12	2 M KCl NO_3^--N µg/g soil DAY 12	Resin NH_4^+-N µg-N /5 cm^2/12days	Resin NO_3^--N µg-N /5 cm^2/12days	Pasture N uptake kg/ha/ 12 days
C 1	3.43	1.54	2.49	1.99	6.00	42.75	5.64
C 2	4.47	4.84	5.23	7.22	9.25	83.75	5.10
C 3	4.43	0.91	2.39	0.88	6.25	11.75	7.98
C 4	2.44	2.69	1.61	1.36	9.00	111.75	6.71
AVG	**3.69 A**	**2.50 A**	**2.93 A**	**2.86 A**	**7.63 A**	**62.50 A**	**6.36 A**
U+N1	2.59	2.59	1.63	0.98	5.50	217.75	16.40
U+N2	4.02	7.22	3.00	5.99	6.75	160.75	16.41
U+N3	3.42	5.32	1.34	1.90	6.00	311.75	19.64
U+N4	3.55	1.24	3.13	8.39	5.50	513.75	19.98
AVG	**3.4 A**	**4.07 A**	**2.27 A**	**4.32 A**	**5.94 A**	**301 B**	**18.11 B**

Site 2

Plot	2 M KCl NH_4^+-N µg/g soil DAY 1	2 M KCl NO_3^--N µg/g soil DAY 1	2 M KCl NH_4^+-N µg/g soil DAY 12	2 M KCl NO_3^--N µg/g soil DAY 12	Resin NH_4^+-N µg-N 5cm^2/12days	Resin NO_3^--N µg-N /5 cm^2/12days	Pasture N uptake kg/ha/ 12 days
C 1	4.54	5.47	1.81	0.00	5.75	19.25	5.71
C 2	3.88	1.38	1.9	0.00	5.50	122.5	16.65
C 3	2.64	0.99	2.13	2.81	19.25	88.00	3.77
C 4	4.73	2.55	3.64	1.82	8.50	20.50	5.48
AVG	**3.95 A**	**2.60 A**	**2.37 A**	**1.16 A**	**9.75 A**	**62.56 A**	**7.90 A**
U+N1	3.58	2.47	3.29	2.94	6.25	168.75	24.52
U+N2	2.49	4.75	1.03	0.00	7.75	612.00	19.35
U+N3	4.97	13.58	4.51	9.12	8.25	884.25	31.58
U+N4	3.45	1.23	3.44	3.55	6.50	236.25	21.91
AVG	**3.62 A**	**5.51 A**	**3.07 A**	**3.90 A**	**7.19 A**	**475.31 B**	**24.34 B**

The amounts of 2 M KCl -extractable soil NH_4^+-N and NO_3^--N in control and N treated plots were low and did not change from day 1 to day 12 at both sites. Further, the levels of 2 M KCl -extractable soil NH_4^+-N and NO_3^--N in controls and N treated plots were not significantly different either on day 1 or day 12 at both sites. Resin-adsorbed NH_4^+-N during the 12-day soil burial period was also low, and no significant differences were observed between control and N treated plots at both sites.

In contrast, levels of resin-adsorbed NO_3^--N in controls and N treated plots were significantly different at both sites. At site 1 resin-adsorbed NO_3^--N in N treated plots was 5 times higher than control while at site 2, N treated plots were 8 times higher than control.

There was a considerable variation among the replicates in resin spike N adsorption. This may due to the existing spatial variability within the experimented plots.

Pasture N uptake was significantly different between the two treatments at both sites. Pasture N uptake related well to resin-adsorbed NO_3^--N but not to 2 M KCl -extractable NO_3 -N.

4.5.2 Field experiment 2

The performance of resin spikes as an *in situ* measure of soil mineral N in hill country pasture was further examined in this second field experiment. This experiment was carried out at the Waipawa AgResearch hill country research station (Experimental site described in Chapter 3). Two plots (0.5 m x 1m) were marked at two contrasting landscape units at the site. One site was a sheep campsite where dung and urine had been deposited and consequently had good pasture growth.

The other site was on a steep slope where less dung and urine had been deposited and where the pasture growth rate was lower. Ten KCl-saturated resin spikes were buried in each plot. After 7 days, resin spikes were removed from the soil and analyzed for resin-adsorbed N. Soil cores were also collected at the beginning of the experiment and after 7 days, and were analyzed for 2 M KCl -extractable N. In addition, soil samples from

the area surrounding the each of the two plots were taken and bulked into two bags. This soil was brought to the laboratory, crumbled, well mixed and placed into six small containers (100 mL cups). A resin spike was buried in each container and left for 7 days. The resin-adsorbed N and 2 M KCl -extractable N were measured.

The results of this experiment are illustrated in Table 4.9. In the field the amounts of 2 M KCl -extractable NH_4^+-N and NO_3^--N at the beginning of the experiment and after 7 days, were low in both soils and the values do not differentiate between the two soils.

However, when the two soils were incubated in the laboratory, 2 M KCl -extractable N did vary between soils. After 7 days incubation 2 M KCl -extractable NO_3^--N in soil collected from campsites had increased. This was not evident in soil collected from steep sites.

Levels of resin-adsorbed NH_4^+-N in field soils were low–as was the case with 2 M KCl -extractable NH_4^+-N. In contrast, there were reasonably large quantities of resin-adsorbed NO_3^--N at both sites. The average amount of resin-adsorbed NO_3^--N in campsite soils was twice as high as in steep soils.

These quantities of NO_3^--N detected by the resin spikes at both sites might suggest that *in situ* mineralisation and nitrification were occurring during the 7 day period. The resulting NO_3^--N however was being utilized rapidly by plant uptake or lost through other processes and so was not detected by extraction with 2 M KCl .

The results of this preliminary experiment were an encouraging evaluation of the potential use of resin spikes as a N measurement technique.

The resin spikes appear to reflect the flux of N through the mineral pool, even although the pool size at any one time may be low.

The quantities of resin-adsorbed N on the ten resin spikes buried within a small area were highly variable. The CVs of resin-adsorbed NO_3^--N values were >100% at both sites. This indicated the resin spike's potential to detect the high soil spatial variability associated with soil mineral N.

Table 4.9 Levels of mineral N in two soils as measured by 2 M KCl extraction and resin spikes. Measurements were made over a 7 day period in the field and also after incubation for 7 days in the laboratory.

A) Camp Site

Field					Laboratory		
2 M KCl -extractable N µg N/g soil					2 M KCl-extractable N µg N/g soil		
Rep	Day 0		Day 7		Rep	After 7 days incubation	
	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N		NH_4^+-N	NO_3^--N
1	5.4	9.7	10	0	1	4.3	38.3
2	7.5	9.7	3.8	0	2	3.2	39.3
3	7.5	9.7	3.7	0	3	5.3	41
Average	**6.8**	**9.7**	**5.8**	**0**	Average	**4.3**	**39.5**
Resin adsorbed N µg N/5 cm^2/7days					Resin adsorbed N µg N/5 cm^2/7days		
Rep	NH_4^+-N		NO_3^--N		Rep	NH_4^+-N	NO_3^--N
1	0		33		1	0	225
2	0		60		2	0	247
3	3		83		3	1	305
4	8		205		Average	**0.33**	**259**
5	3		85				
6	3		93				
7	0		3				
8	13		25				
9	0		58				
10	3		73				
Average	**3.3**		**71.8**				

B) Steep site

Field					Laboratory		
2 M KCl -extractable N µg N/g soil					2 M KCl-extractable N µg N/g soil		
Rep	Day 0		Day 7		Rep	After 7 days incubation	
	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N		NH_4^+-N	NO_3^--N
1	5	0	6	0	1	6	0
2	5	0	6	0	2	9	0
3	5	0	6	0	3	5	0
Average	**5**	**0**	**6**	**0**	Average	**6.7**	**0**
Resin adsorbed N µg N/5 cm^2/7days					Resin adsorbed N µg N/5 cm^2/7days		
Rep	NH_4^+-N		NO_3^--N		Rep	NH_4^+-N	NO_3^--N
1	5		3		1	0	10
2	8		10		2	8	20
3	0		0		3	0	15
4	0		120		Average	**2.7**	**15**
5	3		20				
6	0		60				
7	0		50				
8	0		0				
9	0		28				
10	0		8				
Average	**1.6**		**29.9**				

4.6 Modelling of *in situ* N adsorption to resin membrane spikes

4.6.1 Introduction

In previous sections, the potential of *in situ* use of ion exchange resin membranes for obtaining a sensitive measurement of the N supplying power of soils over time was identified. When using ion exchange resin membranes for the measurements of N dynamics in soil, it is necessary to understand the process of N adsorption to the resin, and the influence of other factors such as N diffusion rate, soil moisture content, and the resin burial period in the soil.

As was noted earlier however, it is very difficult to design experiments to measure changes in resin-adsorbed N under different levels of a single factor. For example, increasing soil moisture is likely to increase the N diffusion rate, but also increase N availability by mineralisation. Thus, the final measurement of resin-adsorbed N is a result of both increased diffusion and increased N availability, and it is difficult to separate out these two effects. Hence, simulation of N adsorption to resin in soil offers an alternative way to identify the influence of experimental conditions on the adsorption process.

This study involved modelling the experimental work described in Section 4.4.1.2. Only NO_3^--N adsorption to resin spikes was modelled, as NH_4^+-N adsorption was complicated by competition from other cations on the resin membrane and the soil exchange surfaces. Once constructed, the model was used to predict N adsorption to the resin spike in a given burial period, the N depletion zone in the soil when N is adsorbed by the resin spike, and the influence of moisture, initial N concentration and temperature on resin N adsorption from soil.

4.6.2 Basic equations for solute diffusion in soil

In this section the basic partial differential equation for NO_3^--N diffusion in soil is derived. To do this we consider a notional rectangular box of soil (Fig. 4.9) with the dimensions of Δx (L) Δy (L) L (L). This notional box receives or loses NO_3^--N by

molecular diffusion along the x and y coordinates. A constant concentration is assumed in the z coordinate and so there is no flux along it.

The flux density ($ML^{-2}T^{-1}$) in the x and y coordinates is described by Fick's first law (Section 4.2.2) as

$$q_x = -\theta D_s \frac{dC}{dx} \tag{4.2}$$

$$q_y = -\theta D_s \frac{dC}{dy} \tag{4.3}$$

where

q_x = Amount of NO_3^--N moving across unit-cross-section per unit time in the x direction

q_y = Amount of NO_3^--N moving across unit-cross-section per unit time in the y direction

θ = Volumetric water content of the soil ($L^3 L^{-3}$)

D_s = Diffusion coefficient for NO_3^--N in the soil (see Section 4.6.3)

C = NO_3^--N concentration in soil solution ($M L^{-3}$)

x = Coordinate in the x direction (L)

y = Coordinate in the y direction (L)

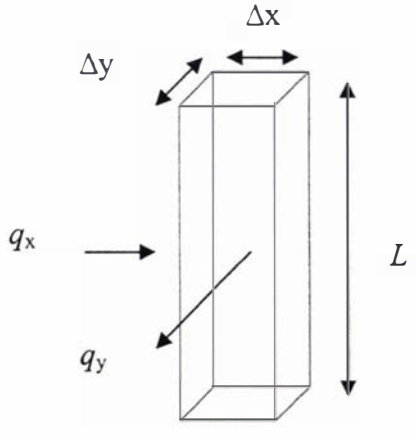


Fig. 4.9 Notional box of soil.

It is assumed that NO_3^--N is conserved over the period of interest. i.e. there is no significant plant uptake, nitrification, denitrification, or immobilization. Thus, during any time interval Δt (T), the net NO_3^--N movement in and out of the box equals the accumulation of NO_3^--N in the box . Now

$$Q_{in} = [(q_x . \Delta y . L) + (q_y . \Delta x . L)] \Delta t \quad (4.4)$$

$$Q_{out} = [(q_{x+\Delta x} . \Delta y . L) + (q_{y+\Delta y} . \Delta x . L)] \Delta t \quad (4.5)$$

where

Q_{in} = quantity of NO_3^--N diffusing into the box (M)
Q_{out} = Quantity of NO_3^--N diffusing out of the box (M)

Given there is no adsorption, the accumulation of NO_3^--N in the box over Δt, ΔM is given by

$$\Delta M = \theta \ \Delta y \ \Delta x \ L \ \Delta C \quad (4.6)$$

and as indicated above conservation of mass implies the

$$\Delta M = Q_{in} - Q_{out} \quad (4.7)$$

Substituting the equations (4.4), (4.5) and (4.6) into equation (4.7) gives.

$$\theta \Delta y \ \Delta x \ L \ \Delta C = [[(q_x \ \Delta y \ L) + (q_y \ \Delta x \ L)]\Delta t] - [[(q_{x+\Delta x} \ \Delta y \ L) + (q_{y+\Delta y} \ \Delta x \ L)]\Delta t] \quad (4.8)$$

Dividing both sides by ($\Delta x \ \Delta y \ L \ \Delta t$) and a little arranging gives

$$\theta \frac{\Delta C}{\Delta t} = -\left(\frac{q_{x+\Delta x} - q_x}{\Delta x}\right) - \left(\frac{q_{y+\Delta y} - q_y}{\Delta y}\right) \quad (4.9)$$

This finite difference equation can be changed into a partial differential equation by taking limits as $\Delta x \to 0$, $\Delta y \to 0$ and $\Delta t \to 0$ (i.e making the box infinitely small in the x and y coordinates and changing the time interval into an instant.) The resulting equation is

$$\theta \frac{\partial C}{\partial x} = -\frac{\partial q_x}{\partial x} - \frac{\partial q_y}{\partial y} \qquad (4.10)$$

Then by substituting the expressions for q_x and q_y from equation (4.2) and (4.3) into equation (4.10) and dividing by θ gives.

$$\frac{\partial C}{\partial t} = D_s\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) \qquad (4.11)$$

This is one form of the equation known as Fick's second law of diffusion as applied to soil.

As it stands, equation (4.11) cannot be solved. It tells how the solute (NO_3^--N) concentration changes with time and distance in the x and y coordinates. To find the solute concentration at a particular point (x,y) and time it is necessary to specify the initial conditions and boundary conditions.

In the box considered here, the initial condition in the soil is

$$C = C_i \text{ for } x > 0,\ y > 0,\ t = 0 \qquad (4.12)$$

where C_i is the uniform concentration of NO_3^--N in the soil solution. The non uniform boundary condition at the surface of the "resin spike" will be discussed later.

Due to the complex geometry of the boundary condition, equation (4.11) could not be solved analytically. Thus, a model was developed to solve this equation numerically.

4.6.3 Model development

The experimental design described in Section 4.4.1.2 was modelled. The effective soil volume for adsorption was considered as a 125 cm^3 (5 x 5 x 5 cm) cube. This had 400 (20x20) cells or compartments, each 0.25 cm (Δy) x 0.25 cm (Δx) x 5 cm (Fig.4.10). The resin membrane was in contact with the soil in cells (Δy, Δx) at (10,9), (10,10), (10,11) and (10,12). To ease computation, it was assumed that diffusion was symmetrical about a line through the mid point of the resin spike (see Fig. 4.10). Diffusion was then calculated for half of the area (shaded area in Fig.4.10). The resulting adsorption in cells (10,9) and (10,10) was then multiplied by 2 to give the total adsorption to the spike.

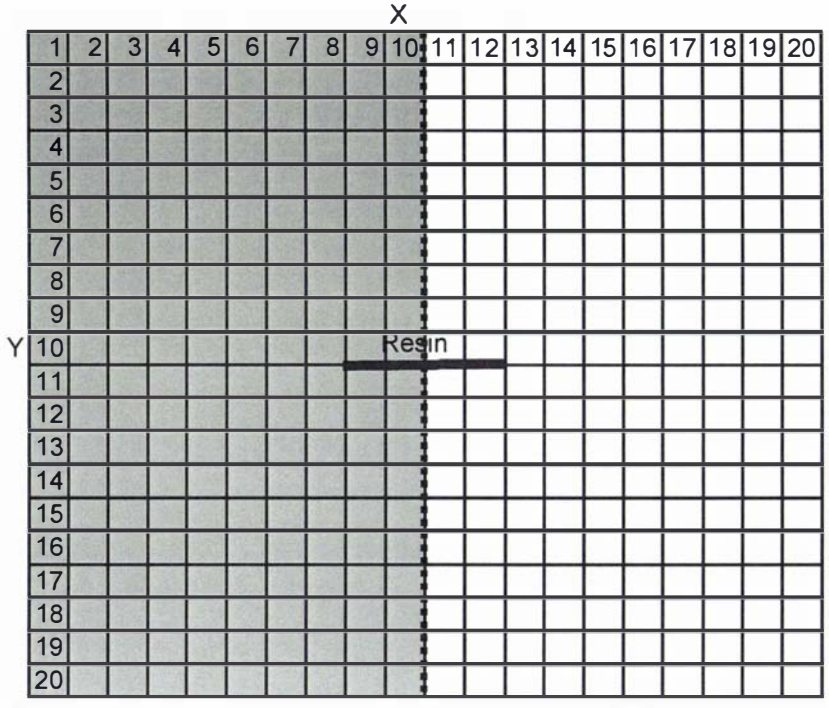


Fig. 4.10 Modelled experimental soil cube with resin spike inserted, viewed from above. The anion exchange resin membrane is facing cells (10,9), (10,10), (10,11), and (10,12) and the cation exchange resin facing the cells (11,9), (11,10), (11,11) and (11,12).

The model recognizes that the quantity of N adsorbed depends on the relation between N in soil solution and N on the exchange complex, and the rate of diffusion of N towards the resin surface.

The relationship between N in soil solution and on the surface is assumed to be given by a 1:1 adsorption isotherm. The 1:1 isotherm assumes that there is no selectivity in NO_3^--N adsorption to resins (see Section 4.4) and that NO_3^--N competes equally with other anions initially in the soil solution and on the resin surface for sorption sites. Thus

$$\frac{C}{C_{max}} = \frac{X}{X_{max}} \tag{4.13}$$

where

C = NO_3^--N concentration of soil solution at the resin contact surface ($\mu g/cm^3$ soil solution)

C_{max} = operational maximum NO_3^--N concentration if NO_3^- was the only anion existing in soil solution. ($\mu g/cm^3$ soil solution)

X = NO_3^--N adsorbed to resin ($\mu g/cm^2$ resin)

X_{max} = maximum NO_3^--N adsorption capacity of resin ($\mu g/cm^2$ resin)

The maximum anion adsorption capacity of the 5 cm^2 of anion membrane was 2179 μg (Section 4.4). Thus, the maximum anion adsorption capacity of one cell is calculated as

$$X_{max} = 2179/4 \tag{4.14}$$

The operational maximum NO_3^--N concentration, if the soil solution contained only NO_3^--N ions, (C_{max}) was estimated using an indirect method. It was assumed in the model that the content of NO_3^--N at the start of the period of N adsorption to the resin was constant at 192 μg NO_3^--N per g soil. This was the measured 2 M KCl -extractable NO_3^--N at 7 and 14 days after resin burial (Fig. 4.8).

The electrical conductivity (EC) of different concentrations of NH_4NO_3 solutions was measured and is plotted in Fig. 4.11. At the same time, the electrical conductivity of the soil that was used in the experiment (4.4.1.2) was measured in a 1:5 (soil:water) suspension.

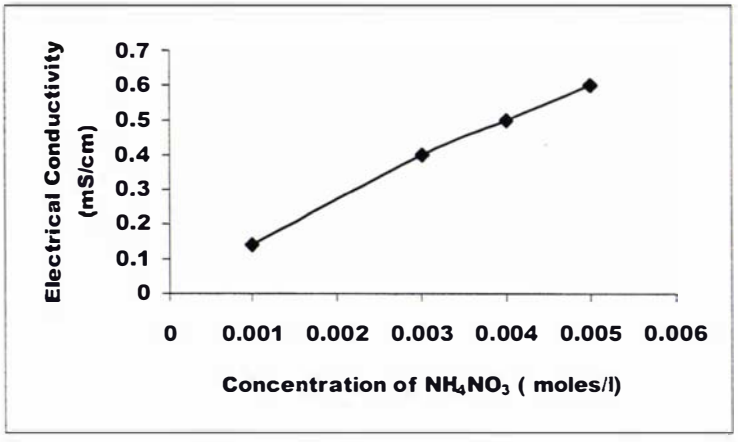


Fig. 4.11: Electrical conductivity of different NH_4NO_3 concentrations at 20° C.

The electrical conductivity of the soil that was used in the experiment was 0.46 mS/cm. The concentration of a NH_4NO_3 solution that has an EC of 0.46 mS/cm is 0.0035 M (Fig. 4.11). Thus the operational maximum NO_3^--N concentration in the soil solution was found as (0.0035)(14) g NO_3^--N/liter or 0.049 g NO_3^--N/liter. In 5 mL of soil suspension this amounts to 245 μg NO_3^--N per g soil.

As the soil suspension was 1:5 (soil: water), this would be the quantity of NO_3^--N in 1 g of soil if the existing soil solution contained only NH_4NO_3. In fact, the experimental soil contained 192 μg NO_3^--N per g soil. Thus the operational maximum soil solution concentration of NO_3^--N was greater than the initial soil solution concentration (C_i , defined below) by a factor of 245/192 or 1.28.

At the beginning of the experiment the resin membrane does not have any adsorbed N. Thus, initially

$$X = 0 \qquad (4.15)$$

Before the simulation process started, the initial soil NO_3^--N concentration in each cell (C_i, μg N/cm^3 soil solution) was calculated as follows:

$$C_i = (G).(\rho_b)/\theta \quad (4.16)$$

where

G = Soil NO_3^--N concentration (μg NO_3^--N/g soil)

ρ_b = Bulk density (g cm^{-3})

The amount of NO_3^--N in each cell (M, μg NO_3^--N) is calculated as follows

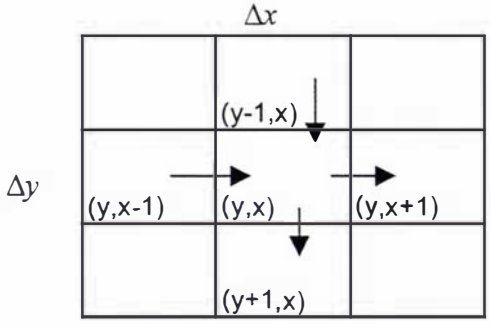
$$M_{(y,x)} = (C_i)\,(\theta)\,(\Delta x\,\Delta y\,L) \quad (4.17)$$

The diffusion coefficient of the solute in soil (D_s) was calculated according to Tinker and Nye (2000).

$$D_s = f\,D_l \quad (4.18)$$

where the diffusion coefficient of the solute in free solution (D_l) was taken as 1.3 cm^2/day at 25°C (Tinker and Nye 2000). The impedance (tortuosity) factor (f) for the relevant soil moisture content was obtained from the relationship in Fig. 4.2 in Section 4.2.2 .

Consider a cell (y,x). The fluxes into the cell in the x and y direction are



$$F_x = \theta\,D_s\,\Delta y\,L\,(C_{(y,x)} - C_{(y,x+1)})/\Delta x \quad (4.19)$$

$$F_y = \theta\,D_s\,\Delta x\,L\,(C_{(y,x)} - C_{(y+1,x)})/\Delta y \quad (4.20)$$

There are similar fluxes out the other side of the cell. The net gain (or loss) of NO_3^--N by the cell over a time interval Δt, $\Delta M_{y,x}$ is given by

$$\Delta M_{(y,x)} = [\ (F_{y\ (y-1,x)} - F_{y(y,x)}) + (\ F_{x\ (y,x-1)} - F_{x(y,x)})]\ \Delta t \qquad (4.21)$$

This then changes the N content in each cell.

$$M_{(t+1)} = M_{(t)} + \Delta M \qquad (4.22)$$

The model then uses the new M value to calculate a new NO_3^--N concentration value (C) for the soil solution in each cell.

$$C = (M/\theta)\ (\Delta y)\ (\Delta x)\ (L) \qquad (4.23)$$

At the first time step the resin membrane in contact with the soil in compartments (10,9), (10,10), (10.11) and (10,12) adsorbs NO_3^--N from the soil surface. As noted earlier, adsorption is modelled for only half of the resin, as adsorption is assumed to be symmetrical. The interface between the soil and the resin surface in compartment (10,9) is designated as s1 and the corresponding interface between the soil and the resin surface in compartment (10,10) is designated as s2. The amount of NO_3^--N adsorbed by the resin is equal to the amount of N diffusing towards the resin surface from compartments (10,9) and (10,10). This flux of N (F_{s1} and F_{s2}) towards the resin is calculated using Fick's law as described previously.

$$F_{s1} = \theta\ D_s\ \Delta x\ L\ (C_{(10,9)} - C_{s1})/\ (\Delta y/2) \qquad (4.24)$$

$$F_{s2} = \theta\ D_s\ \Delta x\ L\ (C_{(10,10)} - C_{s2})/(\ \Delta y/2) \qquad (4.25)$$

C = NO_3^--N concentration (μg NO_3^--N/cm^3 soil solution)

C_{s1} = NO_3^--N concentration at the resin membrane surface in cell (10,9)

C_{s2} = NO_3^--N concentration at the resin membrane surface in cell (10,10)

θ = Volumetric moisture content

D_s = Diffusion coefficient of the solute in soil (cm^2/day)

L = Length of resin membrane (5 cm)

The flux towards the surface calculated in each time step is then added to the quantity adsorbed on the resin

$$X_{1(t+\Delta t)} = X_{1(t)} + F_{s1} \quad (4.26)$$

$$X_{2(t+\Delta t)} = X_{2(t)} + F_{s2} \quad (4.27)$$

Where

X_1= NO_3^--N adsorbed to resin from (10.9) compartment
X_2= NO_3^--N adsorbed to resin from (10.10) compartment
Δt = time step

As the NO_3^--N is adsorbed onto the resin membrane, the NO_3^--N concentration in the soil solution adjacent to resin membrane surface changes. The new NO_3^--N concentration in soil solution at the resin membrane surface is calculated using the 1:1 adsorption isotherm

$$C_{s1(t+\Delta t)} = (X_{1(t)}/X_{max})\ (C_{max}) \quad (4.28)$$

$$C_{s2(t+\Delta t)} = (X_{2(t)}/X_{max})\ (C_{max}) \quad (4.29)$$

As the resin surface solution concentration (C_{s1} and C_{s2}) has changed, a concentration gradient will develop in the cells of the soil matrix near the resin membrane.

The change of NO_3^--N concentration in cells of the soil matrix leads to diffusion of NO_3^--N towards the resin membrane surface and NO_3^--N adsorption to the resin. The model simulates these actions continuously at given time steps for the period that the resin spike is buried in the soil.

4.6.4 Model output

4.6.4.1 The effect of time of burial on N adsorption by a resin spike in soil

Overall, the model predictions of resin adsorption of NO_3^--N are reasonably close to the actual measured values (Fig. 4.12). Although the model forecast the final adsorption

reasonably accurately, it slightly overestimated the rate of adsorption in the early stages. The model estimation of NO_3^--N adsorption to resin depends on N diffusion towards the resin. As pointed out in Section 4.6.2, the value for the diffusion coefficient (D_s) in the model was obtained from the literature. This may account for the overestimation of N adsorption in the early days after placement of the resin spike.

It was found in Section 4.4 that the 5 cm^2 resin membrane has a capacity to adsorb 2179 μg NO_3^--N. However, the measured and modelled N adsorption is less than the maximum capacity, reflecting competition from other anions.

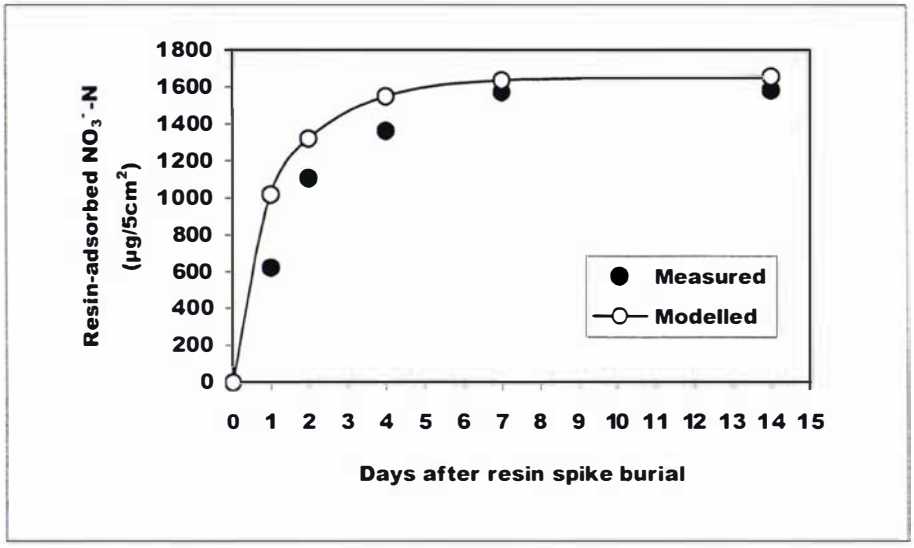


Fig. 4.12 Measured and modelled NO_3^--N adsorption to resin spikes with time.

The modelled concentrations of NO_3^--N in soil solution in each cell, 1 day after the resin spike has been placed in the soil, are presented in Fig. 4.13. It is apparent that there are marked concentration gradients in the direction of resin spike. These concentration gradients encourage diffusion of NO_3^--N towards the resin. The data recalculated as the quantity of NO_3^--N (μg) in each cell are presented in Fig. 4.14 to visually depict the depletion zone

By day 7 (Fig. 4.15 and 4.16) all soil compartments in the system have similar N levels and therefore the rate of diffusion approaches to zero. By this time, the resin membrane has slightly reduced the soil nitrate concentration throughout the 5 cm x 5 cm zone under consideration around the spike

cm	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.25	2.50	
0.25	737	737	737	736	735	733	732	730	729	728	
0.50	737	737	736	735	733	732	729	728	726	725	
0.75	737	736	735	733	731	728	725	722	720	718	
1.00	736	735	733	731	727	723	718	713	709	707	
1.25	735	734	731	728	722	716	708	700	694	690	
1.50	734	732	729	724	717	707	695	683	672	666	
1.75	733	731	727	720	711	697	681	662	645	634	
2.00	732	729	725	717	705	689	667	639	610	592	
2.25	731	729	724	716	703	684	657	618	567	537	
2.50	731	729	724	716	704	687	660	614	548	461	Resin
2.75	732	730	728	719	710	697	682	671	691	699	
3.00	733	732	728	723	717	708	700	698	702	708	
3.25	734	733	731	727	723	718	713	711	713	714	
3.50	735	735	733	731	728	725	722	721	721	721	
3.75	736	736	735	733	732	730	728	728	727	727	
4.00	737	737	736	735	734	733	732	732	732	732	
4.25	738	737	737	737	736	735	735	735	734	734	
4.50	738	738	738	737	737	737	736	738	736	736	
4.75	738	738	738	738	738	737	737	737	737	737	
5.00	738	738	738	738	738	738	738	738	738	738	

Fig. 4.13 Modelled NO_3^--N concentration (µg/cm^3 soil solution) in each soil compartment (0.25 x 0.25 x 5 cm) 1 day after placement of the resin spike in soil. The asymmetrical depletion pattern is caused by the placement of the anion resin strip on the side of the spike apparently closest to the top of page. (This diagram shows only half of the system).

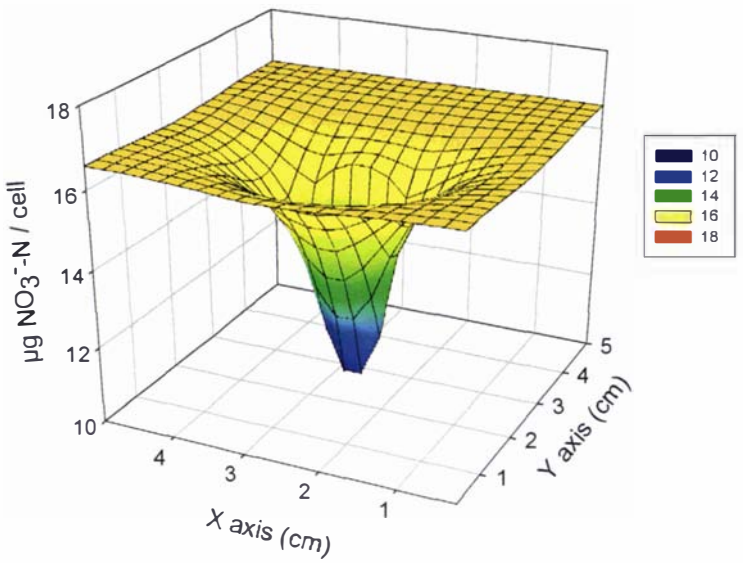


Fig. 4.14. Soil NO_3^--N (µg/cell) distribution in each soil compartment (0.25x 0.25x1 cm) 1 day after placement of the resin spike in soil. The resin spike is placed at 2-3 cm on the X axis and at 2.5 cm on the Y axis. The asymmetrical depletion pattern is caused by the placement of the anion resin strip on the side of the spike apparently closest to the reader.

cm	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.25	2.50
0.25	696	698	697	697	697	696	696	696	696	695
0.50	696	698	697	697	697	696	696	696	695	695
0.75	696	696	696	697	697	696	696	696	695	695
1.00	696	696	696	697	697	697	696	696	695	695
1.25	699	698	698	698	697	697	696	696	695	695
1.50	699	699	699	698	696	697	696	696	695	695
1.75	700	699	699	699	696	697	697	696	695	695
2.00	700	700	700	699	699	696	697	696	695	694
2.25	701	701	701	700	700	699	696	697	695	694
2.50	702	702	702	701	701	700	699	698	694	692 Resin
2.75	703	703	703	703	702	702	701	701	703	703
3.00	704	704	704	704	704	703	703	703	704	704
3.25	706	705	705	705	705	705	705	705	705	705
3.50	707	707	707	706	706	706	706	706	706	706
3.75	706	706	706	707	707	707	707	707	707	707
4.00	709	709	709	706	706	706	706	706	706	706
4.25	709	709	709	709	709	709	709	709	709	709
4.50	710	710	710	710	710	710	710	710	710	710
4.75	711	711	710	710	710	710	710	710	710	710
5.00	711	711	711	711	711	710	710	710	710	710

Fig. 4.15 Modelled NO_3^--N concentration (µg/cm^3 soil solution) in each soil compartment (0.25 x 0.25 x 5 cm) 7 days after placement of the resin spike in soil (This diagram shows only half of the system).

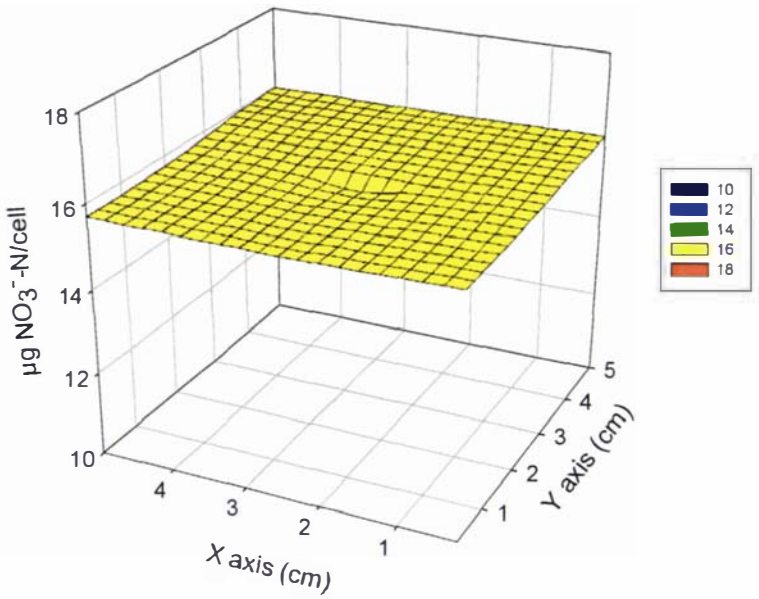


Fig. 4.16. Soil NO_3^--N (µg/cell) distribution in each soil compartment (0.25x 0.25x1 cm) 7 days after placement of the resin spike in soil. The resin spike is placed at 2-3 cm on the X axis and at 2.5 cm on the Y axis.

It can be seen that the concentration gradients in the cells on one side of the spike are much steeper than on the other side. This is because only one side of the resin spike has anion resin membrane attached.

4.6.4.2 Effect of soil moisture on N adsorption by resin spikes

Adsorption of NO_3^--N to resin with time was estimated by the model at different soil moisture levels and illustrated in Fig.4.17. Under very dry conditions N adsorption by resin spikes in soil is predicted to be much slower than under moist conditions. However, in wetter soils (W = 0.3 and 0.4) the effect of changes in moisture content on NO_3^--N adsorption is not as great. Thus in wet soils, resin spikes would need to be buried in soil for shorter periods to achieve satisfactory comparisons while in dry soils longer burial periods may be more suitable.

This is further illustrated by the effect of soil moisture on the soil N depletion zone after N adsorption to resin (Fig. 4.18).

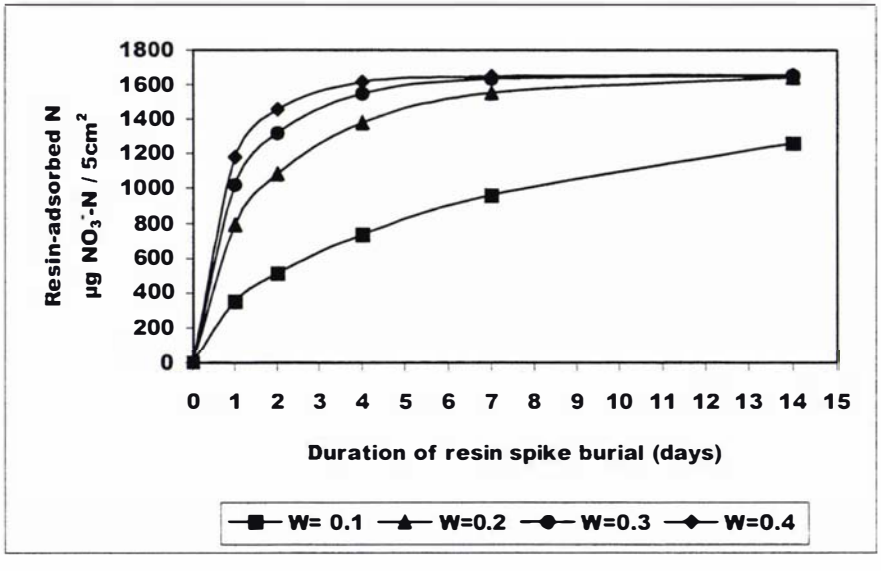
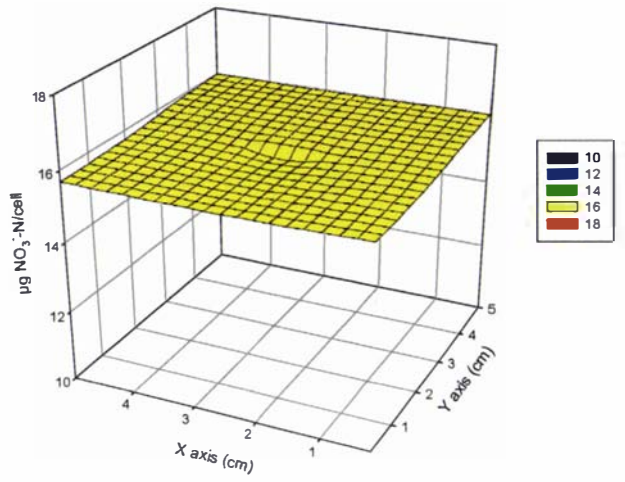


Fig. 4.17 Modelled effect of soil moisture content on NO_3^--N adsorption by resin spikes with time after burial. W = gravimetric moisture content.

A) Soil moisture = 0.26 (W/W)



B) Soil moisture = 0.1 (w/w)

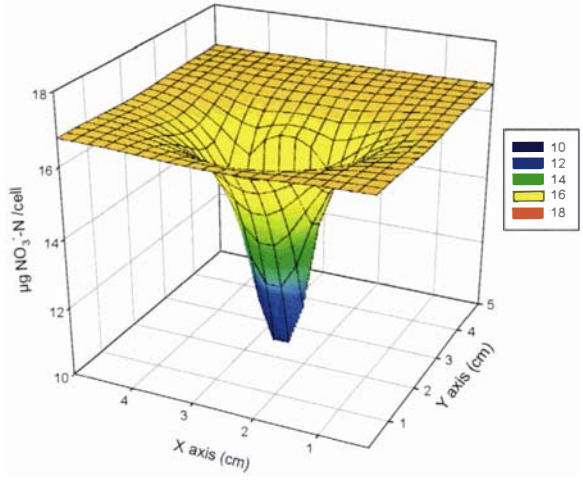


Fig. 4.18. Effect of soil moisture on soil NO_3^--N (µg/cell) distribution 7 days after placement of the resin spike in soil. The resin spike is placed at 2-3 cm on the X axis and at 2.5 cm on the Y axis. The asymmetrical depletion pattern is caused by the placement of the resin strip on the side of the spike 'apparently closest' to the reader.

4.6.4.3 Effect of initial soil N concentration

The model was used to estimate N adsorption to resin membrane spikes with time at different initial soil NO_3^--N concentrations (Fig 4.19). It can be seen that as the soil NO_3^--N concentration increases, the time taken to reach equilibrium decreases.

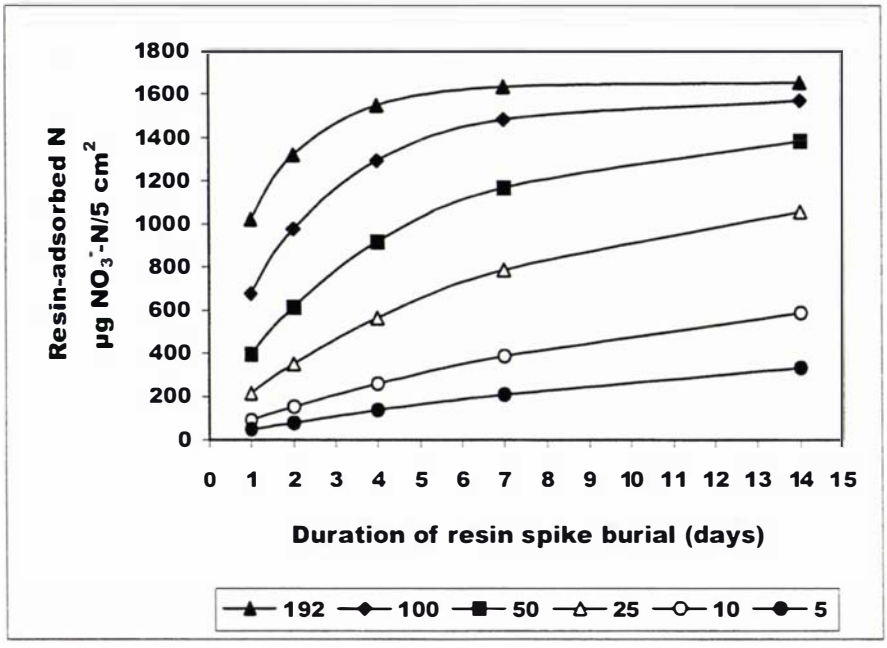


Fig. 4.19 Modelled effect of initial soil NO_3^--N concentration (µg NO_3^--N/g soil) on NO_3^--N adsorption by resin spikes with time after burial. The gravimetric moisture content is 0.26 (w/w).

At low soil NO_3^--N concentrations, resin spikes need to be buried for longer periods for better comparisons. At higher soil NO_3^--N concentrations, resin spikes would need to be buried in soil for shorter periods to achieve satisfactory comparisons. Hence, in experiments with N fertilizer and urine application the resin spike would need to remain in the soil for only short periods.

4.6.4.4 Effect of temperature on N adsorption by resin spike in soil

As discussed in Section 4.6.2, the diffusion coefficient of the solute in soil is calculated using the diffusion coefficient of the solute in free solution (D_l) and the impedance factor (f). The diffusion coefficient of the solute in free solution (D_l) is generally affected by solution temperature through a change in solution viscosity. The diffusion

coefficient in solution (D_l) is directly proportional to temperature (K) and inversely proportional to viscosity (Scotter D.R. pers.comm). Hence, new values were calculated for D_l using the viscosity values of water at different temperatures. These values of D_l were 1.3 cm^2/day (25°C), 0.98 cm^2/day (15°C) and 0.71 cm^2/day (5°C). The N adsorption by the model (Fig. 4.20) was then estimated at these 3 temperatures. It can be seen that during the early period of the adsorption, under warm soil temperatures, the resin would adsorb more N than under cool conditions. After longer burial periods there seems to be no significant effect of temperature on N adsorption to resin.

The effect of temperature is not as large as the effect of soil moisture and initial soil NO_3^--N concentrations on N adsorption to resin spikes.

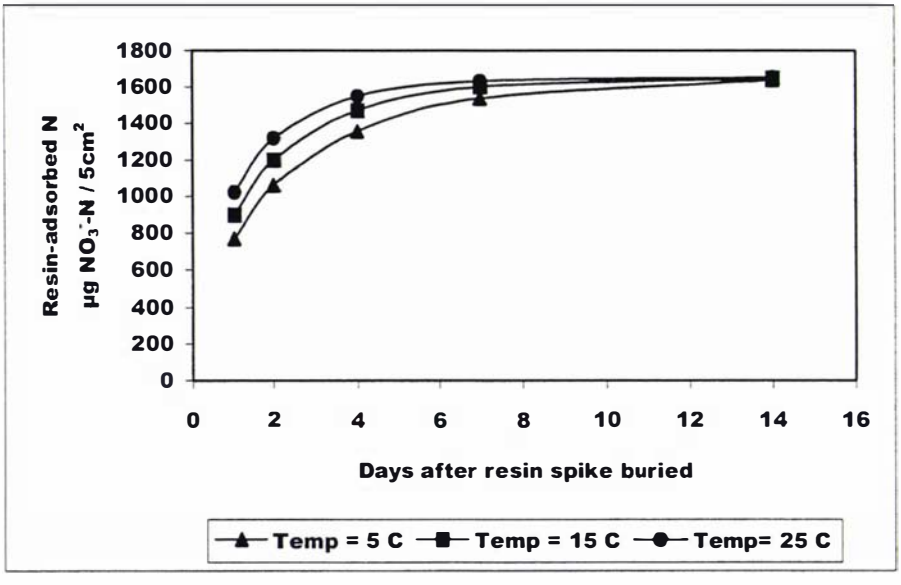


Fig. 4.20. Modelled effect of temperature on N adsorption by resin spikes with time. The moisture content of the soil is 0.26 (w/w).

4.7 Recommended procedure

Following the preliminary experiments described in the previous sections the recommended method for *in situ* measurement of soil mineral N using resin spikes is as outlined below.

a) Spike construction:

Strips of cation and anion membranes (1 x 6 cm) are taped to both sides (one strip per side) of an acrylic spike (2 x 0.5 x 8 cm) using water resistant tape, leaving 5 cm^2 of membrane area for adsorption.

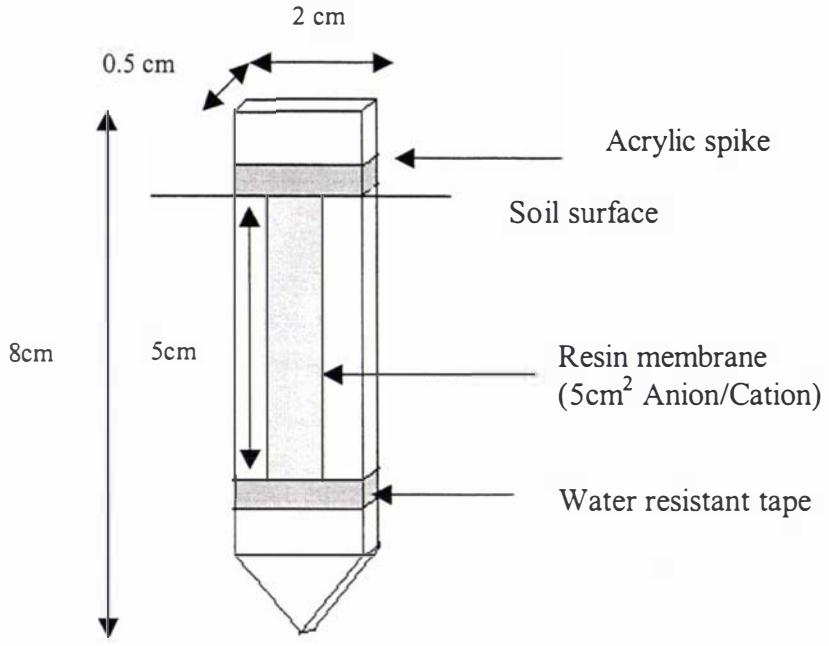


Fig. 4.21.Schematic diagram of resin spike.

b) Procedure:

The spikes should be kept in a 2-3M KCl solution overnight for regeneration before use. To bury resin spikes, a thin vertical slot is made in the soil using a small steel bar of similar dimensions to the spike. The resin spike is placed into the slot carefully without disturbing the soil further. The resin spike is removed from the soil after an appropriate time, rinsed with deionized water, placed in a centrifuge tube containing 25 mL of 2 M KCl , and shaken for 1 hour. The NH_4^+-N and NO_3^--N adsorbed to the resin are displaced into the KCl eluent and their concentrations determined by a Technicon Auto Analyser (Searle, 1975; Blakemore *et al.*, 1987).

The length of time the resin spike is left in the soil depends on the soil N concentration and moisture content. Shorter burial periods are suitable under moist and high soil N situations while longer periods (7 or 14 days) are necessary for dry and low soil N situations.

4.8 Discussion

In this study, it has been demonstrated that the *in situ* measurement of mineral N availability using resin spikes may be an effective technique to adopt in field experiments.

Initial experiments described in this chapter demonstrated that when cation and anion exchange membranes are directly buried in soil, N is adsorbed on to the membrane and this resin-adsorbed N bears a relationship to soil N availability to pasture plants. It was evident that adsorption of NO_3^--N was more efficient and uniform than adsorption of NH_4^+-N. This appeared to be due in part to the greater competition for NH_4^+-N adsorption from other cations in the soil/membrane system.

Experiments conducted in the field demonstrated that *in situ* measurement of N availability by resin membrane spikes was able to detect measurable quantities of N even when the standard 2 M KCl extraction method could detect only negligible amounts of soil N. This probably reflects in part the greater volume of soil influenced by the resin strip. More importantly the resin procedure could discriminate soil fertility differences, both in intensively managed experimental plots and also among different hill country landscapes. The apparent advantages of the resin method can be explained as follows:

The most common method of estimating soil mineral N availability in soil is the 2 M KCl extraction method (see Section 3.3.4). This measurement gives an estimate of the available N pool at the time the soil sample is collected. There are many processes that affect the available soil N pool as illustrated in Fig. 4.22. Additions to the pool through mineralisation are countered by losses, such as leaching and plant uptake. Thus, although considerable quantities of mineral N may be produced and consumed, the amount in the soil at any one time may be small. This applies equally to soils with high

and low fertility. It is for this reason that N extractable with 2 M KCl is not usually a good indicator of N availability to plants.

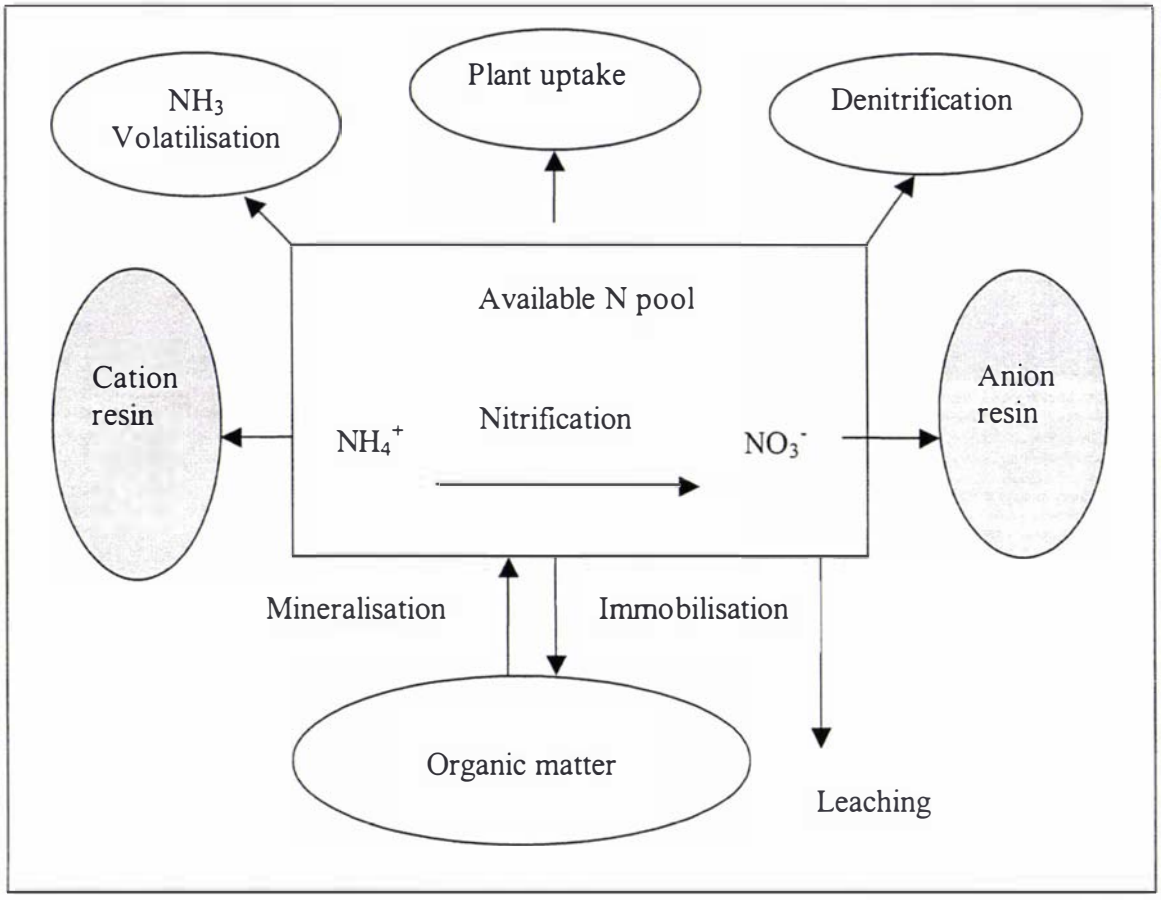


Fig. 4.22 Schematic diagram of processes controlling the available soil N.

It appears that *in situ* N measurement using resin membrane spikes may have the potential to at least partially overcome this problem. When resin spikes are embedded in the soil they can adsorb N over time, simultaneously with other processes. Therefore, the resins act as a net sink for mineral N and so give a better estimate of N availability over time. In this way, the resin data indicates a measure of the N flux through the available N pool.

Resin-adsorbed N may be able to be used as a potential mineralisation index. The results in Section 4.5.2 give some evidence for this. When the soils were incubated in the laboratary, larger amounts of resin-adsorbed NO_3^--N were found in the campsite soils than in the soils from the steep slope. Similarly, when resin spikes were directly buried in the field, the average resin-adsorbed NO_3^--N from 10 resin spikes was twice as

high in campsites as in steep slopes. As discussed in the literature review, campsites receive large amounts of dung and urine, and have large amounts of easily decomposable organic material, whereas in steep slopes substantial amounts of resistant organic matter accumulates. Qian and Schoenau (1995) used anion exchange resin membranes (AEM) in an incubation experiment to determine the influence of different tillage systems and landscape positions on mineralisable N. The NO_3^--N accumulated on AEM strips buried in soil for 2 weeks showed the expected difference among soils due to tillage treatments and slope position.

During the experiments described in this chapter, the resin spike's potential ability to detect spatial variability in soils was noted. Cain *et al.* (1999) used resin membranes to study spatial and temporal variation in N availability in coastal dunes. Huang and Schoenau (1996), also used resin membranes to study microsite assessment of forest soil nitrogen, phosphorus and potassium supply rates. It was noted in the literature review that recently scientists have been suggesting precise N application for hill country pasture using GIS and GPS systems (Gillingham *et al.*, 1999). Resin spikes may be useful in developing spatial N maps of the hill country landscapes.

The computer model developed in this chapter based on the diffusion of NO_3^--N closely simulated the actual experimental data. This has enabled an understanding of the N adsorption process and the influence of other factors on N adsorption by resin spikes. The model suggested that resin adsorption would continue until the rate of diffusion approached zero.

As N adsorption to resin is diffusion dependent, soil moisture, soil temperature, and soil tortuosity will also be major factors influencing N adsorption. In warm, moist, relatively high soil N conditions, N diffusion to resin is fast. However, in dry soils the diffusive resistance is high. Under such conditions, resin-adsorbed N would probably not correlate well with soil N concentration. This is because the mobility of the N rather than its quantity, would control the resin-adsorption. However, resin-adsorbed N under these conditions might still provide a useful index of N flux and plant N availability in the soil. Even at high concentrations, soil NO_3^--N is largely unavailable for plant uptake, when its movement in the soil is restricted by low soil moisture.

Resin-adsorbed N may therefore be a better measurement of the actual plant availability of mineral N under natural conditions.

The experiment described in Section 4.4.1.2 and the diffusion model described in Section 4.6 could be used as an effective way of determining the diffusion coefficient of NO_3^- ion in different soil conditions and soil types.

Estimates of resin-adsorbed N are not expressed as the quantity of N per unit weight of soil. This is one disadvantage of the resin method. This can be overcome to some extent by estimating the N depletion zone when resin spikes are kept in the soil. It was demonstrated in Section 4.6.3.5 that the depletion zone depends on other factors such as resin spike burial time and soil moisture.

The possible potential of N measurement by resin spikes has been outlined in this Chapter. Resin spikes were then used in the field experiment described later in Chapter 5 and the incubation experiment described in Chapter 6. As the N availability was also measured by the standard 2 M KCl method in these experiments, relationships between resin-adsorbed N and 2 M KCl -extractable N in different soils are discussed in detail in Chapters 5 and 6.

CHAPTER 5

FIELD INVESTIGATION OF NITROGEN DYNAMICS UNDER URINE PATCHES IN NORTH ISLAND HILL COUNTRY PASTURES

5.1 Introduction

The literature review revealed the importance of N cycling via animal excreta, especially in hill country where there are significant losses of N due to transfer of excreta from sloping land to flat camp areas. The preliminary experiment conducted at Waipawa, and described in Chapter 3, investigated the fate of urine N in steep and flat sites within a hill country pasture. In that experiment only about 20% of the added urine N was utilised by pasture and the rest appeared to be lost in some way from the mineral N pool.

A concern with the conduct of the preliminary experiment at Waipawa was that the frequency of sampling was not sufficient to detect rapid changes in the mineral N pool. In particular, although little NO_3^--N appeared to form after urine application, the possibility could not be ruled out that nitrification was occurring but the NO_3^--N so formed had then been leached from the profile before it could be detected.

In Chapter 4, a method, using ion exchange resin membrane spikes, for *in situ* N measurement over time was described. These resin spikes can be used to effectively monitor mineral N changes in a urine patch and overcome in part the difficulty of monitoring continuous changes in soil mineral N by sampling at particular points in time.

Also, it was suggested in Chapter 3 that urine N loss by NH_3 volatilisation was substantial in hill country even during the cold and moist winter. There have been limited studies that have measured NH_3 volatilisation in North Island hill country

pasture in New Zealand. Thus, it is important to obtain more information about NH_3 volatilisation losses in hill country pasture.

The objective of this study was to further monitor and understand the transformations and fate of urine N in different landscapes with contrasting topography in North Island hill country pasture. The use of resin spikes in this experiment would be useful to elaborate on the N transformations in urine patches and as well as providing further assessment of the technique.

5.2 Materials and methods

5.2.1 Site description

This experiment was carried out at Ballantrae AgResearch hill country research station, 20 km north of Palmerston North in the southern Ruahine range, during the mid-winter to early spring of 2000. The soils at this experimental site are Yellow Brown Earths and Intergrades to Yellow Grey Earths (NZ genetic soil classification). In addition, these soils can be identified as Brown soils (NZ soil classification version 3) and Dystrochrepts (US soil Taxonomy), according to Hewitt (1998). As many field studies have been carried out on this site in recent years, well-defined landscapes of contrasting fertility could be identified easily. Some soil properties of low and high fertility landscapes of the site were described in Sakadevan (1991), Machado (1994) and Carran *et al.* (1995).

5.2.2 Field layout and soil sampling

This experiment was carried out at two contrasting adjacent sites. The first was a flat site (F) that was a campsite for sheep and the second was a more steeply (20-25°) sloping site (S). The total C %, total N %, C/N ratio, Olsen P and soil pH of steep and flat sites were 5.5, 5.4; 0.4 ,0.5; 14 ,12; 29.8 μg/g, 49.3 μg/g and 5.8, 5.4 respectively. In each experimental site, twelve 0.5 x 1 m plots were established and arranged into four blocks of three plots. Three treatments were assigned at random within each of four blocks to give a randomised complete block design. The plots were established with buffer zones around the edges to prevent interference from other treatments by run

off etc. Each 0.5 x1m plot was divided into two 0.5 x 0.5 m sections. One section was used to take soil samples and the other was used for resin spike burial and for measurement of pasture yield.

5.2.3 Treatments

The treatments described in Chapter 3 were changed for this experiment based on measurements of available mineral N (NH_4^+-N + NO_3^--N) in newly-deposited urine patches at the site just before the experiment. The quantities of available soil mineral N in newly deposited urine patches were higher than the quantities of soil mineral N found in the 400 kg urine N/ha treated plots in the Waipawa experiment described in Chapter 3, suggesting that the N application rate in the urine patches may have been higher than 400 kg urine N/ha. Other works have also suggested 500 kg N/ha as the equivalent application rate per urine patch (Haynes and Williams, 1993; Sherlock and Goh, 1984), although Sakadevan *et al.* (1993) used 280 kg N/ha. Hence, the urine application rates for this experiment were taken as, 0 N (control), 280 kg urine N/ha and 560 kg urine N/ha (Table 5.1).

Table 5.1 Treatments used in the experiment at Ballantrae AgResearch hill country research station investigating the fate of simulated urine N applied to hill country pasture.

Rate N kg/ha	Site	
	Flat	Steep
0	F0	S0
280*	F280	S280
560**	F560	S560

* Applied as 2 litres of 0.7% N solution ** Applied as 2 litres of 1.4 %N solution

Table 5.1A Constituents of the synthetic urine solution (pH=7.8).

Constituent	0.7% N solution (g/l)	1.4% N solution (g/l)
Urea	13.7	27.4
Glycine	3.78	7.56
KCl	3.64	7.28
K_2SO_4	1.4	2.8
$KHCO_3$	10.5	21.0

Synthetic urine solution was made using the same constituents used in the Waipawa experiment, described in Chapter 3. As in that experiment, two litres of urine solution was added to the experimental plots. Thus, the quantities of constituents used to make the urine solution in the Waipawa experiment were changed to give the new urine N rates in the current experiment (Table 5.1A).

Two litres of 0.7 or 1.4 % N urine solutions were added evenly using a small watering can to relevant plots at a rate which avoided surface runoff.

As discussed in Chapter 3, it was decided that control plots should receive nothing- as opposed to 2 litres of water containing no N.

5.2.4 Soil sampling

At 4, 12, 27, 45, 66 and 88 DAUA soil samples were taken from the 0-100, 100-200 and 200-300 mm depths of each plot. Soil sampling was done as described in Chapter 3.

5.2.5 Ammonia volatilisation

NH_3 samplers were placed and analysed as described in Chapter 3.

5.2.6 Soil mineral and mineralisable nitrogen

Soil NH_4^+-N and NO_3^--N were extracted with 2 M KCl and analysed as described in Chapter 3. Soil samples from 3 DAUA were extracted with 0.5M K_2SO_4 rather than 2 M KCl to use the extractions for analysis of mineral nitrogen, dissolved organic C and dissolved organic N.

Soil samples from 4, 12 and 27 DAUA were analysed for mineralisable nitrogen after anaerobic incubation as described in Chapter 3.

5.2.7 Dissolved organic carbon and dissolved organic nitrogen

At 3 DAUA, 4 g of soil was extracted using 30 mL of 0.5M K_2SO_4. The extracts were used to measure dissolved organic carbon (Sparling and West, 1988) and total soluble N (Cabrera and Beare, 1993). Mineral N content was deducted from the total soluble N to calculate the dissolved organic N.

5.2.8 Resin-adsorbed nitrogen

Resin spikes were constructed as described in Chapter 4. Before commencement of the experiment, the reproducibility of the resin spikes was checked using an ammonium nitrate solution containing 10 μg NH_4^+-N/mL and 10 μg NO_3^--N/mL .

It was found in Chapter 4 that shorter burial periods of resin spikes in soil would be more suitable for moist soil and for soils containing high amounts of N. As the current experiment was carried out in mid winter with moist soil conditions and high N concentrations due to urine addition, it was decided to keep the resin spikes in the soil for a short period of only 3 days.

After urine solution was added to the soil, three KCl-saturated resin spikes were buried in random locations within the undisturbed section of each plot. After 3 days, the resin spikes were removed from the soil, washed with deionised water, shaken with 25 mL of 2 M KCl and the extracts were analysed for resin-adsorbed NH_4^+-N and NO_3^--N using a Technicon Auto Analyser as described in Chapter 4. When the three spikes were removed from the soil another three KCl-saturated resin spikes were buried for the next 3 days. The subsequent resin spikes were buried at different locations within the undisturbed section of each plot. This routine was continued until the first harvest at 33 DAUA. Thereafter resin spikes were buried for 3 days in every week until the last pasture harvest.

5.2.9 Plant dry matter production and pasture nitrogen uptake.

Four pasture harvests were taken 33, 66, 97 and 144 DAUA. At each harvest, pasture dry matter production and plant N uptake were measured as described in Chapter 3.

5.2.10 Statistical analysis

Analysis of variance was carried out using SAS for Windows version 8. Resin-adsorbed NH_4^+-N and NO_3^--N, 2 M KCl -extractable NH_4^+-N and NO_3^--N in 0-10 cm soil depth and total mineral N in 0-30 cm depth data were analysed using a repeated measures model in a mixed procedure (Littell *et al.*, 1998) to examine and compare response trends over time. Autoregressive co-variance structure was used in the model. Log transformed data were used in the statistical analysis. Log-transformed means were compared by a Least Mean Square method at a 5% significance level and based on this, the significance of observed means was expressed.

Analysis of variance for NH_3 volatilisation, herbage DM, and herbage N uptake data were analysed using a GLM procedure. Mean comparisons were done using the Duncan multiple range test at 5% significance. Log-transformed data were used in NH_3 volatilisation statistical analysis.

5.3 Results

5.3.1 Climate

The mean air temperatures and mean rainfall (mm/month) during the period of 1970-1995 and mean wind speed km/h for 1994 at Ballantrae AgResearch hill country research station are presented in Table 5.2. Average annual rainfall received at the experimental site for the last 25 years was 1188 mm/year. The 25-year average rainfall for the July to October period was 421 mm.

Rainfall, air temperature and soil temperature data during the experimental period are presented in Fig. 5.1 and Fig. 5.2. The total amount of rainfall received during the experimental period (14/7/2000 to 19/10/2000) was 316 mm.

Table 5.2 Average meteorological conditions for 1970-1995 at Ballantrae AgResearch Hill country research station (wind speed data was only available for 1994).

Month	Mean air temp (°C)	Max. air temp (°C)	Min air temp (° C)	Rainfall (mm)	Wind speed (km/h)
Jan	16.6	18.4	14.7	78.8	15.8
Feb	16.6	19.0	14.4	82.5	12.1
Mar	15.5	17.9	13	100.3	14.6
Apr	12.8	15.2	10.1	90.9	14.7
May	10.4	12.0	7.9	103.2	18.6
Jun	8.6	10.7	8.0	110.2	13.8
Jul	7.9	9.4	6.0	108.1	16.3
Aug	8.5	10.9	7.2	97.7	17.1
Sep	10.0	11.8	8.2	108.1	18.8
Oct	11.5	12.6	9.9	106.0	15.1
Nov	13.3	15.4	11.1	98.3	22.3
Dec	15.1	16.8	13.2	104.6	16.8

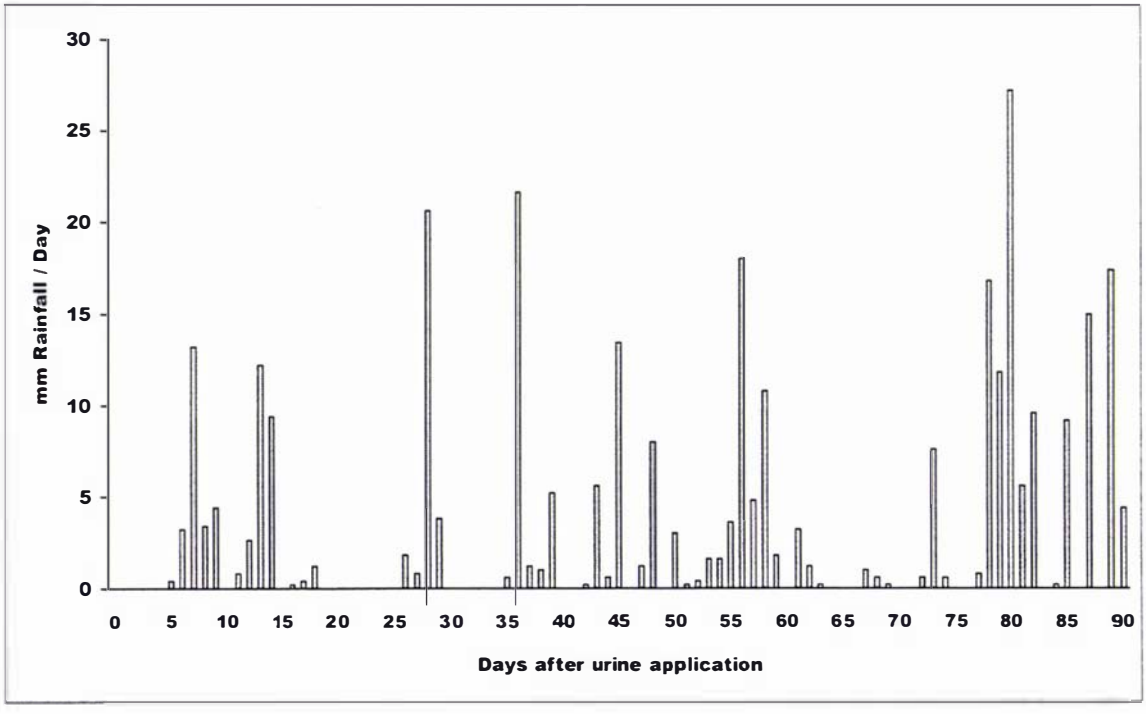


Fig. 5.1 Rainfall during the experimental period (14/7/2000-19/10/2000).

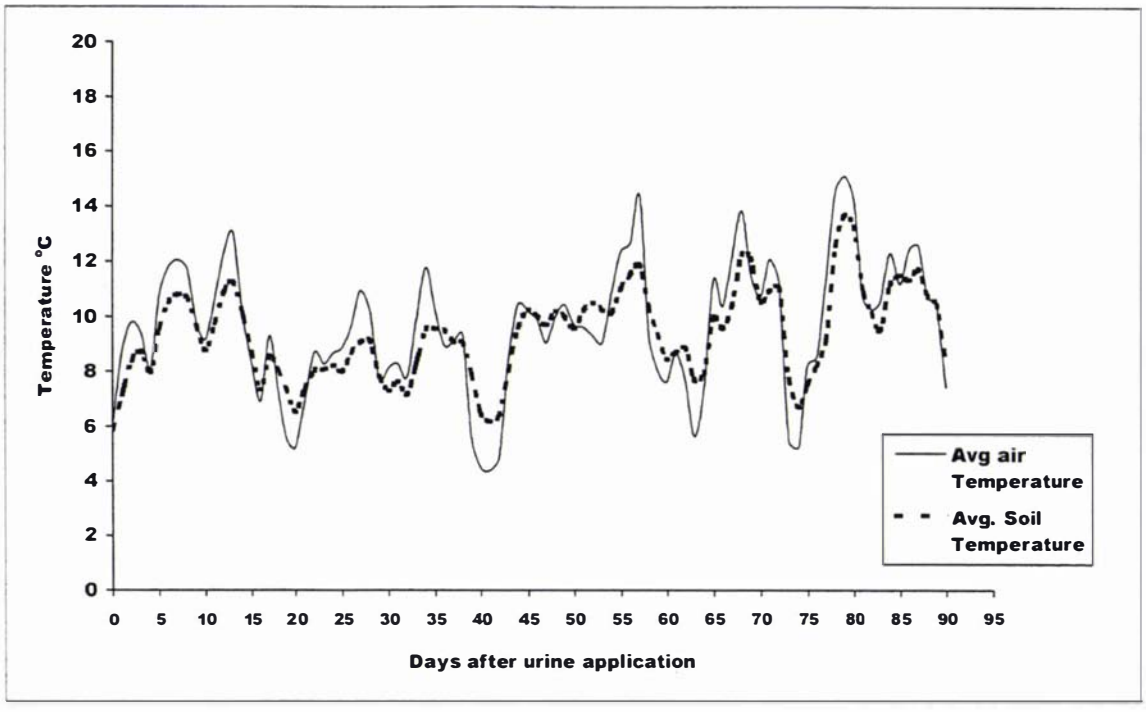


Fig. 5.2 Air and soil temperature (0-10 cm) during the experimental period (14/7/2000-19/10/2000).

5.3.2 Statistical interpretation

As pointed out in Section 3.4.2, the repeated measures model in a mixed procedure made it possible to compare the treatment means at a particular sampling time as well as treatment means between sampling times within a site. As in the Waipawa experiment described in Chapter 3, no comparisons were made between sites, as the site locations were not replicated appropriately. The least squares mean procedure for mean comparison supplied mean comparisons for all possible comparisons. This caused some difficulties in tabulating the statistical data. This detailed information is tabulated in Appendix 2. When necessary, any important statistical significant differences within and between samplings are identified and discussed in the text.

5.3.3 Mineral nitrogen

Mineral N comprises NH_4^+-N and NO_3^--N. These two components are discussed separately in Sections 5.3.4 and 5.3.5. This section provides some general comments on the combined quantities of NH_4^+-N and NO_3^--N extractable by 2 M KCl in the soils.

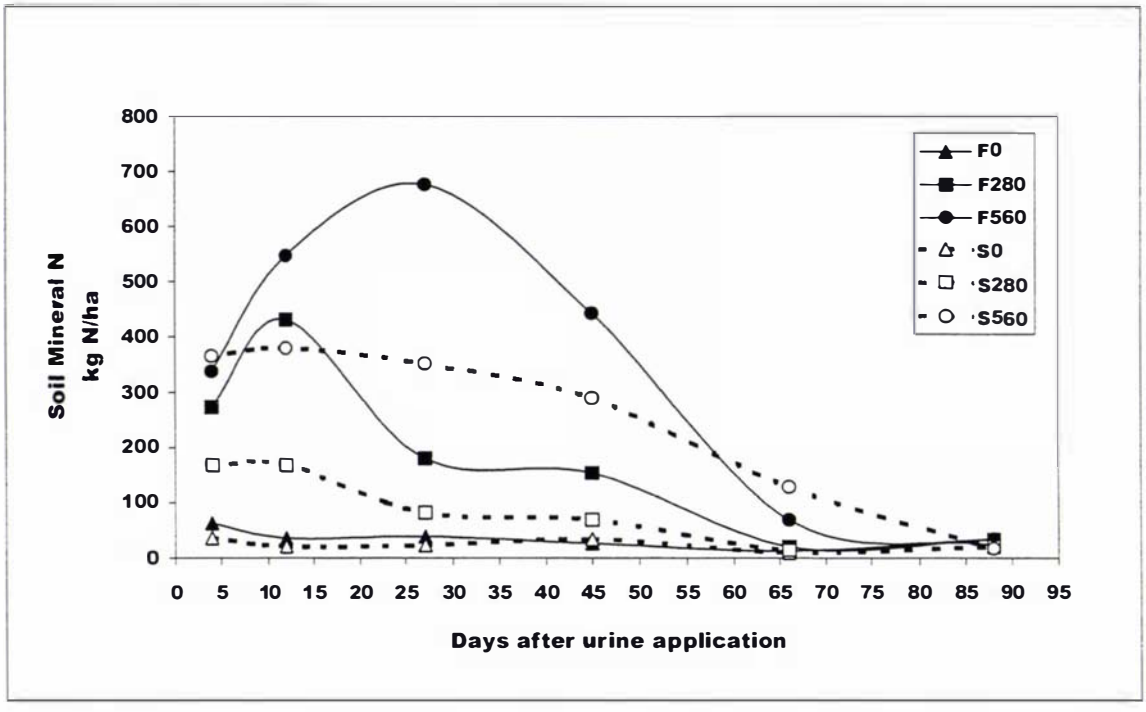


Fig. 5.3 Effect of urine application on soil (0-30 cm) mineral N levels.

Urine application resulted in highly significant (Table 2.1 of Appendix 2) increases in the levels of 2 M KCl -extractable mineral N in soil, to a depth of 30 cm, at both the flat site and steep site (Fig. 5.3). These increases in mineral N were greater at the flat site than the steep site and, not surprisingly, were greater when urine was applied at 560 kg N/ha than when it was applied at 280 kg N/ha.

At the steep site, soil (0-30 cm) mineral N levels in the urine-treated plots tended to be close to their maxima 3 DAUA, and declined thereafter towards the control levels. In the S280 treatment, mineral N levels were not statistically different from the control values from 45 DAUA onwards. In the S560 treatment, mineral N levels were still significantly higher than the control at 66 DAUA, but not at 88 DAUA.

In contrast to the steep site, soil (0-30 cm) mineral N levels in the urine-treated plots at the flat site tended to increase further, beyond 3 DAUA. In the F560 treatment, this increase in mineral N levels continued until 27 DAUA, and this increase over time was statistically significant (Table 2.1 of Appendix 2). In the F280 treatment, the increase

continued only until 12 DAUA and was not statistically significant. In both treatments, mineral N levels then decreased towards the control values.

Table 5.3 Net mineral N (extracted by 2 M KCl) in the soil profile (0-30 cm) (i.e. treatment minus control values).

Treatment	Day	Soil Depth						
		0-10cm		10-20cm		20-30cm		% recovery in soil
		NH_4+-N	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	
		kg N /ha						
F280	3	159	11	24	10	4	1	75
	12	277	56	13	30	0	18	141
	27	106	23	3	6	2	3	51
	45	25	37	11	35	1	18	45
	66	0	0	1	0	1	3	2
	88	6	0	1	0	0	0	2
F560	3	208	29	15	12	7	4	49
	12	316	75	60	49	0	12	91
	27	334	153	51	76	2	17	113
	45	91	157	29	93	9	38	74
	66	2	5	7	24	5	38	15
	88	0	0	0	0	0	0	0
S280	3	118	8	0	0	8	0	48
	12	88	17	20	8	11	2	52
	27	26	22	5	8	0	4	23
	45	5	15	3	9	1	2	12
	66	0	0	0	2	1	3	2
	88	0	0	0	0	0	0	0
S560	3	279	14	18	9	4	4	59
	12	259	44	20	26	2	7	64
	27	209	76	12	29	0	7	60
	45	77	97	6	51	2	21	45
	66	10	10	8	47	5	38	21
	88	1	0	1	0	0	0	0

In both the F280 and F560 treatments, mineral N levels were still significantly higher than control at 45 DAUA, but not at 66 DAUA.

When soil (0-30 cm) mineral N levels were at their peak at the flat site, the differences in the quantities of mineral N between the treated and control plots were greater than the total amount of urine N added (Table 5.3). In other words, the apparent recovery of urine N in the soil mineral form alone was greater than 100%. This was the case for both rates of urine addition, and suggests a possible priming effect.

Although at the first sampling (3 DAUA), most of the mineral N resulting from urine addition was in the 0-10 cm soil depth, there was clear evidence of some movement of urine N to the 10-20 cm and 20-30 cm soil depths (Table 5.3). As there had been no rainfall over this time (Fig. 5.1), this movement probably resulted from preferential flow through soil macro-pores during urine addition. At later samplings, greater quantities of urine N were detected in the 10-30 cm soil depths, presumably as a result of leaching. This is discussed in more detail in Section 5.3.10.

5.3.4 Ammonium

Concentrations of 2 M KCl -extractable NH_4^+-N (μg NH_4^+-N/g soil in 0-10 cm depth) and resin-adsorbed NH_4^+-N (μg NH_4^+-N/5 cm^2 resin/3 days) over the duration of the trial are presented in Fig. 5.4.

The patterns for 2 M KCl -extractable NH_4^+-N in the 0-10 cm soil depth, are similar to those for soil mineral N, to a depth of 30 cm, (discussed in the previous section), particularly shortly after urine application. This was because at that time, NH_4^+-N was the dominant component of mineral N in all the urine-added treatments (Fig. 5.5), and most of the added nitrogen was in the 0-10 cm soil depth.

Thus, urine application resulted in highly significant (Table 2.2 of Appendix 2) increases in the levels of 2 M KCl -extractable NH_4^+-N, to a depth of 10 cm, at both the flat site and steep site (Fig. 5.4). As for mineral N, these increases in NH_4^+-N were larger at the flat site than the steep site, and larger for the 560 kg/N/ha than for the 280 kg N/ha rate of urine application.

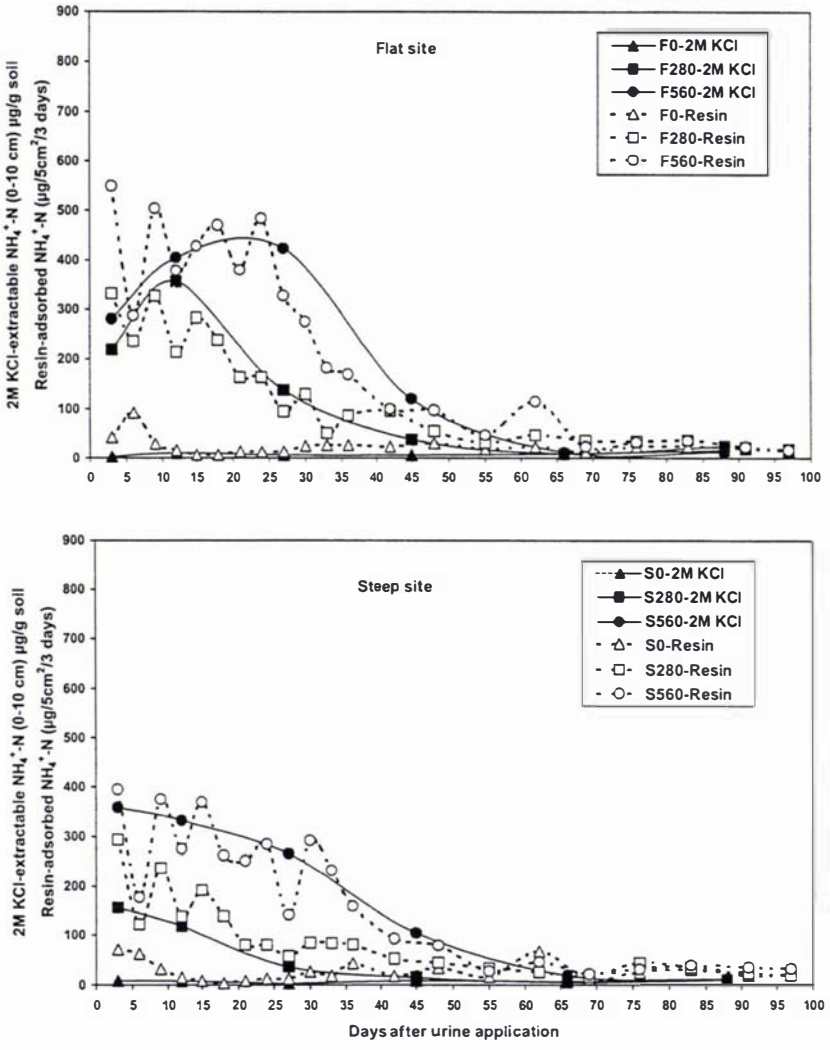


Fig. 5.4 Effect of urine application on soil NH_4^+-N levels (0-10 cm) as determined by 2 M KCl extraction and resin adsorption methods.

As was the case for mineral N, there was an apparent, continuing increase in 2 M KCl -extractable NH_4^+-N after 3 DAUA, for both rates of urine application at the flat site. However, for NH_4^+-N in the 0-10 cm soil depth, these increases after 3 DAUA were not statistically significant–although for the F560 treatment the increase between 3 and 27 DAUA nearly reached statistical significance (P=0.08).

As the trial progressed, the levels of NH_4^+-N in the treated plots decreased towards those in the control plots. At both the flat site and steep site, 2 M KCl -extractable NH_4^+-N (0-10 cm) levels in the 280 kg urine N/ha treatments were significantly higher

than in the control plots, up to 27 DAUA. In the 560 kg urine N/ha treatments, the significantly elevated levels of 2 M KCl -extractable NH_4^+-N (0-10 cm) persisted until 45 DAUA.

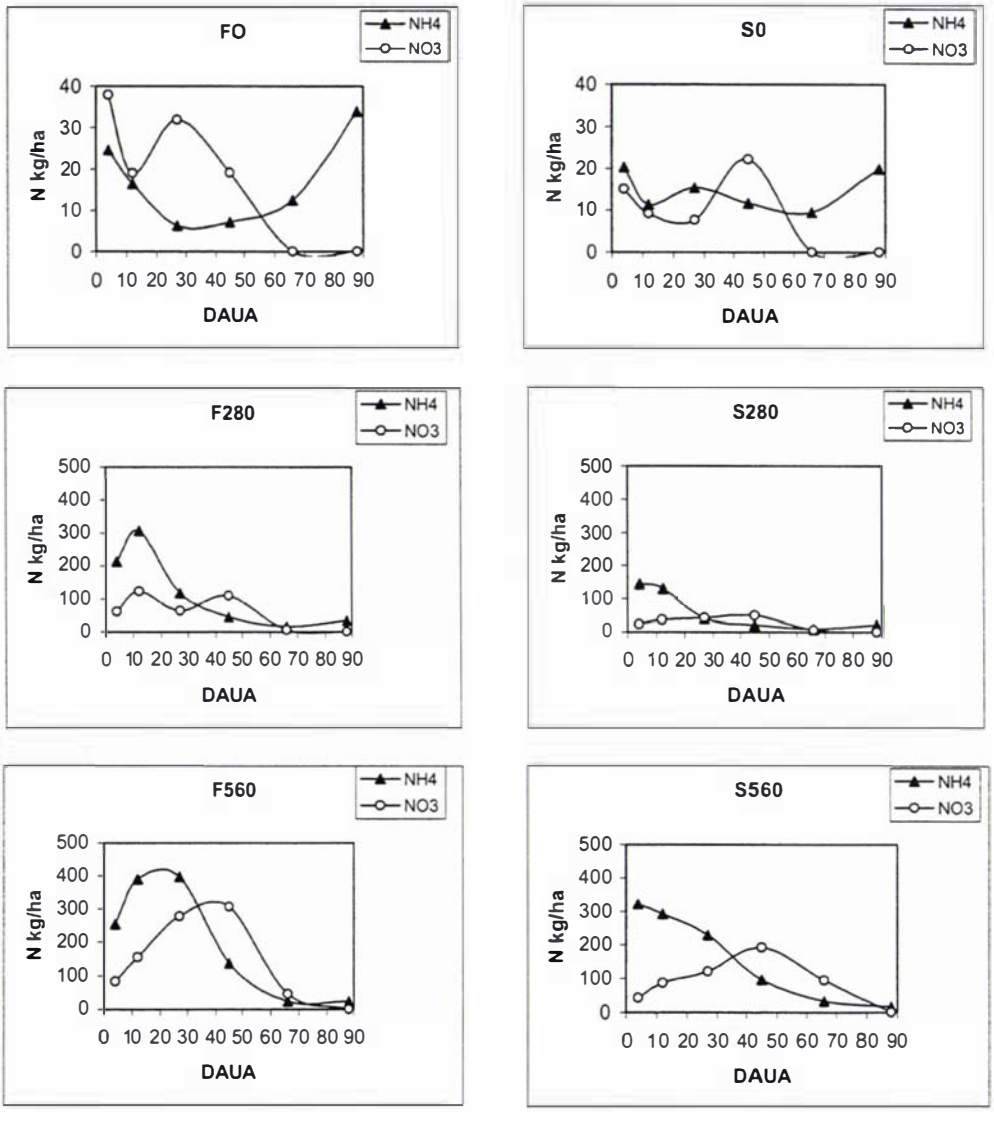


Fig. 5.5 Quantities of 2 M KCl extractable NH_4^+-N and NO_3^--N in the 0-30 cm soil depth during the experimental period. Note. change in scale between control and treated plots.

Resin-adsorbed NH_4^+-N followed similar trends to the 2 M KCl -extractable NH_4^+-N in the 0-10 cm soil depth, but there were some large variations between sampling times (Fig. 5.4). Some of these variations were statistically significant, and there were some consistent patterns between treatments–providing further evidence that the variations

with time were not solely due to chance. For example, from 3 to 6 DAUA all urine-added treatments showed a drop in resin-adsorbed NH_4^+-N, which was then recovered by 9 DAUA. This could be due to high volatilisation losses in first few days and later recovery from a priming effect.

One theoretical explanation of the variation in resin extractable NH_4^+-N with time relates to the observation that NH_4^+-N adsorption by resin spikes in the soil can vary with soil moisture content, as the NH_4^+-N adsorption to resin is governed by diffusion. This was demonstrated in Section 4.6.4.2 in Chapter 4. In this instance however, the observed variations of resin-adsorbed NH_4^+-N levels with time were not likely to be due to soil moisture differences because the soil moisture contents were usually close to field capacity due to the high rainfall (Fig. 5.2) that occurred during the experiment.

5.3.5 Nitrate

Concentrations of 2 M KCl -extractable NO_3^- -N (μg NO_3^- -N/g soil in the 0-10 cm depth) and resin-adsorbed NO_3^--N (μg NO_3^- -N/5 cm^2 resin /3 days) over the duration of the trial are presented in Fig. 5.6. Although urine application resulted in highly significant increases in 2 M KCl -extractable NO_3^--N (Table 2.3 of Appendix 2), the pattern of increase was very different to that for NH_4^+-N, described in Section 5.3.4.

At the first sampling (3 DAUA), there were no significant differences in 2 M KCl - extractable NO_3^--N between the control and urine-treated plots at either site. Soil NO_3^--N levels then built up with time in the urine-treated plots at both sites. These elevated levels of 2 M KCl - extractable NO_3^--N were apparent throughout the 0-30 cm soil depth (Table 5.3). Presumably, NO_3^--N was produced in the 0-10 cm depth by nitrification of added urine N, and was then transported to the deeper soil depths by leaching. These processes are discussed in more detail in later sections.

The 2 M KCl - extractable NO_3^--N levels at both sites in the 0-10 cm soil depth were at their maximum between 35-45 DAUA (Fig. 5.6). Thereafter, NO_3^--N levels in the surface soil decreased markedly, to reach the levels in the control plots by 66 DAUA. The elevated NO_3^--N levels in the 10-20 and 20-30 cm soil depths persisted for

somewhat longer (Table 5.3), but by 88 DAUA there was no difference in NO_3^--N levels between the control and treated plots in any of the 3 soil depths at both sites.

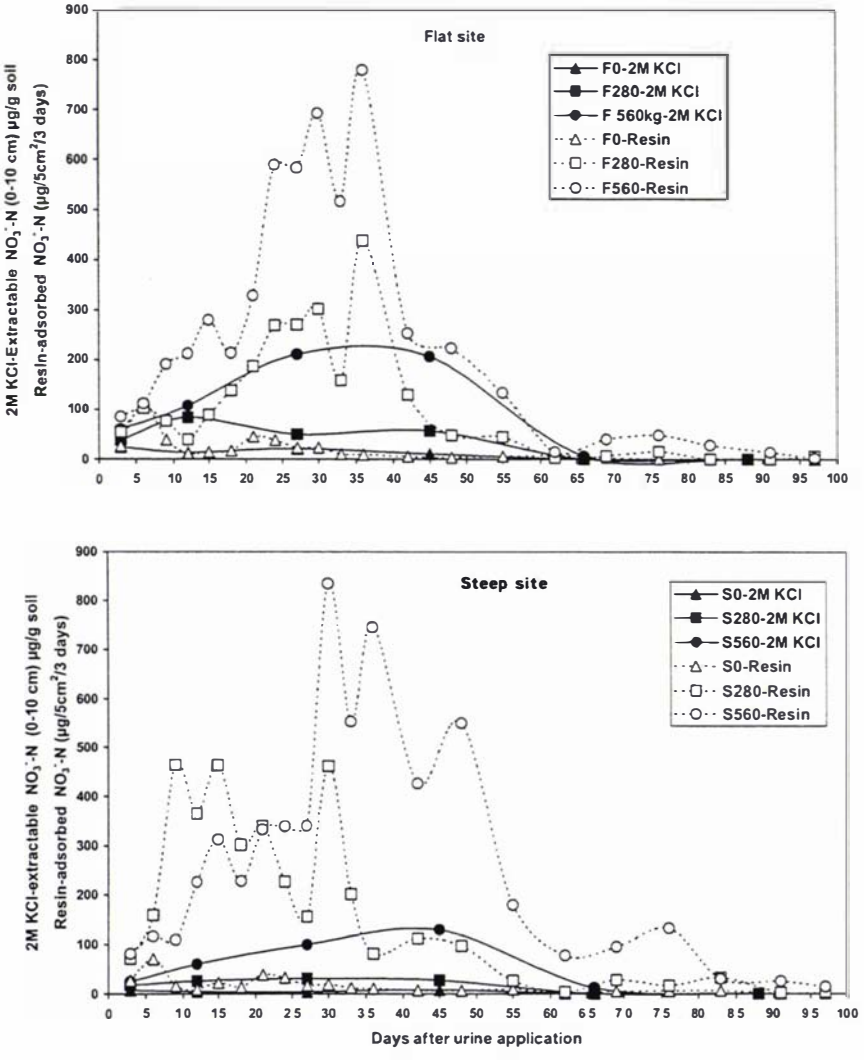


Fig. 5.6 Effect of urine application on soil NO_3^--N levels (0-10 cm) as determined by 2 M KCl -extraction and resin-absorption methods.

The quantities of 2 M KCl -extractable NO_3^--N (0-10 cm) appeared to be higher on the flat site than the steep site, but the trial was not designed to test these differences statistically.

Resin-adsorbed NO_3^--N followed a similar pattern to 2 M KCl -extractable NO_3^--N. However, NO_3^--N extracted by the resin showed a much greater range than that by 2 M

KCl for both rates of urine addition at both sites. This is discussed in more detail in Section 5.3.6.

Although after 66 DAUA, no significant differences in 2 M KCl -extractable NO_3^--N were observed between treated and control plots, there were still some statistically significant differences (Table 2.5 of Appendix 2) observed in resin-adsorbed NO_3^--N levels. This is also discussed in more detail in Section 5.3.6.

It was interesting to note that when the 2 M KCl -extractable NO_3^--N levels were at their maximum at both sites, there was a more than three-fold difference in the amounts of NO_3^--N between the 560 kg urine N/ha and the 280 kg N/ha urine treatments. In contrast, levels of resin-adsorbed NO_3^--N were more in proportion to the two-fold difference in application rates.

5.3.6 Performance of resin spikes

It is difficult to compare directly resin adsorbed N and N extracted by 2M KCl , as resin spikes do not measure from the same volume of soil as the 2 M KCl extraction method. Also, these two methods are measuring different properties. Data from the 2 M KCl extraction method report the pool size of available N at a particular time while resin data may reflect the N flux over time as well as the available N pool size at a given moment. A possible example of this is given below.

After about 66 days, 2 M KCl extraction could detect very little NH_4^+-N or NO_3^--N, but the resin method could still detect sufficient NO_3^--N to show statistically significant treatment differences (Table 2.5 of Appendix 2). To illustrate this, Fig. 5.7 shows the data from 55 to 97 DAUA in Fig. 5.6, redrawn with an expanded scale.

At the steep site, the amounts of resin-adsorbed NO_3^--N in the S560 plots were significantly ($P<0.01$) higher than the control plots from 62 to 97 DAUA and in the S280 plots, NO_3^--N levels were significantly ($P<0.01$) higher at 69 and 76 DAUA. At the flat site, the amount of resin-adsorbed NO_3^--N in the F560 treatment plots was significantly ($P<0.05$) higher than in the control plots from 69 to 91 DAUA, while the F280 plots had significantly ($P<0.01$) higher resin adsorbed NO_3^--N levels than the

control plots only at 76 days. At both the sites, during this period, significant differences in resin adsorbed NO_3^--N levels between the two urine treatments were also observed (Table 2.5 of Appendix 2).

The increase in levels of resin-adsorbed NO_3^--N from 62 DAUA may arise from remineralisation of urine N. However, the fact that the remineralised N was not detected by the 2 M KCl extractions suggests that the NO_3^--N was taken up by plants, or lost almost as soon as it was formed. In such cases, a method that measures the flux of N through mineral N pool, such as the resin method, has particular value.

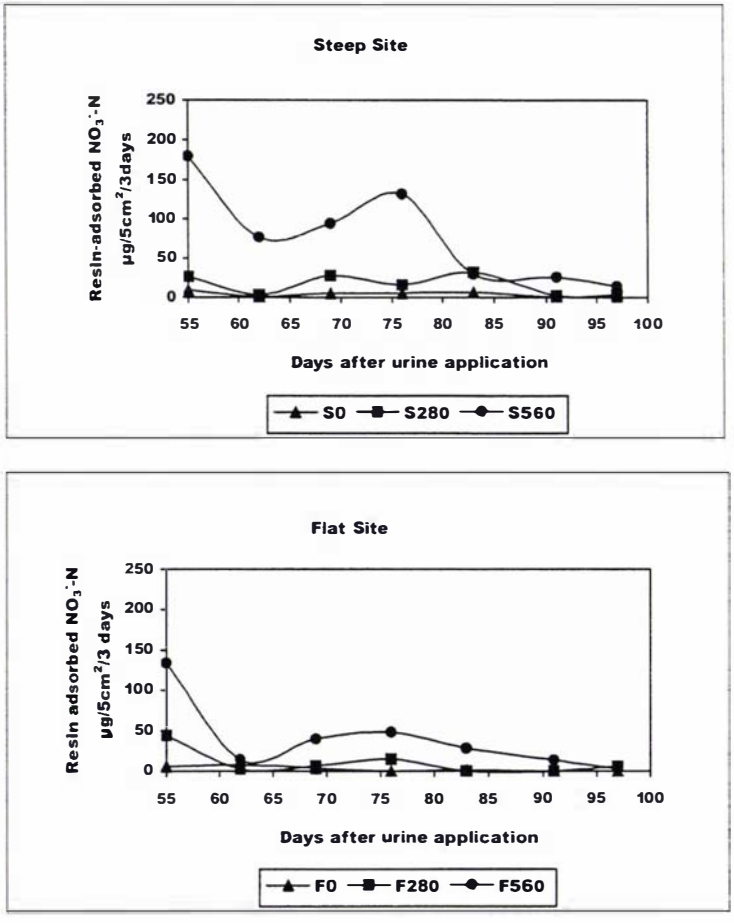


Fig. 5.7 Effect of urine treatments on resin-adsorbed NO_3^--N at 55 to 97 DAUA.

5.3.6.1 Relationships between 2 M KCl -extractable N and resin-adsorbed N

Developing relationships between resin-adsorbed N and other soil parameters is complicated by the high variability in the resin-adsorbed N. For example, at 27 DAUA, resin-adsorbed NH_4^+-N assessed by the twelve individual spikes in each of S0, S280 and S560 treatments varied from 0-34, 17-143, and 54-251 μg/5 cm^2/3 days respectively, with corresponding co-efficients of variation of 88, 61, and 55%. At the same sampling, NO_3^--N varied among the twelve spikes from 5-34, 14-326, and 60-804 μg/5 cm^2/3 days, with co-efficients of variation of 60, 84, and 72% for the S0, S280 and S560 treatments respectively.

As was indicated in Chapter 4, this variation reflects actual spatial variability of mineral N concentrations in the field, rather than errors within the technique itself. Resin-adsorbed values are equivalent to analysing individual soil cores, whereas 2 M KCl -extractable NH_4^+-N and NO_3^--N are from bulked samples of five soil cores.

In an attempt to overcome some of this variability the relationships between resin-adsorbed N and 2 M KCl -extractable N illustrated in Fig. 5.8 were developed by comparing mean resin-adsorbed N values in each plot (average of 3 resin spikes in each plot) and 2 M KCl -extractable N (plot value obtained from a bulk sample of 5 soil cores) values in each plot. Data were obtained from both sites at 3, 12, 27 and 45 DAUA. Thus, a total of 96 data points (3 treatments x 4 replicates x 4 sampling times x 2 sites) from each method were used for the relationships.

For both NO_3^--N and NH_4^+-N, there was some evidence of linear relationships between resin-adsorbed and 2 M KCl -extractable N values. Although, the relationships were statistically significant they were weak.

As the resin method and 2 M KCl methods are measuring different things (see Section 5.3.6), exact 1:1 relationships between resin-adsorbed N and 2 M KCl -extractable N are unlikely.

Resin spikes tend to adsorb more NO_3^--N than NH_4^+-N at a particular N concentration as measured by the 2 M KCl extraction method (Fig. 5.8). This was also observed in

Chapter 4 when resin spikes adsorbed higher amounts of NO_3^--N than NH_4^+-N from a NH_4NO_3 solution containing 10 μg NO_3^--N/mL and 10 μg NH_4^+-N/mL .

To further minimise the variability observed in the resin-adsorbed N data, the linear relationships were re-developed (Fig. 5.9) using the average of each treatment (average of four replicates) for both resin and 2 M KCl extraction methods. Relationships were also developed separately for the flat and steep sites. Thus, a total of 12 data points (3 treatments x 4 sampling times x 1 site) for each method were used for the relationship.

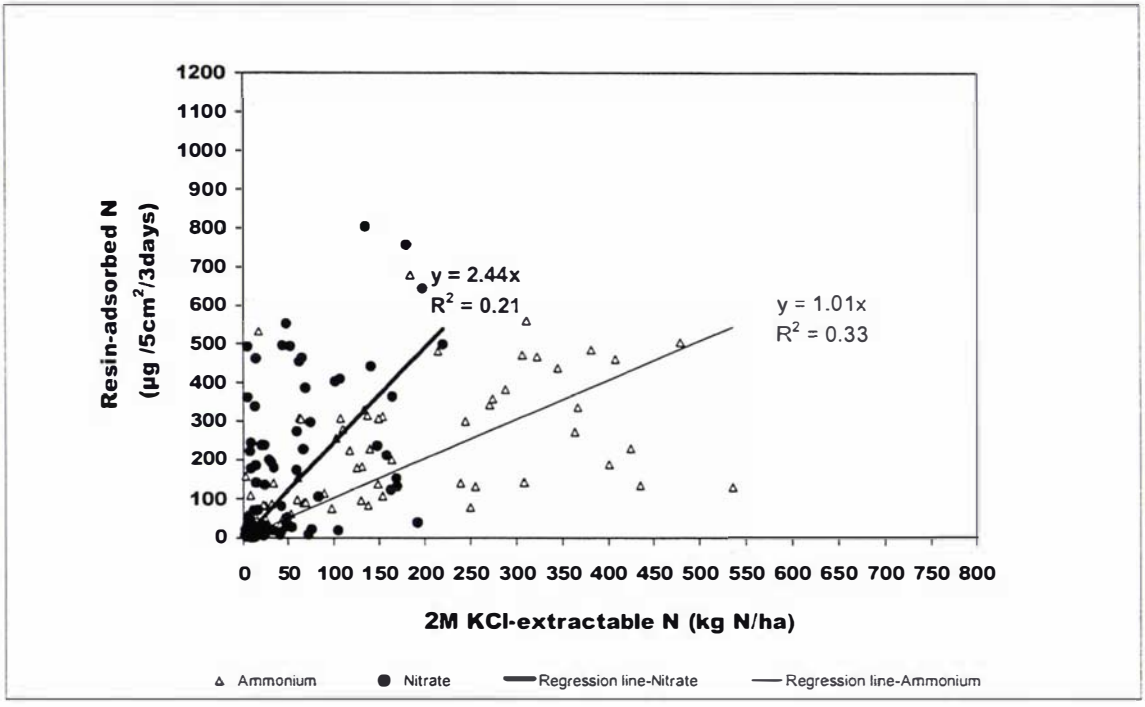


Fig. 5.8 Relationship between resin-adsorbed N and 2 M KCl extractable N when both steep and flat site data are used.

Both the NO_3^--N and NH_4^+-N data then produced strong linear relationships (Fig. 5.9). The resin spikes tended to adsorb higher quantities of NO_3^--N at the steep site than at the flat site at a particular 2 M KCl -extractable NO_3^--N concentration (Fig. 5.9A). Higher NO_3^--N adsorption to resin can occur at higher soil moisture contents (see Section 4.6.3.2 in Chapter 4). However, it is not clear, why the wetter flat site had less resin-adsorbed NO_3^--N than the steep site for a given value of 2 M KCl extractable NO_3^--N.

In contrast, resin-adsorbed NH_4^+-N was similar at both sites at a particular 2 M KCl -extractable NH_4^+-N concentration.

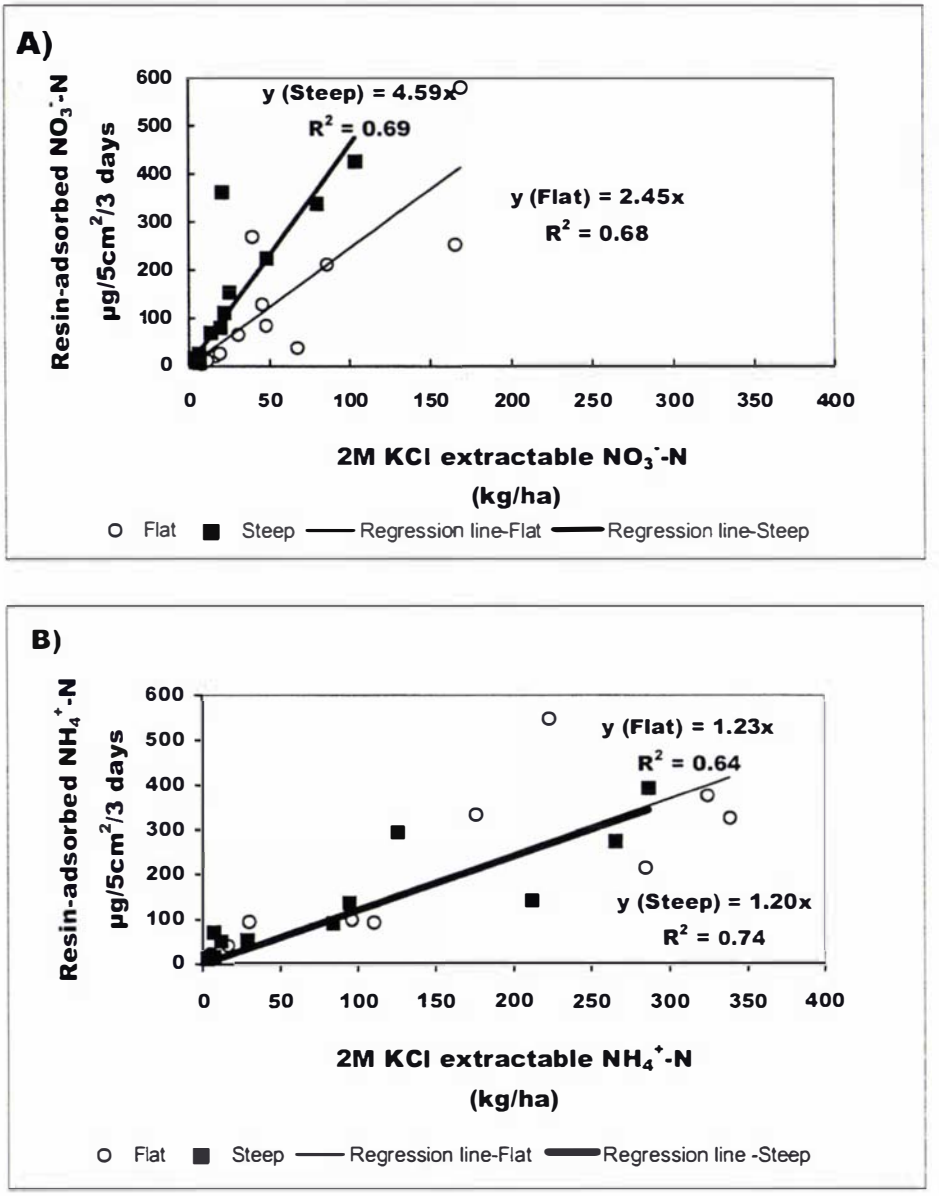


Fig. 5.9 Relationships between (A) resin adsorbed NO_3^--N and 2 M KCl -extractable NO_3^--N. (B) Resin-adsorbed NH_4^+-N and 2 M KCl adsorbed NH_4^+-N.

5.3.7 Mineralisable N

It was observed in Section 5.3.3, that the apparent recovery of urine N in the mineral form was greater than 100% up to 27 and 66 DAUA in the F280 and F560 treatments

respectively, suggesting a priming effect after urine application. To investigate this, an attempt was made to see if there were any changes in soil mineralisable N during the period of the observed priming effect. Soil samples from 3, 12 and 27 DAUA, which had been stored at 4° C at field moisture content, were analysed for mineralisable N using the anaerobic incubation procedure described in Section 5.2.5. These incubations and analyses were conducted after the completion of the field trial.

In the control soils at both the sites, the highest mineralisable N levels were found in the 0-10 cm soil depth (Table 5.4). Also at both sites, mineralisable N in the 10-20 cm and 20-30 cm soil depths was not affected by urine treatments. Therefore, only changes in mineralisable N in the 0-10 cm soil depth are discussed (Fig. 5.10 and 5.11).

Higher mineralisable N levels were observed in the flat site control plots than in the steep site control plots (Table 5.4).

Table 5.4 Mineralisable N levels (kg/ha) in control soils at different depths. Values are the average of soils from sampling times at 3, 12 and 27 DAUA.

Soil Depth	Steep site	Flat site
0-10 cm	200	301
10-20 cm	115	131
20-30 cm	84	92

At both sites, mineralisable N levels in the control plots did not change significantly ($P< 0.05$) between any of the three sampling times.

Although an increase in mineralisable N might normally be expected after urine application, the soil mineralisable N levels were significantly reduced compared to control. This decrease was first observed with the lower urine N application rate of 280 kg urine N/ha treatment at 3 DAUA at both sites. The mineralisable N in the S560 treatment was significantly lower than the control at 12 and 27 DAUA, while the F560 treatment had significantly lower mineralisable N values than the control plots at 27 DAUA only.

Mineralisable N in the F560, S280 and S560 treatments also decreased significantly with time from 3 to 27 DAUA.

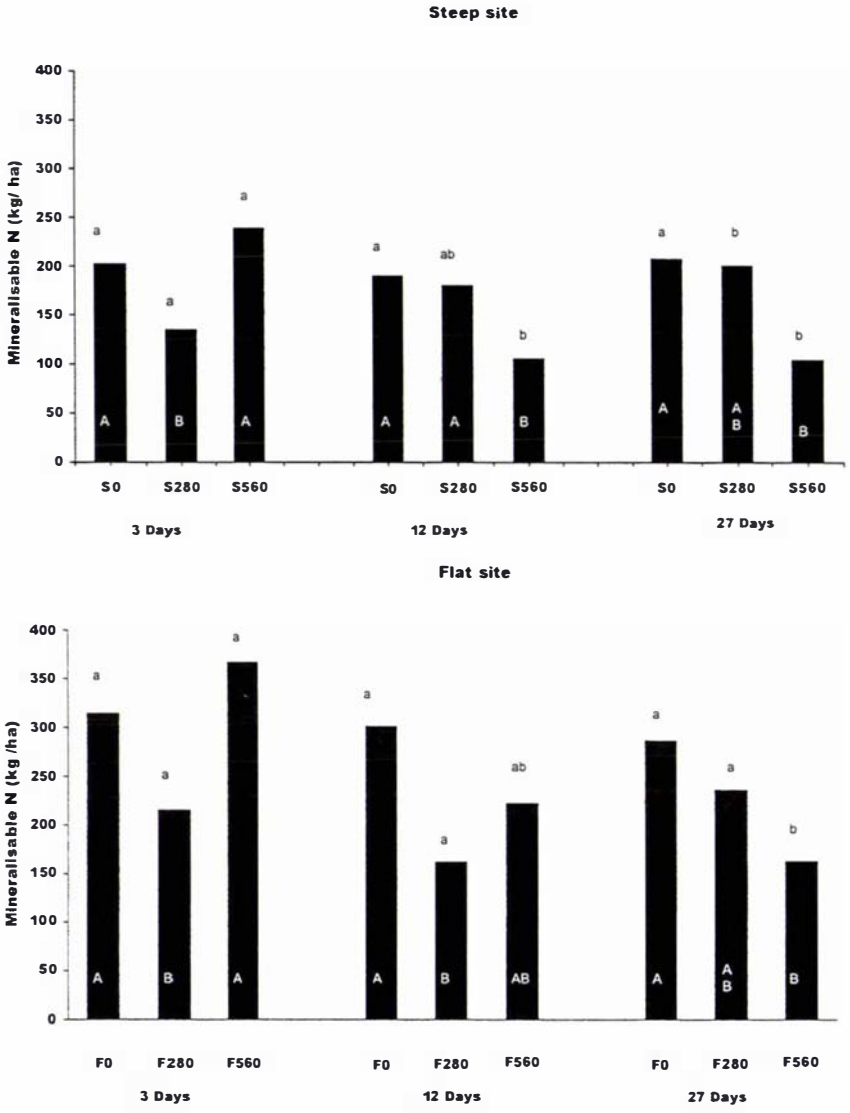


Fig. 5.10 Effects of urine treatments on soil (0-10 cm) mineralisable N levels at 3, 12, 27 days after urine application. Treatments with common upper case letters do not differ at $P<0.05$ level within a sampling day. Treatments with common lower case letters do not differ at $P<0.05$ level between sampling days of the same treatment.

When the levels of mineralisable N at the each site are plotted on the same graph as the level of mineral N (Fig. 5.11), there is an apparent relationship in some treatments.

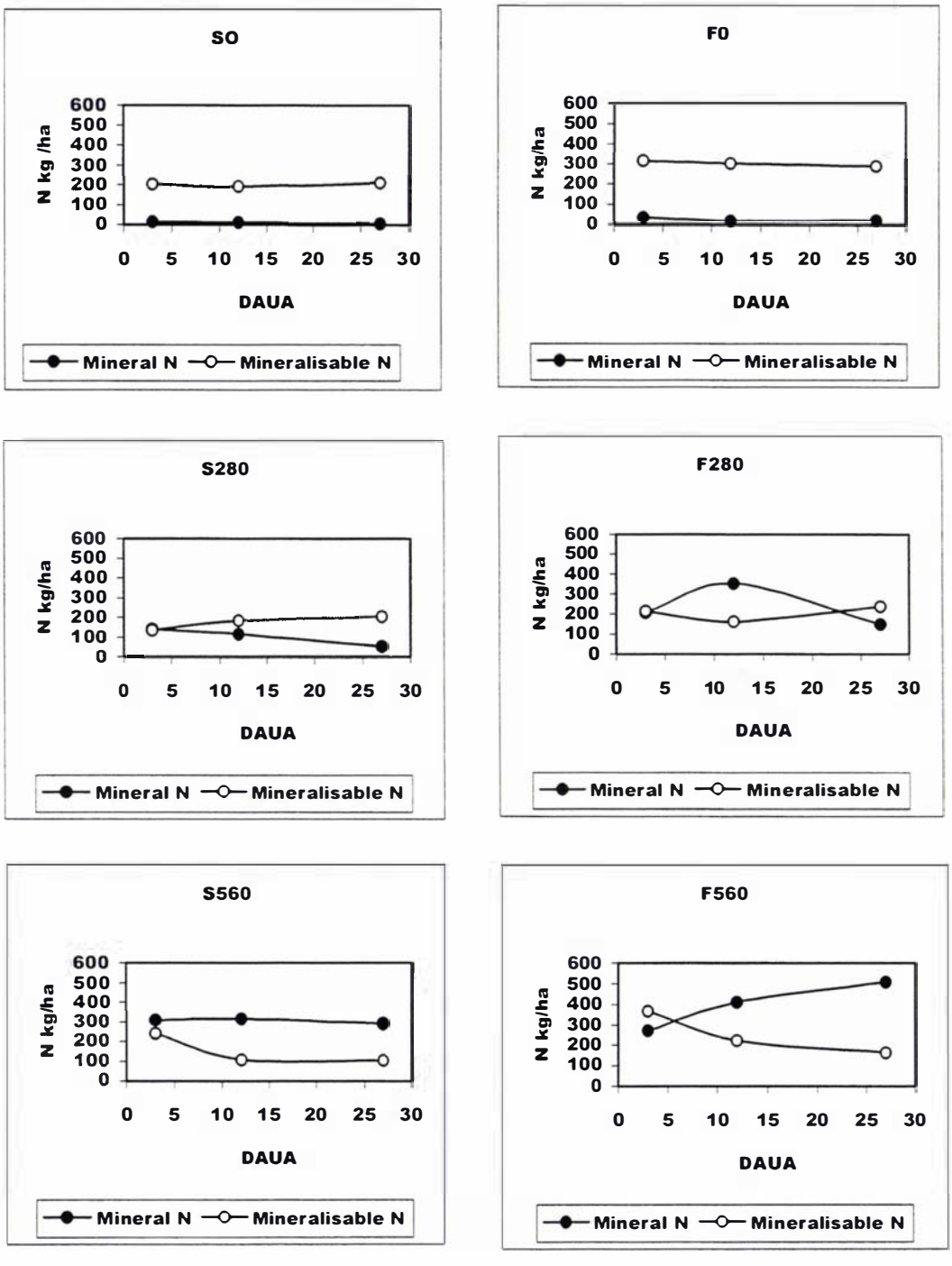


Fig. 5.11 Effect of urine application on soil mineralisable and mineral N levels (0-10 cm depth) at 3, 12 and 27 days after urine application (DAUA).

At the flat site in particular, it appears that increases in mineral N from 3 DAUA are closely paralleled by decreases in mineralisable N. This relationship between increases

in mineral N and decreases in mineralisable N from 3 DAUA to 12 DAUA and from 12 DAUA to 27 DAUA across all sites is displayed in Fig. 5.12.

It is apparent that a linear relationship (R^2=0.6) exists with a slope of 1.1. This close coincidence with the 1:1 line, suggests that the observed mineral N increase was possibly due to mineralisation of soil organic matter. When the relationships were redrawn separately for the two sites (data not presented) it was apparent that the linear relationship was much stronger on the flat site (R^2=0.8) than on the steep site (R^2=0.3).

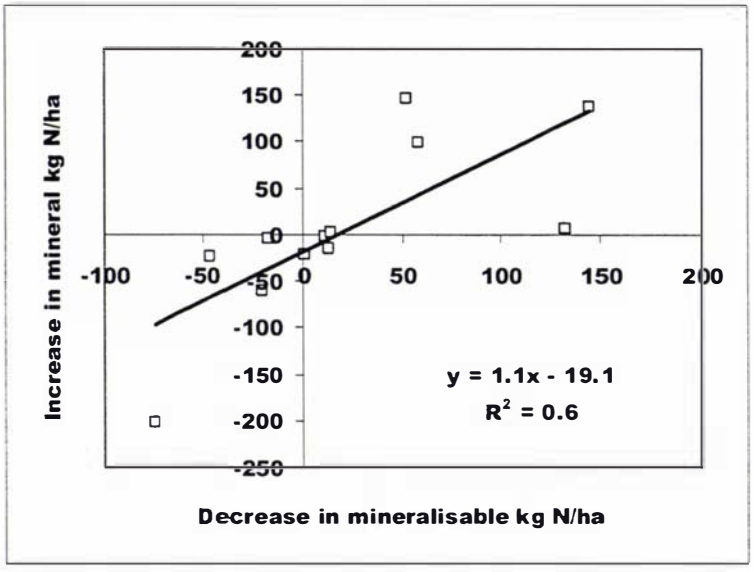


Fig. 5.12 Relationship between increase in soil mineral N and decrease in soil mineralisable N from 3 to 12 and from 12 to 27 DAUA.

5.3.8 Pasture response

Pasture yield cuts and associated herbage N analyses were conducted on four occasions covering the period 0-144 DAUA (14/7/2000 to 7/12/2000). Soil measurements had ceased at 88 DAUA – corresponding to cut 3 - when no further residual effects of urine addition on soil N status could be detected. However one further pasture cut was taken 144 DAUA to check whether there was any observable residual effect of urine addition on either pasture growth rate or N concentration.

Dry matter (DM) accumulation during the experiment is illustrated in Fig. 5.13. When all the cuts are combined, over the whole experimental period, urine treatments significantly increased pasture accumulation only at the flat site.

When the cuts were considered individually (Fig. 5.13), it was apparent that most of the pasture response at the flat site occurred at the second and third cuts. And at the steep site, where there was no growth response overall, there was some evidence of a significant DM response to urine application at the second harvest.

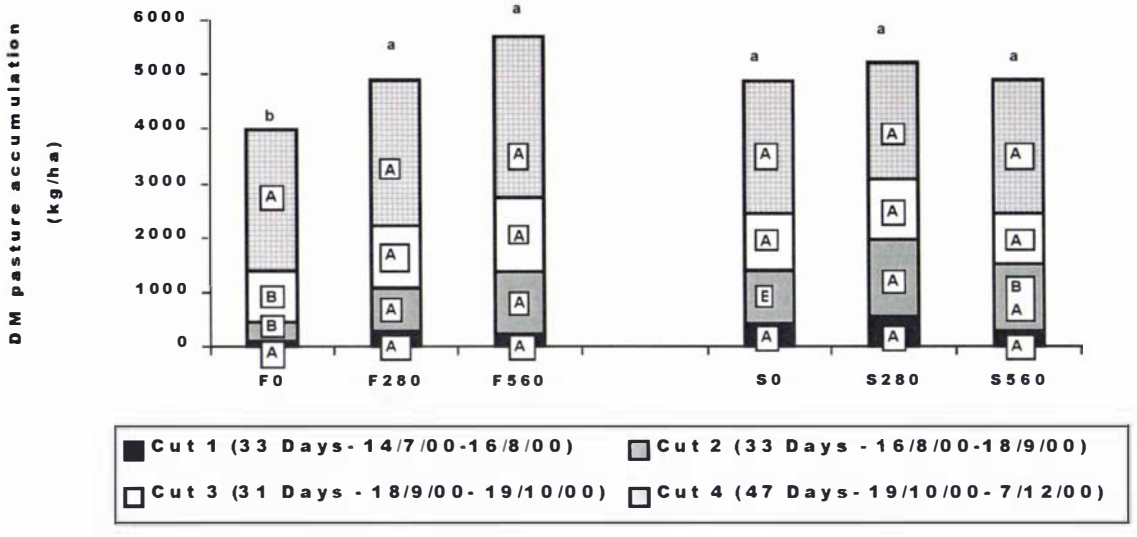


Fig. 5.13 Effect of urine treatments on pasture DM accumulation at the flat and steep sites. Dry matter yields with common letters between treatments within same cut and same site do not differ at $P<0.05$. Total DM accumulation with common lowercase letters between treatments within same site do not differ at $P<0.05$.

N accumulation by herbage (Fig. 5.14) followed a similar pattern to DM accumulation. The N concentration in dry matter increased in urine-treated plots at the first and second cuts only (Table 5.5). Although the N concentration had increased markedly in the urine-treated plots at both sites during the first growth period, the N uptake by pasture was low. This was due to the low rates of pasture growth resulting from the cold and wet winter conditions during this period.

As noted above, the growth period between cuts 3 and 4 was after the cessation of soil monitoring. In this growth period there was no evidence of a residual effect of urine addition on either pasture growth rate or N concentration.

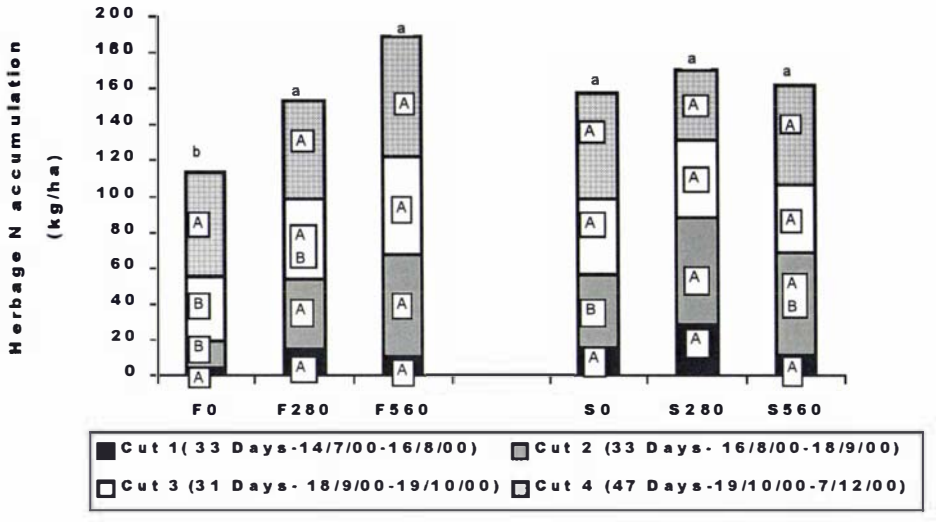


Fig. 5.14 Effect of urine treatments on herbage N accumulation. Herbage N accumulations with common uppercase letters between treatments within the same cut and site do not differ at $P<0.05$. Total herbage N accumulations with common lowercase letters between treatments within same site do not differ at $P<0.05$.

Overall, urine N recoveries by pasture during the experiment were 14, 13, 4, and 1 % of added N for the F280, F560, S280 and S560 treatments respectively.

The trial design precludes any statistically valid comparison of pasture production and N uptake between the flat and steep sites. However, the greater response in pasture production observed on the flat site, suggests that pasture growth was more limited by N at this site than on the steep site.

Table 5.5 Pasture DM production, herbage N concentration and N uptake following urine application.

Treatment	Cut 1 14/7/00-16/8/00			Cut 2 16/8/00-18/9/00			Cut 3 18/9/00-19/10/00			Cut 4 19/10/00-07/12/00		
	DM kg/ha	N Conc. %	N Uptake kg/ha	DM kg/ha	N Conc. %	N Uptake kg/ha	DM kg/ha	N Conc. %	N Uptake kg/ha	DM kg/ha	N Conc. %	N Uptake kg/ha
F0	109	3.4	5	349	3.9	14	932	3.9	37	2595	2.2	58
F280	293	4.9	15	798	4.6	39	1113	4.0	45	2686	2.0	54
F560	215	4.7	10	1157	4.8	57	1364	4.0	55	2959	2.3	66
S0	439	3.5	15	950	4.2	41	1049	4.0	43	2434	2.5	59
S280	535	5.2	28	1439	4.2	60	1099	3.9	43	2141	1.9	39
S560	286	4.9	11	1231	4.7	57	941	4.1	38	2439	2.3	55

5.3.9 Ammonia volatilisation

Urine treatments significantly ($P<0.05$) increased the amount of ammonia volatilisation at both sites (Fig. 5.15). The statistical analysis was done on log- transformed data, due to the high variability between replicates at the high rates of urine addition. The volatilisation losses from urine treated plots, as measured by the amount of ammonia trapped by the samplers, were much larger than from the control plots at both sites (Fig. 5.15).

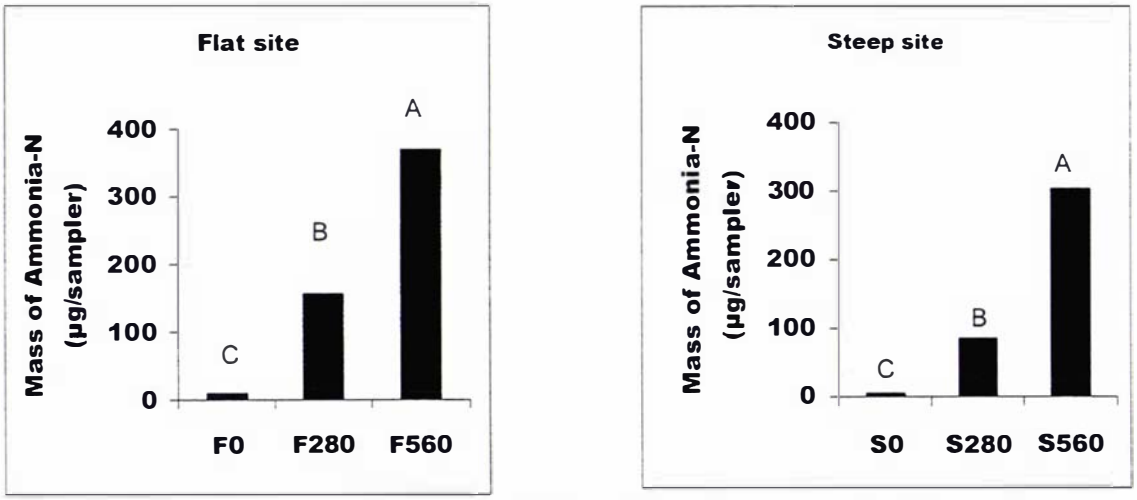


Fig. 5.15. Effect of urine treatments on NH_3 volatilisation during the first 6 days after urine application. Values with common upper case letters between treatments within same site do not differ at $P<0.05$.

The relationship described in Section 3.3.5 was used to gain some idea of the actual quantities of ammonia being lost through volatilisation during this experiment. The resulting estimates of volatilisation losses after urine application were very large, ranging from 24% to 51% of added urine N (Table 5.6).

Table 5.6 Quantities of NH_3 trapped by samplers and estimated losses of NH_3 by volatilisation.

Treatment	Measured ammonia in samplers μg NH_3-N/sampler	Estimated loss of ammonia through volatilisation kg NH_3-N/ha	% of added urine N
S0	4	3	-
S280	85	68	24%
S560	302	242	43%
F0	9	7	-
F280	156	125	42%
F560	369	295	51%

Although the amounts of urine N estimated to have been lost by volatilisation were very large, they may not be unreasonable. When these losses are added to the urine N recovered in soil at 3 DAUA (Table 5.7), the overall N recoveries were close to 100%.

Table 5.7 Amounts of urine N lost through NH_3 volatilisation and overall recovery of added urine N at 3 DAUA. # = data from Table 5.3

Treatment	NH_3 volatilisation kg NH_3 -N /ha	% added urine N	Urine N recovery in soil at 3 DAUA (%) #	Total N recovery at 3 DAUA (%)
F280	118	42	75	117
F560	288	51	49	100
S280	65	24	48	72
S560	239	43	59	102

5.3.10 Leaching

The change with time in the distribution of urine N down the 0-30 cm soil profile, shown in Table 5.2, suggests that the urine treatments may have increased N leaching. For example, the resin-adsorbed NO_3^--N in the 0-10 cm soil depth, in urine-treated plots at both sites decreased considerably between 30 and 45 DAUA (Fig. 5.6). This coincided with a period of high rainfall (Fig. 5.2), and at the same time in the F280 and F560 plots the 20-30 cm soil depth contained 7% and 8% of the added urine N respectively by day 45 (Table 5.3).

However, no direct measurements of nitrate leaching were made, so it was decided to develop a simple model as a Microsoft Excel worksheet to estimate NO_3^--N leaching during the experimental period, and to assess whether leaching could realistically account for the apparent loss of NO_3^--N from the soil profile.

5.3.10.1 Leaching model development

The leaching model required as inputs, the daily soil drainage (mm) and the daily soil NO_3^--N concentration (g/m^2) at each of the three depth intervals, 0-10, 10-20 and 20-30 cm.

Drainage was estimated using a daily water balance. The soil field capacity required for the water balance calculation had to be estimated as described below, because it was not measured during the experiment.

A considerable rainfall was received on the experimental site on 6 July 2000. Thus, it was assumed that the soil had drained to field capacity 3 days later on 9 July 2000. Therefore, the soil moisture content on 9 July was considered to be the soil field capacity at the experimental site. However, the soil moisture content at 9 July 2000 was not available, as the experiment started on 14 July 2000. To overcome this, the moisture content on 9 July was estimated as follows:

The gravimetric moisture content at the first sampling (3 DAUA) was converted to volumetric moisture content by multiplying by bulk density and dividing by the density

of water. Then the depth of soil water at 3 DAUA was obtained by multiplying the volumetric moisture content and the soil depth (100 mm). This value was put into the water balance as the depth of soil water on 17 July 2000. Then the depth of soil water was calculated backwards to earlier dates using rainfall (R) and evapotranspiration values. The water balances for the flat and steep sites are in Appendices 2.6 and 2.7.

The depths of soil water in the top 100 mm of soil on 9 July estimated from the water balance, were 48 mm and 38 mm on the flat and steep sites respectively.

Drainage was assumed to occur whenever the depth of soil water exceeded field capacity.

The model assumed piston flow of water, and that between days the water becomes effectively well mixed within each of the three soil depth intervals in the soil, i.e. the soil water within each depth interval has a uniform nitrate concentration.

Estimation of the daily soil NO_3^--N concentrations to input to the model was more difficult. This was because large quantities of NO_3^--N were being added to and removed from the system daily, by processes such as nitrification, plant uptake and immobilisation. It was not the intention of the simple leaching model to simulate these complex biological processes.

It was assumed that NO_3^--N additions to the system by mineralisation and nitrification, or losses by immobilisation and plant uptake, could only take place in the 0-10 cm soil depth. Thus, nitrate-N could only enter or leave the 10-20 and 20-30 cm soil depths by leaching. Actual measurements of soil NO_3^--N were then used to estimate the daily NO_3^--N levels in the 0-10 cm soil depth as follows.

Soil NO_3^--N extractable by 2 M KCl had been measured for all three depths on 3, 12, 27, 45, 66 and 88 DAUA. Resin-adsorbed NO_3^--N in the surface layer had been measured more frequently; generally with 2-4 measurements between each of the measurements of 2 M KCl -extractable NO_3^--N. Use was made of the linear relationships presented in Fig. 5.9, between 2 M KCl -extractable NO_3^--N and resin-adsorbed NO_3^--N, to estimate values for 2 M KCl -extractable NO_3^--N, in the 0-10 cm

soil depth, on the days when only the resin measurements had been made. This then gave actual or estimated values for 2 M KCl -extractable NO_3^--N in the 0-10 cm soil depth on 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 33, 36, 42, 45, 48, 55, 62, 66, 69, 76, 83 and 88 DAUA. Soil (0-10 cm) NO_3^--N levels in the intervening days were estimated by linear interpolation. The complete daily data set of soil (0-10 cm) NO_3^--N for the F560 treatment estimated in this way, is presented in Fig. 5.16.

The 2 M KCl -extractable NO_3^--N concentrations at 3 DAUA for the 10-20 and 20-30 cm soil depths were taken as the initial values for those depths. From then on the quantities of NO_3^--N in the lower two soil depths were calculated from the quantities of NO_3^--N entering and leaving each depth by leaching (Table 5.8).

Leaching of NO_3^--N from the depth interval n on day t [$L_{n(t)}$ g/m^2] was calculated as follows:

$$L_{n(t)} = N_{n(t)} \left[D_{(t)} / W \right] \qquad (5.1)$$

$N_{n(t)}$ = NO_3^--N concentration is at depth n on day t (g/m^2)

$D_{(t)}$ = drainage on day t (mm)

W = Water depth at field capacity

where n ranges from 1 to 3 corresponding to soil depths 0-10, 10-20 and 20-30 cm respectively and t ranges from 3 to 88.

The NO_3^--N concentration in the 10-20 cm and 20-30 cm depth intervals was calculated as follows:

If $D_{(t-1)} = 0$

$$N_{n\,(t)} = N_{n\,(t-1)} \qquad (5.2)$$

If $D_{(t-1)} > 0$

$$N_{n\,(t)} = N_{n\,(t-1)} + L_{n-1\,(t-1)} - L_{n\,(t-1)} \qquad (5.3)$$

Final leaching was estimated by summing the daily leaching from the 20-30 cm layer during the experimental period. This was called Model 1

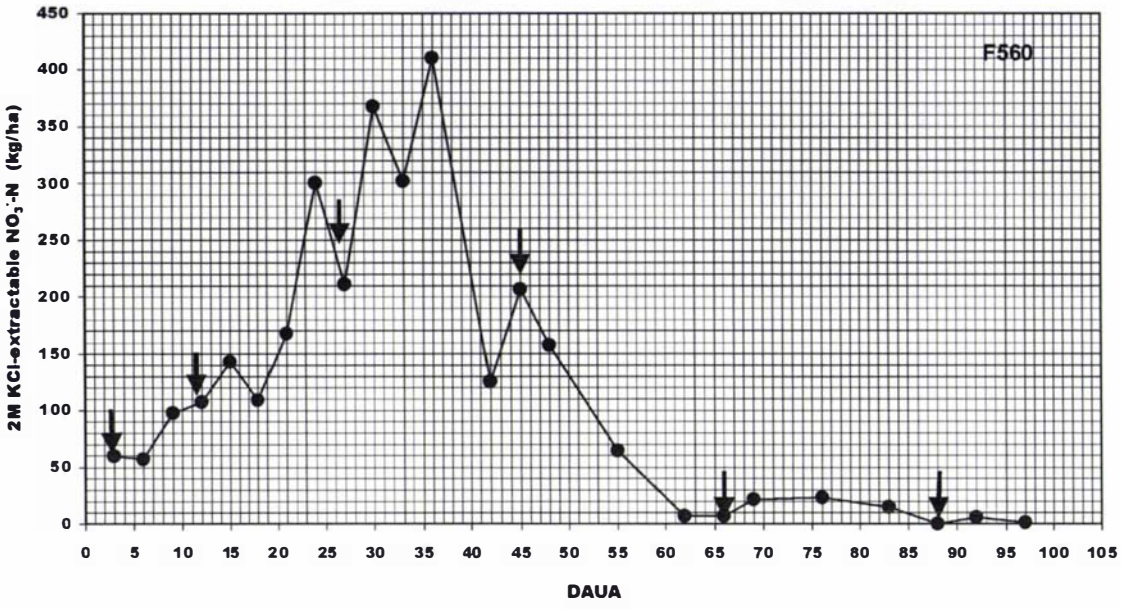


Fig. 5.16 Estimated and measured 2 M KCl -extractable NO_3^--N in the 0-10 cm soil depth during the experimental period. Arrows indicate measured 2 M KCl -extractable NO_3^- N. Other marked data points (•) are estimated 2 M KCl -extractable NO_3^--N values from the relationship with resin adsorbed NO_3^--N illustrated in Fig. 5.8.

Table 5.8 Example of leaching calculation by the model. Data extracted from leaching model of the F560 treatment.

Day	Drainage (mm)	N_1 (g/m^2)	L_1 (g/ m^2)	N_2 (g/m^2)	L_2 (g/ m^2)	N_3 (g/m^2)	L_3 (g/m^2)
6	0	5	0	3	0	2	0
7	10	5	**5 x (10/48)** =1.0	3	**3 x (10/48)** =0.7	2	**2x (10/48)** =0.4
8	3	7	**7x (3/48)** =0.4	**(3 + 1- 0.7)** = 3.3	**3 x (3/48)** = 0.2	**(2+0.7- 0.4)** =2.3	**2x (3/48)** = 0.13

As noted above, in Model 1, measured values of 2 M KCl -extractable NO_3^--N in the 10-20 and 20-30 cm soil depth at 3 DAUA were used to initialise the model and from then on daily NO_3^--N concentrations in the 10-20 and 20-30 cm soil depths were calculated from inputs and outputs to each depth by leaching. In fact, however, 2 M KCl -extractable NO_3^--N was measured at these depths on several occasions throughout

the trial. This therefore gave an opportunity to check the predictions of Model 1 against measured values.

First, Model 1 was run as described above using the inputs of daily NO_3^--N levels in 0-10 cm over the whole experimental period and soil NO_3^--N levels in 10-20 and 20-30 cm soil depths only at 3 DAUA. Then the predicted values of the NO_3^--N concentrations in the 10-20 and 20-30 cm soil depths at 3, 12, 27, 45, 66 and 88 DAUA were replaced in the model by the measured 2 M KCl -extractable NO_3^--N values on these days. Then the model was rerun. This second version of the model was termed Model 2. Finally, the outputs of the two models were compared.

5.3.10.2 Leaching model output

The simple model described in Section 5.3.10.1 suggested that substantial leaching of urine N as NO_3^--N during the experiment was likely. Predicted leaching during the experimental period using Model 1 (Table 5.9) was large in all treatments. The predicted leaching losses from urine-treated plots ranged from 130 to 320 kg N/ha, which is 38-48% of added urine N. In addition, the predicted N leaching from the flat site controls was 50 kg N/ha.

These predicted loses were large and when the predicted soil NO_3^--N concentrations in the 10-20 and 20-30 cm depths at 12, 27, 45, 66 and 88 DAUA were compared with the measured values of 2 M KCl -extractable NO_3^--N (Fig.5.17), it was apparent that Model 1 was overestimating the quantities of NO_3^--N at depth-particularly towards the end of the trial. This might then have led to overestimation of leaching levels by Model 1 (Table 5.9 and Fig. 5.18)

The overestimation of NO_3^--N levels at depth by the model probably resulted from the assumption that changes in the NO_3^--N concentrations in the 10-20 and 20-30 cm depth intervals could only occur through leaching. In reality, NO_3^--N could also have been lost from these depths by plant uptake, denitrification and immobilisation.

As described in section 5.3.10.1, Model 2 made use of measured values of soil NO_3^--N at the 0-10, 10-20, 20-30 cm soil depths where data were available. When the Model 2 was run the predicted leaching was markedly decreased (Table 5.9).

Table 5.9 Estimated leaching losses from urine treatments by the two models.

Treatment	Leaching kg NO_3^--N /ha Model 1	% of added urine (Treatment-control)/added N)	Leaching kg NO_3^--N /ha Model 2	% of added urine (Treatment-control) /added N)
F0	51	-	22	-
F280	157	38	83	21
F560	320	48	188	30
S0	25	-	22	-
S280	137	40	48	09
S560	267	43	207	33

Thus, in Model 2, updating of the NO_3^--N concentration by measured values at several times, may account for the influence of some of the other N transformations noted above. Because of this, Model 2 outputs are likely to be the closer to the actual amount of leaching. Although the model presented here makes many simplifying assumptions, it is clear that the potential for nitrate leaching is very high in these hill pasture urine patches. The predicted leaching losses from the urine treated plots by Model 2 ranged from 48 to 207 kg N/ha which is 9 to 33% of added urine N.

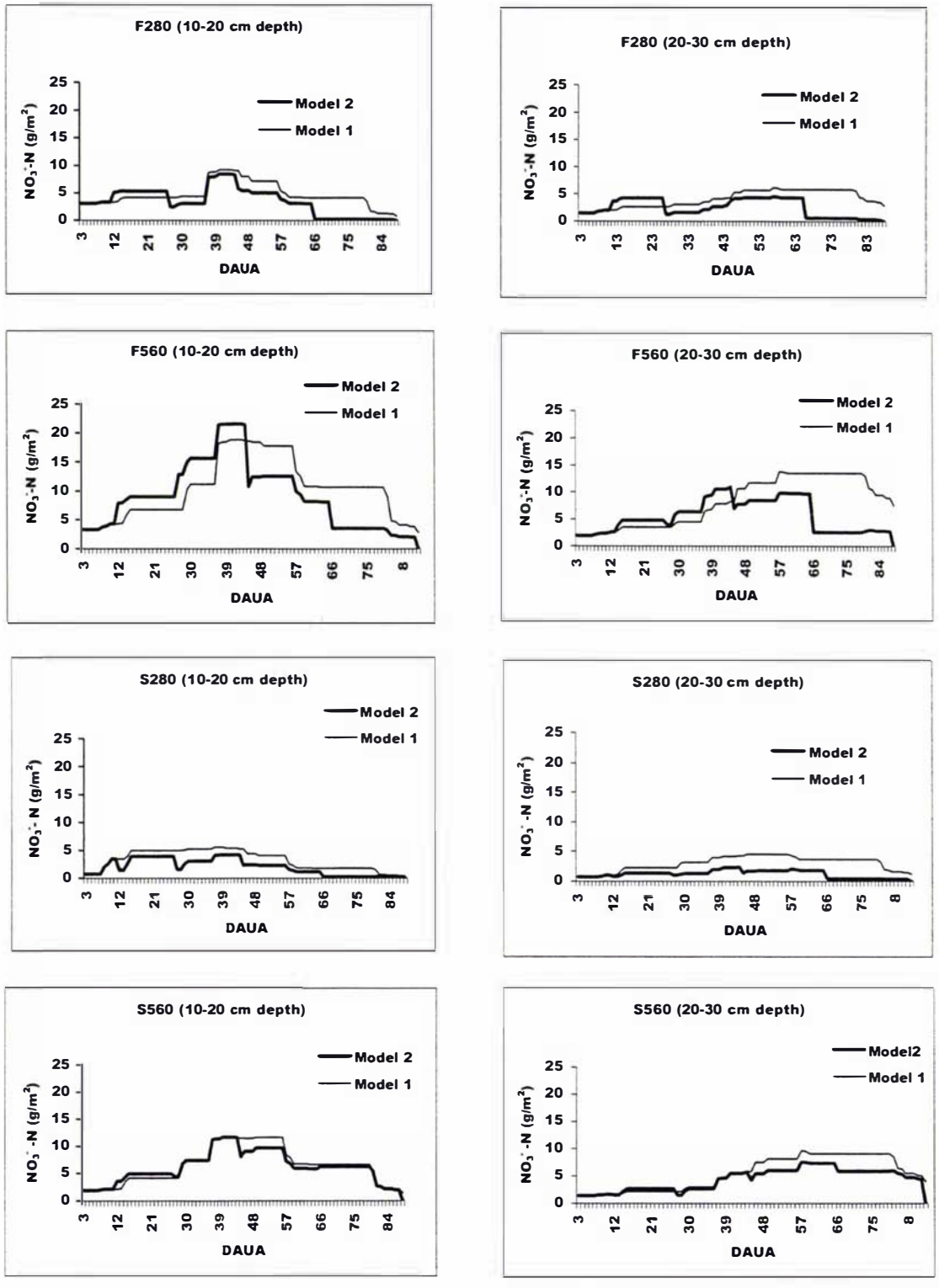


Fig. 5.17 Estimated quantities of soil NO_3^--N (g/m^2) in the 10-20 cm and 20-30 cm depths from the two models during the experimental period.

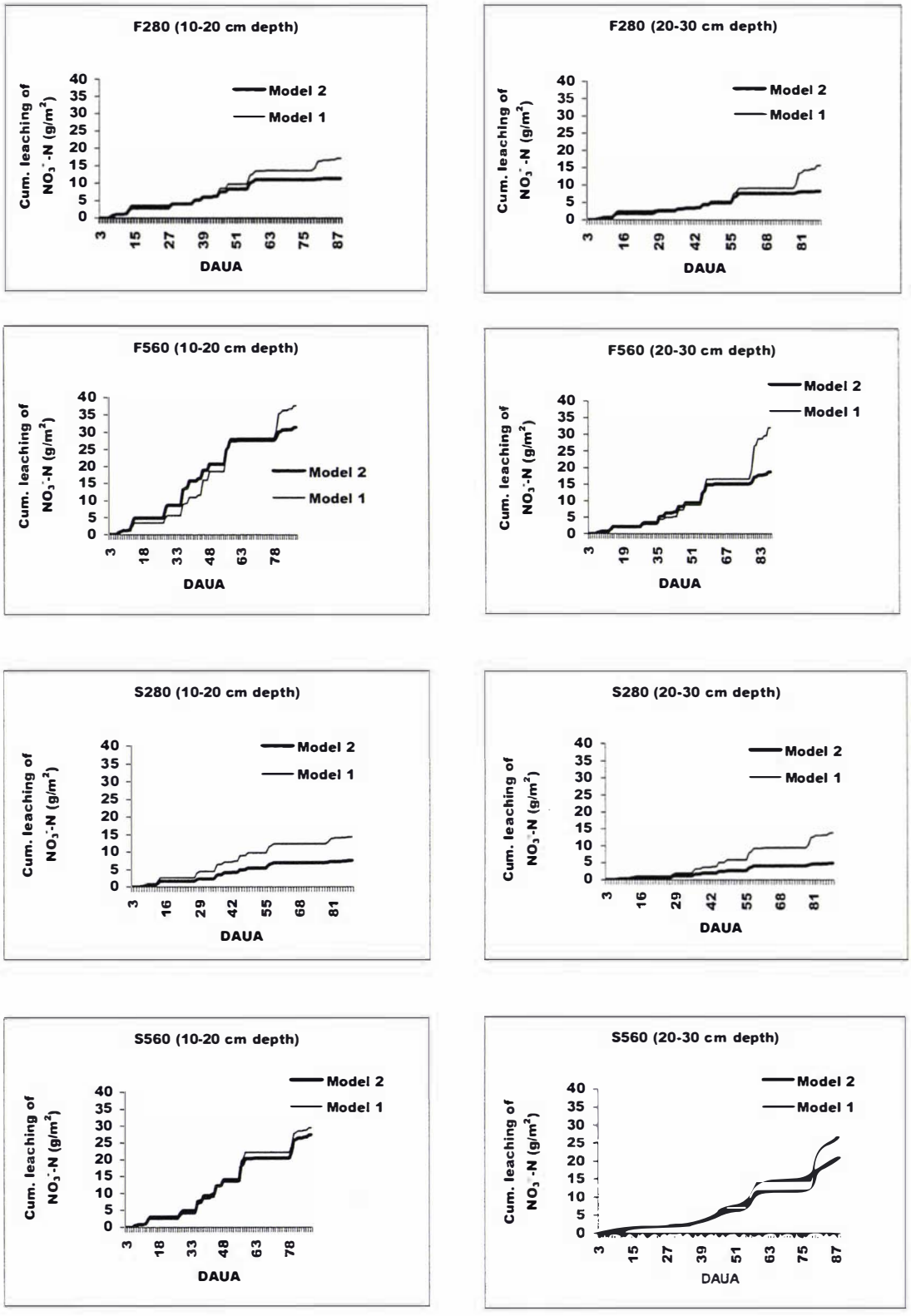


Fig. 5.18 Estimated cumulative leaching of NO_3^--N (g/m^2) from 10-20 cm and 20-30 cm soil depths from urine treatments from the two models during the experimental period.

5.3.11 Nitrification

In the Waipawa experiment described in Chapter 3, it appeared as if there was relatively little nitrification after urine application (Fig. 3.8). In contrast, in the current experiment there was active nitrification after urine application (Fig. 5.5 and 5.6).

The gross nitrification rate is the net rate of NO_3^--N accumulation plus the rate of NO_3^--N consumption. However, while the net rate of NO_3^--N accumulation in soils can be measured reasonably easily, it is very difficult to measure the rate of NO_3^--N consumption as it can be taken by plants and microbes or lost through denitrification and leaching. An attempt was made to obtain an approximate estimate for the nitrification rate in the current experiment by assuming that leaching was the major contributor to NO_3^--N loss/consumption. This leaching component was then estimated from the simple model described in the previous section.

Nitrification was calculated as follows:

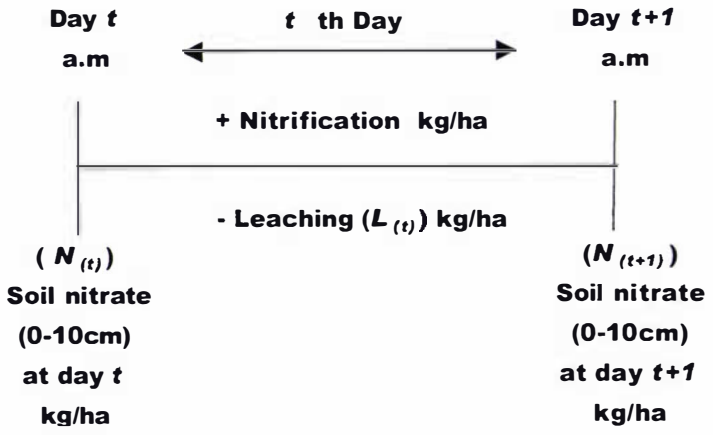


Fig. 5.19 Schematic diagram to illustrate nitrification rate calculation.

Daily NO_3^--N leaching values ($L_{(t)}$) and daily soil NO_3^--N ($N_{(t)}$) values in the 0-10 cm depth increment were obtained from the leaching model data. Daily nitrification rate was then estimated as follows:

Nitrification rate on t^{th} day (kg NO_3^-- N/ha/day) = $(N_{(t+1)}) - N_{(t)} + L_{(t)}$

Table 5.10 Example of nitrification calculation. Calculations up to day 8 are presented for the F560 treatment plots.

Day	NO_3^--N (0-10cm) kg/ha	Difference	Daily leaching (0-10cm) kg/ha	Daily nitrification kg/ha/day	Cumulative nitrification kg/ha
3	51.2	-0.6	0	-0.6	-0.6
4	50.6	-0.9	0	-0.9	-1.5
5	49.7	-0.6	0	-0.6	-2.1
6	49.1	2.3	0	2.3	0.2
7	51.4	21.5	10	31.5	31.7
8	72.9	10.8	5	15.8	47.5
9	83.7				

Cumulative daily nitrification plotted for all treatments is shown in Fig. 5.20. Very low cumulative nitrification was observed in the controls compared to urine-treated plots (Fig 5.20A). This is not unexpected, as after urine addition, and subsequent urea hydrolysis, large amounts of NH_4^+-N would have been present to provide a substrate for nitrifiers. The controls at the flat site had higher cumulative nitrification (6.8 kg NO_3^--N/ha) than control plots at the steep site (0.4 kg NO_3^--N/ha).

Similarly, higher and faster nitrification was observed in the flat site than the steep site in the 560 kg urine N/ha treatments (Fig. 5.20C). In the F560 treatment, cumulative nitrification at the end of the experiment was 321 kg NO_3^--N/ha. This is 56% of added urine N. In the S560 treatment, cumulative nitrification by the end of the experiment was 267 kg NO_3^--N/ha, which was 48% of added urine N.

When urine was applied at 280 kg N/ha, nitrification rates were similar at both the flat site and the steep sites, with 116 and 124 kg NO_3^--N/ha respectively being nitrified. This equated to 41 and 44% of added urine N respectively.

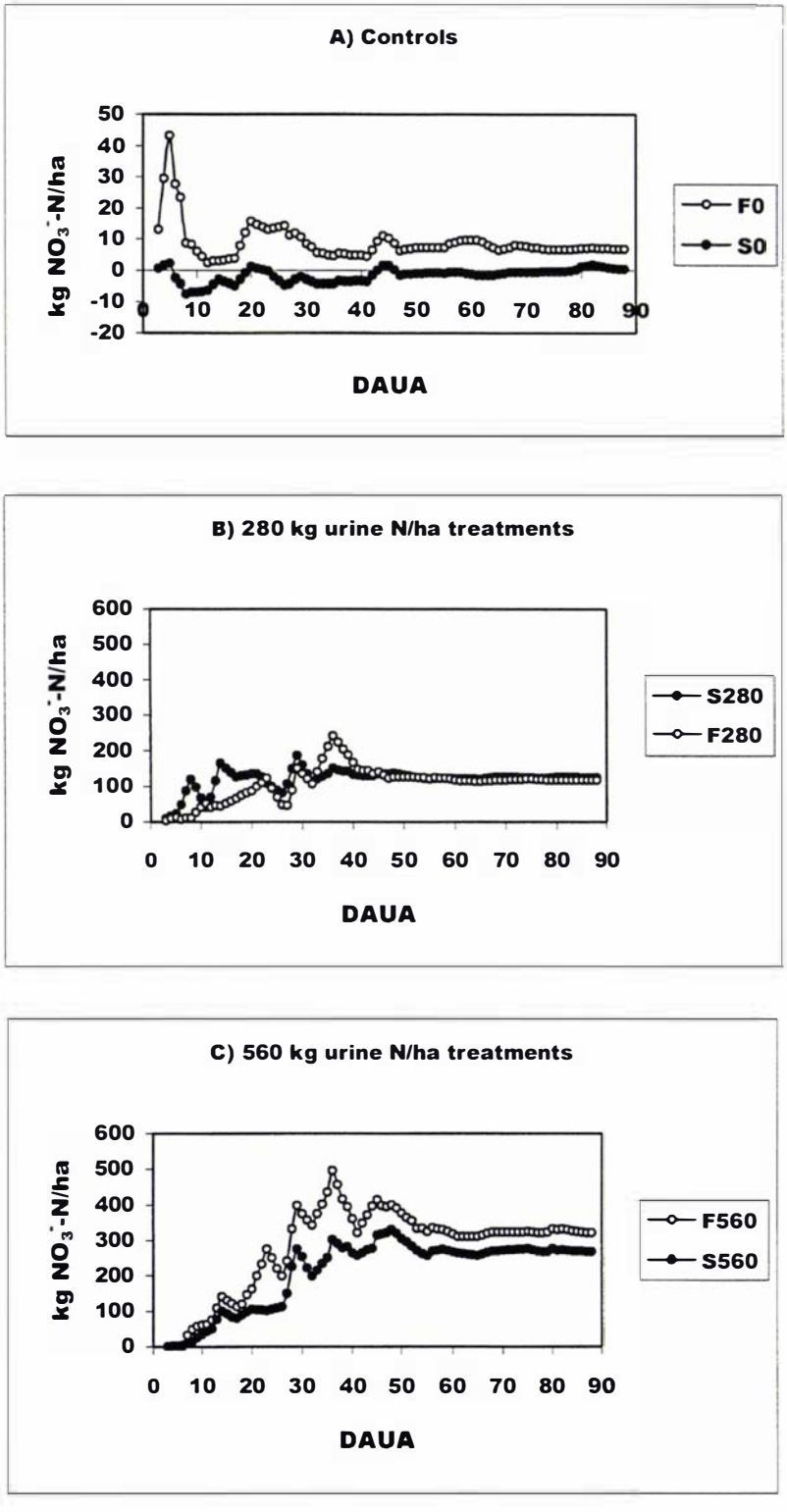


Fig. 5.20 Cumulative daily nitrification during the experimental period.

It was observed in Section 5.3.5 that when the levels of 2 M KCl - extractable NO_3^--N were at their maximum at both sites, they were more than three times as high in the 560 kg urine N/ha treatments as in the 280 kg N/ha urine treatment. A similar trend can be seen in the cumulative nitrification values at the flat site. The cumulative nitrification in the F560 treatment was 2.8 times higher than in the F280 treatment. In the S560 treatment, cumulative nitrification was 2.2 times higher than in the S280 treatment.

It can be seen in Fig. 5.20 that the apparent cumulative nitrification decreased with time on some occasions. This was not surprising as the nitrification calculation assumed that NO_3^--N could only be lost by leaching. In reality however, NO_3^- -N can be consumed by plants, microbes, and denitrification. Losses of NO_3^--N by these processes produced apparently negative nitrification rates.

The variation in daily nitrification rates during the experiment is illustrated by the frequency diagrams shown in Fig. 5.21. Only the nitrification rates up to 45 DAUA were considered for the histograms. This is because, following 45 DAUA, very low NH_4^+-N levels were observed in the soil (Fig. 5.4) and as a result nitrification rates would have been constrained by lack of substrate.

On most days, the daily nitrification was <5 kg NO_3^--N/ha/day in controls at both sites (Fig. 5.21A and 5.21B). In the 280 kg urine N/ha treatments, daily nitrification values ranged up to 45 kg NO_3^--N/ha/day at both sites (Fig. 5.21B and 5.21C). The most prominent differences between the two sites occurred in the daily nitrification values in the 560 kg urine N/ha treatments. For the S560 treatment, there were only 7 days nitrification rates were >20 kg NO_3^--N/ha/day, compared with 17 days for the F560 treatment.

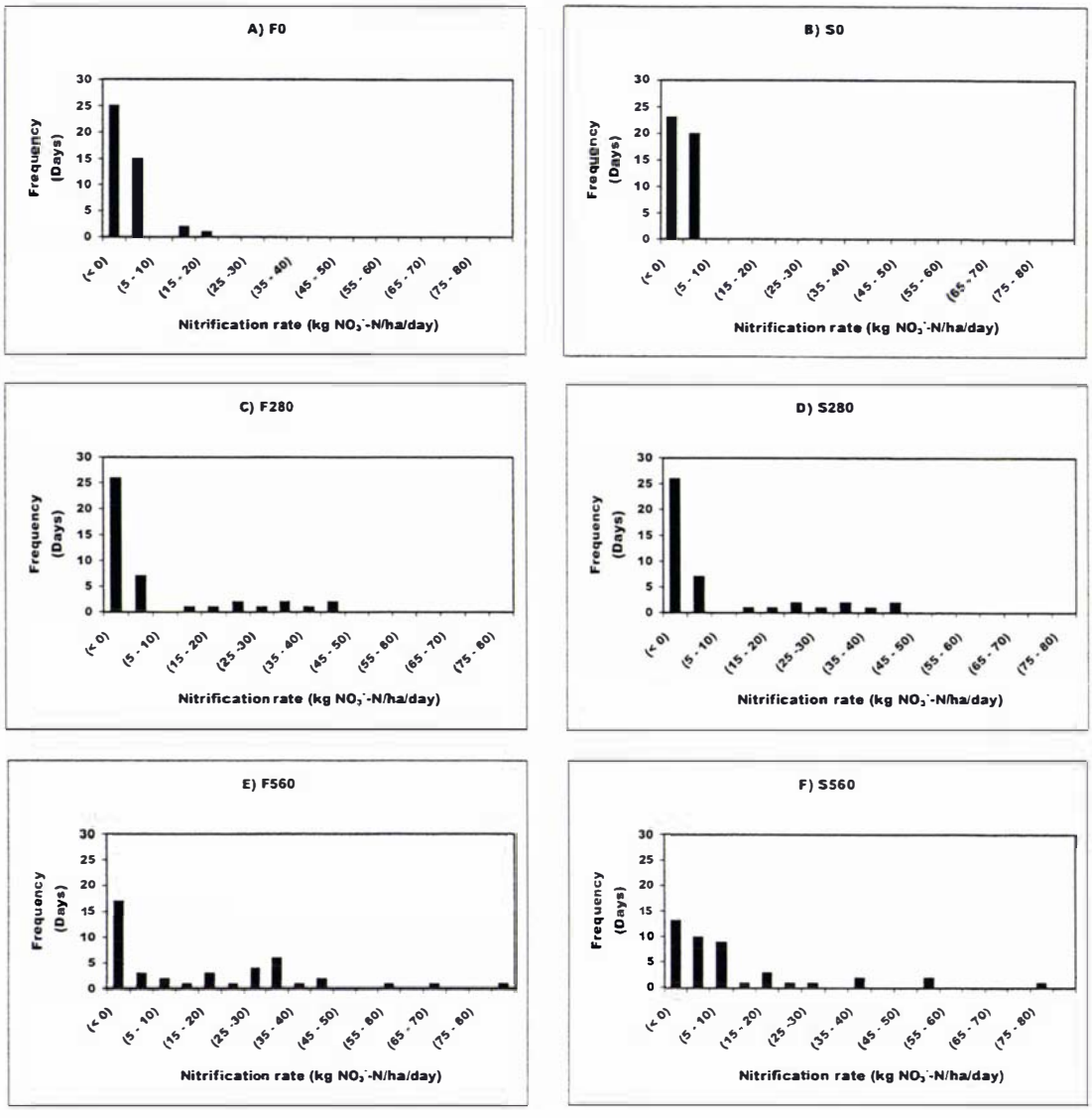


Fig. 5.21 Frequency distribution of daily nitrification rates calculated at each site for the period up to 45 DAUA.

5.4 Discussion

5.4.1 Urine N recovery

The apparent recovery of urine N in soil mineral N, ammonia volatilisation, leaching, and plant uptake, throughout the experiment is illustrated in Fig. 5.22. Immediately after urine application (3 DAUA), complete recoveries of added N were apparent in all treatments except in the S280 treatment. Thereafter, the recoveries at the flat site were more than 100% for some time but this was not apparent at the steep site. Urine N

recoveries decreased towards the end of the experiment. At the end of the experiment (88 DAUA), 80%, 91%, 45% and 79 % of added urine N had been recovered by the sum of soil mineral N, ammonia volatilisation, leaching, and plant uptake from the F280, F560, S280 and S560 treatments respectively.

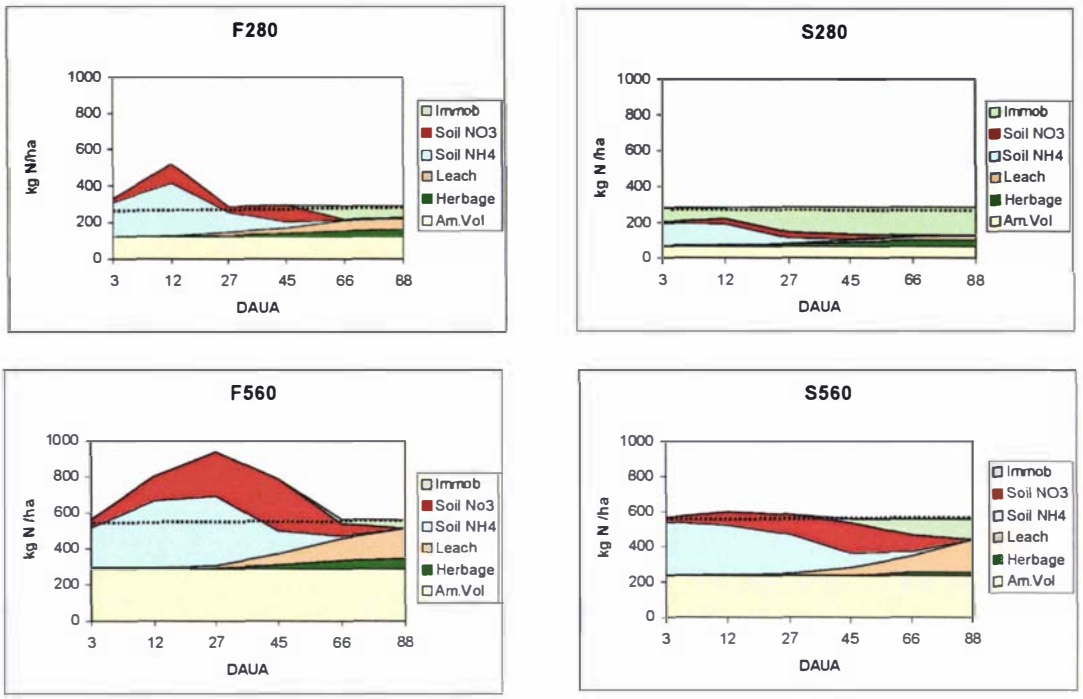


Fig. 5.22 Urine N recovery during the experimental period. The dotted line indicates the application rate.

The general pattern for the total recovery (Fig. 5.22) was different for the two sites and the two treatments. In the F560 treatment, total recovery was above 100% up to 27 DAUA and then decreased towards the end. In contrast to this, the urine N recovery in S560 treatment remained closer to 100% up to 27 DAUA then gradually decreased towards the end.

In the F280 treatment, recoveries were more than 100 %, but only up to 12 DAUA. In the S280 treatment recoveries were less than 100% throughout the experiment.

Urine N losses by ammonia volatilisation and leaching during the experiment period were large. The estimated combined urine N loss through ammonia volatilisation and

leaching by the end of the experiment ranged from 93 to 423 kg urine N/ha and 179 to 453 kg urine N/ha in steep and flat sites respectively. The urine N losses from ammonia volatilisation and leaching are discussed in detail later in Sections 5.4.4 and 5.4.6 respectively.

Urine N recoveries by herbage were low ranging from 1-14% of added urine N. This is also discussed in detail later in Section 5.4.7.

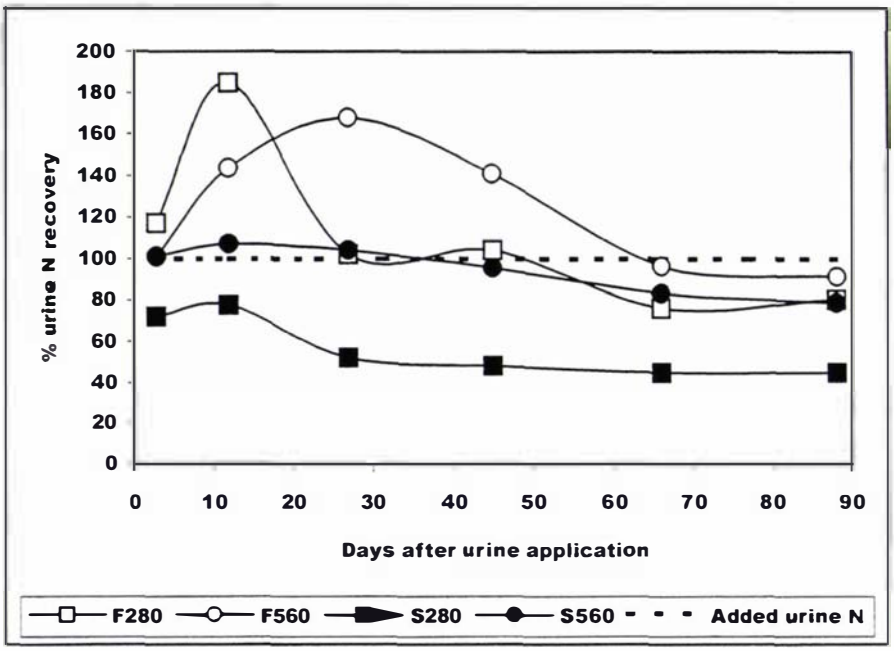


Fig. 5.23 Urine N recoveries (%) during the experimental period, estimated as the sum of soil mineral N, NH_3 volatilisation, plant uptake and leaching of NO_3^--N.

High urine N recoveries were observed in the F280, F560 and S560 treatments, particularly in the early stages (Fig. 5.23). Low urine N recoveries were observed in the S280 treatment throughout the experiment. In addition, lower recoveries were observed in the S560 treatment in the latter part of the experiment when compared to the F560 treatment.

It was assumed that urine N not recovered by soil mineral N, ammonia volatilisation, leaching and plant uptake during the experiment was immobilized to complex organic matter in the soil and converted to non-mobile N. Thus, according to Fig. 5.22, the

estimated immobilisation was larger and occurred earlier in the steep site than in the flat site. Also, immobilisation in the 280 kg urine N/ha treatment was higher than in the 560 kg urine N/ha treatment at both sites (Fig. 5.22). By the end of the trial at 88 DAUA the estimated percentages of added urine N that had been immobilised into soil organic matter were 24, 8, 57 and 21 for the F280, F560, S280 and S560 treatments respectively.

5.4.2 Mineral N

As with the experiment at Waipawa, described in Chapter 3, this experiment again demonstrated that increased soil mineral N levels would remain for the first 2 months after urine application. For example, by 66 DAUA, 81 and 118 kg urine N/ha were still present in soil in the mineral form, which was 21 and 29% of the added urine N in the S560 and F560 treatments respectively. However by the end of the experiment (88 DAUA), urine N recovery in the mineral form was very small, ranging from 0 to 3%.

During the first month after urine application, NH_4^+ was the dominant form of mineral N and during the second month NO_3^- was the dominant form. In contrast to the current experiment, NO_3^--N was not present in large quantities throughout the experiment described in Chapter 3, highlighting differences in soil nitrification activity between the soils of Waipawa (see Chapter 3) and Ballantrae.

A pasture response to urine N was observed only in the flat site, suggesting pasture growth was limited more by N at the flat site than the steep site. However, this was not reflected in the soil mineral N levels in the flat and steep site control plots. The resin adsorbed N levels during the experimental period in flat and steep site control plots (Fig. 5.24) indicated that soil mineral N levels were similar. Similarly, no differences in mineral N levels between control plots at flat and steep sites were observed in the Waipawa experiment described in Chapter 3.

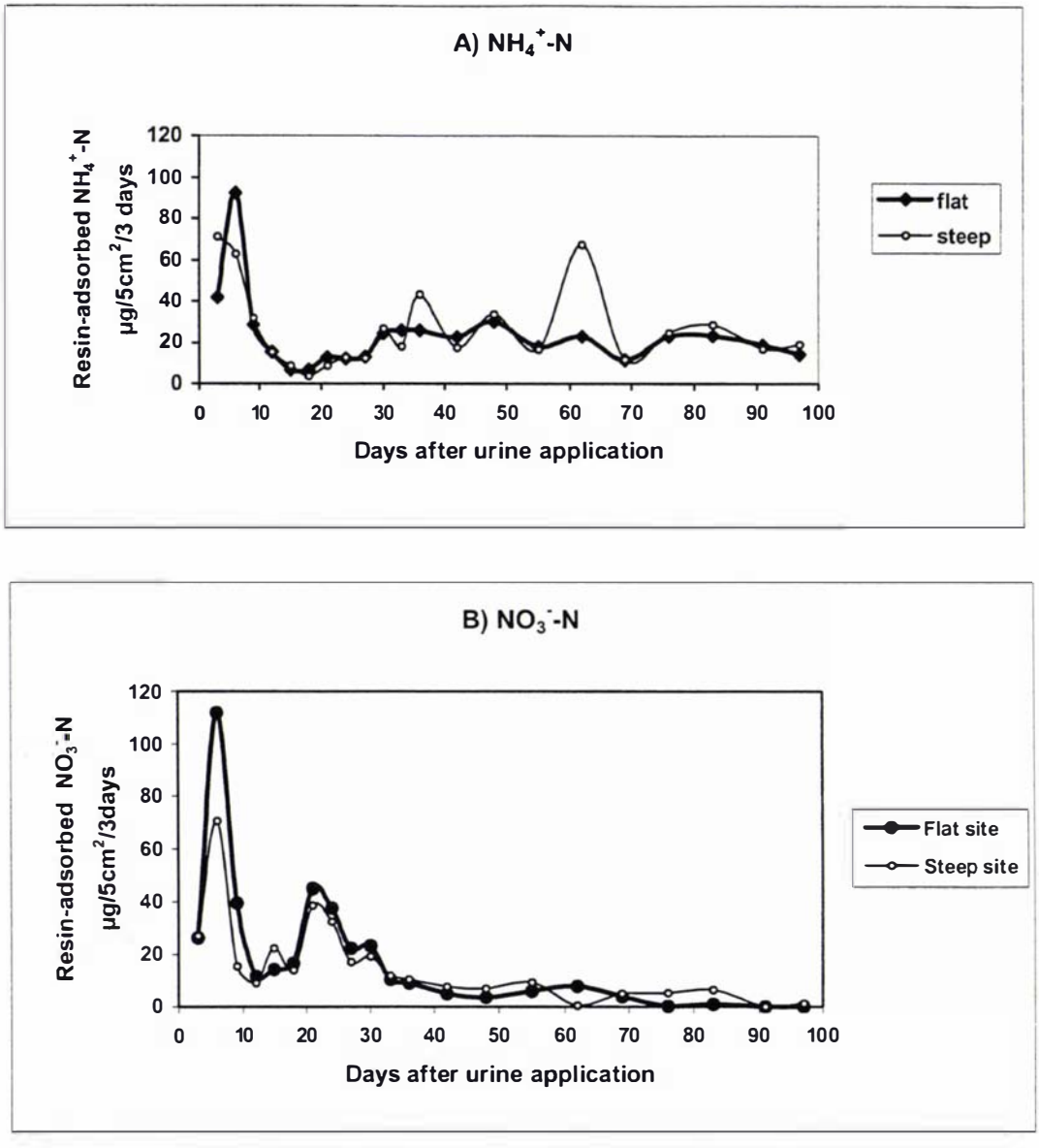


Fig. 5.24 Resin adsorbed NH_4^+-N (A) and NO_3^--N (B) levels during the experimental period in control treatments at both sites.

5.4.3 Priming effect

As noted in Section 5.4.1, urine N recoveries at the flat site were greater than 100% suggesting a priming effect after urine application. At the time of the maximum apparent priming effect (12 DAUA for F280 and 27 DAUA for F560), 237 and 379 kg N/ha in excess of that added in urine were recovered from the F280 and F560 treatments. These quantities of N are equivalent to 85 and 68 % of added urine N for

the F280 and F560 treatments respectively. Priming effects could be observed up to 27 and 45 DAUA for the F280 and F560 treatments respectively (Fig. 5.22).

It is interesting to note that the urine N recovery by soil mineral N alone could detect the priming effect. In the F280 treatment, at 12 DAUA, an additional 114 kg N more than the added urine N/ha was measured as soil mineral N. In the F560 treatment, at 27 DAUA, an additional 73 kg N more than the added urine N/ha was measured as soil mineral N

This suggests that the addition of urine induced soil N mineralisation. This was reinforced by the subsequent measurement of mineralisable N (Fig. 5.10 & 5.11). Mineralisable N levels in the urine treated plots were significantly decreased compared to controls. For example, at 27 DAUA, the mineralisable N in the F560 treatment had decreased by 124 kg N/ha from the levels in the control plots

As illustrated in Fig. 5.10 and 5.11, the mineralisable N levels at 3 DAUA in the 560 kg urine N/ha treatments at both sites had decreased significantly by 27 DAUA. In the F560 treatment, this decrease was 204 kg N/ha. This release of mineralisable N appeared to be reflected in an increase in soil mineral N from 3 to 27 DAUA (Fig. 5.11). In the F560 treatment the mineral N levels increased by 236 kg N/ha from 3-27 DAUA. The correspondence of decreases in mineralisable N and increases in mineral N are illustrated in Fig. 5.12.

Priming effects were not so prominent at the steep site, with an apparent excess recovery of only 39 kg N/ha over and above that added in urine to the S560 treatment. The greater priming effect on the flat sites indicates that there was a difference flat and steep sites in their mineralisation/immobilisation balance. Norton (1999) suggested that indicators of mineralisation/immobilisation turnover include the availability of substrate for decomposition and the C/N ratio of the substrate. Sakadevan (1991) observed higher mineralisation of N from soil samples taken from easy slopes than from medium slopes at a site adjacent to this experiment. This result was associated with the narrower C/N ratio in the soils from easy slopes. Further, Sakadevan (1991) commented that the narrower C/N ratio of soils taken from low slopes mainly results from the greater deposition of dung and urine on the low slopes.

However, the C/N ratios of the soils at the two sites in the current experiment do not differ very much. They are 12 and 14 for the 0-30 cm soil depth for the flat and steep sites respectively.

Several other studies (discussed in Section 3.2.3.6) have pointed out that stimulation of N mineralisation appears to be caused by added salt. After urine application, as urea hydrolysis proceeds, there is a rapid rise in soil pH in the urine patch. This could increase solubility of soil organic matter as well as increase NH_3 volatilisation. A large amount of NH_3 volatilisation after urine application appeared to occur in this experiment. Free NH_3 in the soil could perhaps have had a lethal effect on soil flora and fauna. Mineralisation of these dead materials could have increased the mineral N level in soil.

Further clarification of the reasons for the differences in priming effect between the two soils after urine application would be useful in future experiments.

5.4.4 Ammonia volatilisation

The predicted large ammonia volatilisation losses clearly indicated the importance of NH_3 volatilisation when studying N balances in urine patches, irrespective of the season. In an N balance study at Ballantrae in which volatilisation was not actually measured, Lambert *et al.* (1982a) used an estimate of 5% of excretal N for volatilisation losses. He argued that this low value was probably appropriate because the conditions at the site were unlikely to be conducive to volatilisation. However, results in this study have shown that there is a high potential for volatilisation even during mid winter. Ball and Keeney (1983) concluded that NH_3 volatilisation losses were 5% in winter, 16% in spring and 66% summer. However, Holland and During (1977) suggested that within the temperature range of 8-18° C, temperature does not have a large effect on volatilisation of ammonia.

The estimated volatilisation losses in the Waipawa experiment described in Chapter 3, were also relatively large compared to the quantity of the added urine N. Thus, both experiments consistently support the view that there is a high potential for volatilisation in urine patches in hill country even during mid winter.

5.4.5 Nitrification

Unlike the experiment described in Chapter 3, nitrification was active at both sites in this experiment. Carran *et al.* (1982), Haynes and Williams (1992) and Williams and Haynes (2000) have also reported active nitrification after urine application. The daily nitrification rate calculation using the leaching model data enabled a comparison of soil nitrification activities between sites. The soil at the flat site had a faster nitrification rate than the soil at the steep site. As nitrification is an important N transformation that governs N losses through leaching and denitrification, observed soil nitrification differences between the flat and steep sites need further clarification in future studies.

Steel *et al.* (1980) reported mean rates of nitrification under field conditions in Kiripaka silt loam of 0.053 μg N/g soil/h which is equivalent to 1.2 kg N/ha/day (assuming a bulk density of 1000 kg/m^3 and soil depth of 10 cm).

The daily nitrification values estimated for controls in the current experiment were reasonably in agreement with this value. However, the daily nitrification rates in urine-treated plots were much higher than this on most days. This reflects the high levels of NH_4^+-N in soil.

5.4.6 Leaching

The simple model used in this experiment suggested that significant leaching losses of NO_3^--N beyond 30 cm might have occurred - up to 30% of added urine N in some treatments. These predicted urine N losses by leaching were large compared to some previous studies.

Whitehead and Bristow (1990) measured a loss of 16% of added N below 30 cm from urine patch areas of pasture during a spring period in which exceptionally heavy rainfall was recorded. Williams and Haynes (1994) observed 11% of the ^{15}N from cattle urine patches leached below the 30 cm soil depth. Monaghan *et al.* (1989) estimated the N losses from urine patches after varying amounts of drainage through undisturbed soil monolith lysimeters. They observed that after 1 pore volume of drainage (136 mm) about 14 % of the applied urine N was leached below a depth of 340 mm.

Sakadevan *et al.* (1993) did not observe leaching of NO_3^--N after adding 280 kg N/ha as urine N in an experiment conducted on a low-slope site, described as low fertility, at Ballantrae AgResearch hill country research station. This site had received 156 kg single super phosphate (SSP)/ha/yr for 7 years and then 125 kg SSP /ha/yr for 8 years, but no Olsen P values were available to compare with the current study.

In contrast to the findings of Sakadevan *et a*l. (1993), estimates of leaching in the current study, at the equivalent application rate of 280 kg urine N/ha, were 21% and 9% of added urine N at the F280 and S280 sites respectively. These sites were classified as high fertility and had received 500 kg SSP/ha/year from 1973 to 1980 and 375 kg SSP/ha per year from 1981 to 1988 (Sakadevan and Hedley, 1993).

These results suggest that the potential for leaching in hill country is variable between sites. In large part, this variation of leaching loss appears to be related to nitrification activity, which in turn may be higher at high fertility sites.

In a typical hill country sheep farm, (stocking rate=14 su ha^{-1}, production = 63 kg wool and 180 kg meat/ha/yr) approximately 178 kg N/ha are recycled annually in urine (Haynes and Williams, 1993). As pointed out in the literature review, most of this N is accumulated in flat campsite areas due to sheep camping behaviour. Sakadeven *et. al.* (1993b) estimated, using the data of Gillingham *et al.* (1980), that 55% of urine was returned to low slope areas (0-12°). The leaching estimate for the F560 treatment in the current experiment was 30% of added urine N. If this figure was applied to all urine N deposited on low slope areas, approximately 29 kg N/ha ((178x 55%) x 30%) could be leached annually from the flat sheep campsites in hill country. Realistically however, extrapolation of the data from this study based on one urine application will be approximate at best since leaching losses of N from urine patches vary considerably throughout the year being highest in winter and practically non-exist in summer (Sherwood and Fanning, 1989). Nevertheless, this calculation suggests that leaching losses of N from hill country may be significant in terms of N likely to be added by N fixation.

In addition, the leaching model used in this experiment demonstrated the importance of measuring climatic data (e.g. rainfall, temperature, evapotranspiration, etc) when

studying N transformations. When such data are available simple models such as that used in this experiment may provide a cost effective way of assessing the likely significance of leaching losses in experiments of this type where it is difficult to measure leaching losses due to the technical difficulties in setting up lysimeters.

The resin technique was valuable in acquiring the daily soil NO_3^--N data in the 0-10 cm soil depth for the leaching model. Studies using resin spikes at different soil depths would also be useful to input daily soil NO_3^--N in 10-20 and 20-30 cm soil depths directly to the model

5.4.7 Pasture response

Over the whole experimental period, significant pasture responses to urine addition, were observed only in the flat site (Fig. 5.13 and 5.14). During the first pasture growth period no response to urine was observed in either site. The winter conditions that were not conducive to rapid pasture growth may have restricted pasture responses. The warmer spring conditions and N availability in urine treated plots would then have created suitable conditions for pasture response during the second and third harvest.

In the current experiment the pasture response was present up to 3 months from urine addition. Haynes and Williams (1993) also indicated that pasture response to added urine N normally lasts for 2 to 3 months. However, Sakadeven *et al.* (1993a) observed a statistically significant response ($P< 0.01$) for up to one-year (June 1990 to June 1991) after adding 280 kg urine N/ha to a low fertility low slope site at Ballantrae.

Urine N recovery by herbage in this experiment was low (1-14%) compared to the experiment described in Chapter 3 and some previous studies. Sakadeven *et al.* (1993a) recovered 19% of urine N added at 280 kg urine N/ha. Ball *et al.* (1979) recovered 22% and 37% of urine N applied at 300 and 600 kg urine N/ha respectively, in herbage within 53 days of application. Williams and Haynes (1994) recovered 19% of ^{15}N- urea labelled urine applied at 290 kg urine N/ha within 5 months after urine application.

The low urine N recovery by herbage in the current experiment was probably due to the high urine N losses by volatilisation and leaching. Sakadevan *et al.* (1993) did not

observe any leaching and consequently they measured relatively high urine N recovery in herbage for a longer period.

5.4.8 Denitrification

No direct observations were made to quantify denitrification. Although, theoretically, the potential for denitrification losses from grazed pastures is high (Ball and Ryden, 1984) due to the high levels of readily available C in surface soil, and the high concentrations of nitrate present in soil under urine patches, several studies in New Zealand have suggested that denitrification losses may be low. Luo *et al.* (2000) measured low denitrification losses (4-6 kg N/ha/yr) from a poorly drained soil on a dairy farm near Palmerston North. Carran *et al.* (1995) also observed very low N_2O emissions (0.5 kg N_2O-N/yr) from the same site as the current experiment and noted that nitrification or other transformations of urine-derived N did not appear to contribute to overall N_2O emissions in an important way at that site.

5.4.9 Immobilisation

As noted previously in Section 5.4.1, urine N recovery at the steep site was higher than at the flat site. The soil C/N ratio is normally used as an indicator of potential immobilisation. However in this case the soil C/N ratios were reasonably similar in both sites (see section 5.4.3). Deluca and Keeney (1993) suggested that total soil C/N ratios do not reflect the status of the internal N cycle and observed that soluble C to inorganic N ratios better reflected the condition of the N cycle. The ratios of soluble organic C to inorganic N in the 0-10 cm depth increment in the control plots of the current experiment were 6 and 15 for the flat and steep sites respectively. This suggests that at the steep site, there is a surplus of soluble organic C leading to a high potential for immobilisation of urine N.

Sakadevan *et al.* (1993) also suggested that the majority of added urine N might have been immobilised in soil, as the proportion of observed leaching was very low from an experiment conducted at a low fertility, low slope farmlet at same site. Williams and Haynes (1992, 1994) reported that significant proportions of urine-derived N are rapidly immobilised to soil organic forms by the active microbial biomass in pastoral soils.

5.5 Conclusions

Urine application markedly increased the soil mineral N availability, and a priming effect after urine application in flat campsites increased the soil mineral N availability still further.

The increased mineral N availability generally resulted in increased pasture growth however, the observed response was small and did not persist for a long period, indicating a high potential for N losses from the available pool in urine patches in hill country.

Ammonia volatilisation after urine application is a major N loss mechanism associated with hill country urine patches. Also, substantial N losses through leaching can occur in some areas in hill country pastures, especially in flat sheep campsites. The differential leaching potentials in different sites in hill country seem to be related to soil nitrification activity

Immobilisation of urine N was high in steep sites in hill country pasture soils. The influence of lower nitrification activity in steep sites might lead to low leaching, and increasing potential for immobilisation. In addition, high amounts of soluble C in steep hill soils could provide a high potential for immobilisation.

The resin spikes showed great potential for use as a N measuring technique. Their potential ability to monitor mineral N changes over time, ability to detect N fluxes in soil, and the ability to estimate daily N levels as inputs for leaching models, were highlighted in this experiment.

CHAPTER 6

LABORATORY INCUBATION STUDY OF NITROGEN TRANSFORMATIONS IN HILL COUNTRY AND LOWLAND PASTURE SOILS AFTER APPLICATION OF URINE

6.1 Introduction

It was clear from the experiments described in Chapters 3 and 5 that the N transformations in urine applied to hill country pasture soils are highly variable across the different sites and different topographic units. Nitrification after urine application was much higher in the Ballantrae experiment than in the Waipawa experiment. In addition, in the Ballantrae experiment, nitrification was higher in the campsites than in the steep sites. These variations led to differences in N leaching after urine application. The other important N transformation observed during the previous experiments was a priming effect after urine application. The observed priming effect was higher in the Ballantrae experiment than in the Waipawa experiment. In the Ballantrae experiment, the priming effect was more prominent in the flat campsite than in the steep site.

It is important to understand why these variations occur in order to improve our understanding of the N cycle in hill country pastoral soils. The previous two experiments were conducted at two different sites under different environmental conditions. Laboratory incubation provides a means to study N transformations in different soils under the same environmental conditions. This makes it easier to identify soil factors responsible for these variations.

The objective of this experiment was to study the N transformations after urine application to different soils collected from hill country. To provide greater contrast in soil properties, which might enable critical soil properties to be identified, a number of soils collected from highly fertile, lowland sites were also included in the study.

6.2 Materials and methods

6.2.1 Soils used for the incubation

Seven different soils were used in this experiment. Hill country soils were taken from the sites of the previous experiments conducted at Waipawa (Chapter 3) and Ballantrae (Chapter 5). From each of the sites, soils were collected from flat campsites and steep slopes. Two lowland soils (Kairanga Silt loam and Karapoti silt loam (both Fluvial Recent Soils)) were collected from ongoing experiments at AgResearch (Grasslands) Palmerston North. For each soil type, samples were taken from experimental plots that had received 1000 kg urine N/ha/year from November 1996 to August 2000. A further lowland soil (Manawatu sandy loam (Fluvial Recent Soil)) was collected from a paddock at Massey University's No.1 Dairy Farm. A summary of the soils used in the experiment is as follows.

1. Summer dry hill country (Waipawa). Flat site (WF)
2. Summer dry hill country (Waipawa). Steep site (WS)
3. Summer wet hill country (Ballantrae). Flat site (BF)
4. Summer wet hill country (Ballantrae). Steep site (BS)
5. Lowland soil with history of urine application (Kairanga silt loam) (KAI)
6. Lowland soil with history of urine application (Karapoti silt loam) (KAR)
7. Lowland soil from dairy farm (Manawatu sandy loam) (MD)

6.2.2 Experimental procedure

Bulk soil samples (10 kg) were collected from the 0-10 cm soil depth and brought from each site to the laboratory. Then herbage, stones, roots and other debris were removed. Soils were crushed by hand and mixed. A sub sample of each soil was used to determine soil moisture content by drying at 105^0C for 16 hours. A weight of field-moist soil, equivalent to 100 g of dry soil, was put in each of 36 small plastic cups, for each soil type. All soil-filled cups were covered by a plastic sheet to prevent moisture loss. These cups were then aerobically incubated at room temperature for 14 days. After 14 days, 6 mL of cattle urine was added to 18 cups of each soil type. This urine was collected from four cows during milking two weeks before the experiment and

frozen until required. For urine addition, soil was removed from the cup, spread in a small tray and mixed with the 6 mL of urine uniformly. Then the soil was replaced in the cup.The rest of the 18 cups were used as controls. No solution was added to the control cups. However, soil in the control cups was also removed from the cup, spread in a small tray, mixed and the cups refilled.

The application rate of 6 mL of urine/100 g dry soil (40 mg urine N/100 g dry soil) was chosen based on the approximate N content of the 560 kg urine N/ha plots 4 DAUA in the Ballantrae experiment (Chapter 5) and the N concentration (0.7%) of the cattle urine used in this experiment

Immediately after urine application, 6 cups (3 urine treated and 3 control) were randomly identified from each soil type for the first sampling to take place 3 DAUA. A KCl -saturated resin spike (see Chapter 4) was buried in each of these cups. These resin spikes remained in the soils for 3 days as described in Section 5.2.7. In addition, immediately after urine addition cylindrical polycarbonate vials to measure ammonia volatilisation (see Section 3.3.5) were placed in each of the cups identified for the first sampling.

Sampling days during the experiment were 3, 9, 15, 21, 28 and 45 DAUA. Three days before each sampling day KCl-saturated resin spikes were buried in the cups identified for the next sampling

At the first sampling (3 DAUA), ammonia samplers were removed, 10 mL of deionised water was added and NH_3 volatilised was measured as described in Chapter 3.

At each sampling day, 3 urine-treated and 3 control soil cups were sampled. From each cup

- resin spikes were removed from soil, shaken with 25 mL of 2 M KCl and extracts were analysed for resin adsorbed NH_4^+-N and NO_3^--N (Section 6.2.3.1).
- 35 g of soil was weighed into a 200 mL centrifuge bottle, 100 mL of 0.5 M K_2SO_4 was added, shaken for 30 minutes, filtered through "Whatman 42" filter paper and the extracts analysed for NH_4^+-N, NO_3^--N (Section 6.2.3.1), total dissolved nitrogen and dissolved organic carbon (Section 6.2.3.2 and 3)

- another 35g of soil was weighed into a 50 mL beaker and fumigated with $CHCl_3$ as described in Vance *et al.* (1987). Then the soil was transferred to a 200 mL centrifuge bottle and 100 mL of 0.5 M K_2SO_4 was added, shaken for 30 minutes and the extracts were analysed for total dissolved nitrogen and dissolved organic carbon (as above).
- 5g of soil was weighed into a 50 mL centrifuge tube, 20 mL of distilled water was added and the soil anaerobically incubated at 30° C for 2 weeks, to measure the mineralisable N content as described in Section 3.2.4.
- a sub sample of soil was used for moisture determination by drying at 105^0C for 16 hours.

6.2.3 Chemical analysis

6.2.3.1 Mineral nitrogen (NH_4^+-N and NO_3^--N)

The NH_4^+-N and NO_3^--N contents of 2 M KCl and 0.5M K_2SO_4 extracts were analysed colorimetrically using a Technicon auto analyser (Searle, 1975; Blakemore *et al.*, 1987)

6.2.3.2 Total dissolved nitrogen

Total dissolved nitrogen was determined as described in Section 5.2.6 from the 0.5M K_2SO_4 extracts of fumigated and non-fumigated soils.

6.2.3.3 Dissolved organic carbon

Dissolved organic carbon was determined from the 0.5M K_2SO_4 extracts of fumigated and non-fumigated soils as described in Section 5.2.6. In this experiment, instead of titrating with ferrous ammonium sulphate, a colorimetric procedure was used. After chromic-sulfuric acid digestion, the dissolved C was determined by the intensity of green colour in the solution at 600 nm wavelength (Heanes, 1984). Glucose solutions were used as C standards.

6.2.3.4 Microbial carbon

Microbial biomass carbon was estimated using the equation of Vance *et al.* (1987)

$$\text{Biomass C} = 2.64\ E_C$$

where Ec = the difference in dissolved organic carbon extracted by 0.5M K_2SO_4 from fumigated and non-fumigated soil.

6.2.3.5 Microbial nitrogen

Microbial biomass nitrogen was estimated using the equation of Brookes *et al.* (1985)

$$\text{Biomass N} = 1.85\ E_N$$

where E_N = the difference in total dissolved nitrogen extracted by 0.5M K_2SO_4 from fumigated and non-fumigated soils.

6.2.3.6 Total carbon and total nitrogen in soil

Total C and N contents of control soils were determined by combustion using a Leco FP-2000 CNS analyser.

6.2.3.7 Hot water soluble carbon

Field moist samples of control soils were sent to AgResearch, Ruakura Research Centre, Hamilton to measure the hot water soluble carbon content (Ghani *et al.*, 1999).

6.2.3.8 Clay fixed nitrogen

Clay fixed N was determined only on Karapoti soils sampled at 45 DAUA, to check the extent of NH_4^+-N fixation to clay minerals after urine application. Air-dried, finely

ground (< 150 μm) 1g soil samples were taken for the analysis from three urine treated cups and three control cups. The analytical procedure followed was that of Silva and Bremner (1966). Analysis includes treatment with alkaline KOBr followed by washing with KCl and decomposition of minerals containing fixed NH_4^+ ions with HF-HCl solution. The NH_4^+ ions released were determined by collection and titration after steam distillation of the soil acid mixture.

6.2.4 Statistical Analysis

Analysis of variance was carried out using SAS for Windows version 8. Data were analysed using a repeated measures model in mixed procedure (Littell, 1998) to examine and compare response trends over time. Autoregressive co-variance structure was used in the model. A Least Mean Square method at the 5% significant level was used to compare the means.

6.3 Results

6.3.1 Organic matter quality of tested soils

The major objective of this experiment was to further study the nitrification and priming effects observed after urine application in the previous experiments described in Chapters 3 and 5. The results observed in the previous chapters seemed to have a relationship with soil fertility and organic matter quality.

Sparling and Schipper (1999) identified total carbon (TC), total nitrogen (TN), soil microbial biomass (SMB), and anaerobically mineralisable N (AMN) as useful parameters to characterise soil quality. Haynes (2000) also suggested that labile organic matter, such as dissolved organic C (DOC) and soil microbial biomass were good indicators of soil organic matter quality.

The soil organic matter properties measured in this experiment are illustrated in Fig. 6.1, 6.2 and 6.3. Relationships between different soil quality parameters are illustrated in Fig. 6.4. The values for DOC, SMB-C, SMB-N, total mineral N (TMN), and AMN were obtained from the grand mean of all sampling days for control soils. These

properties in controls were relatively constant throughout the experiment (data will be presented in following sections). The values for TC, TN, and hot water carbon (HWC) were analysed only once, from control soils collected before the experiment.

The TC levels of tested soils were arranged in descending order from the left in Fig. 6.1A. To facilitate the comparison of trends in soil properties the same order of soils was continued in all the other graphs illustrated in this section.

Total C levels in the soils collected from hill country (BS, WF, BF, WS) were higher than the soils collected from flat land (MD, KAR, KAI) (Fig. 6.1A). This is not a surprise, as other studies have also indicated the presence of a large pool of partially decomposed organic residues in hill soils (Ball *et al.*, 1982). In developed flatland, most of the organic material is decomposed rapidly by active microrganisms. The higher ratio of SMB-C to TC in flat soils than in hill soils (Fig. 6.1E) supports this view.

The order of soils according to the TC levels was generally followed by the various measures of labile organic C (Fig. 6.1B, 6.1C, 6.1D). HWC level in the WS soil was an exception to this trend

It is interesting to note that the Ballantrae soils (BF and BS) have the highest levels of DOC, SMB-C and HWC (Fig. 6.1). Within Ballantrae, these labile organic matter levels were higher in flat campsites (BF) compared to the steep slopes (BS). This is mainly due to the high dung and urine return to the flat campsites.

The KAI and KAR soils had low concentrations of labile organic matter (DOC, SMB-C, HWC). The KAR and KAI soils were collected from experimental plots that had received 1000 kg urine N/ha for each of the last five years. As observed in previous chapters (3 and 5), a priming effect after urine application might have resulted in the low levels of easily decomposable organic matter in KAR and KAI soils. The labile organic fraction is the main energy source for soil microorganisms and it is a primary source of mineralisable N (Haynes, 2000). The KAR and KAI soils had lower SMB-C (Fig. 6.1C) and mineralisable N levels (Fig. 6.2D) compared to the other soils used in the experiment.

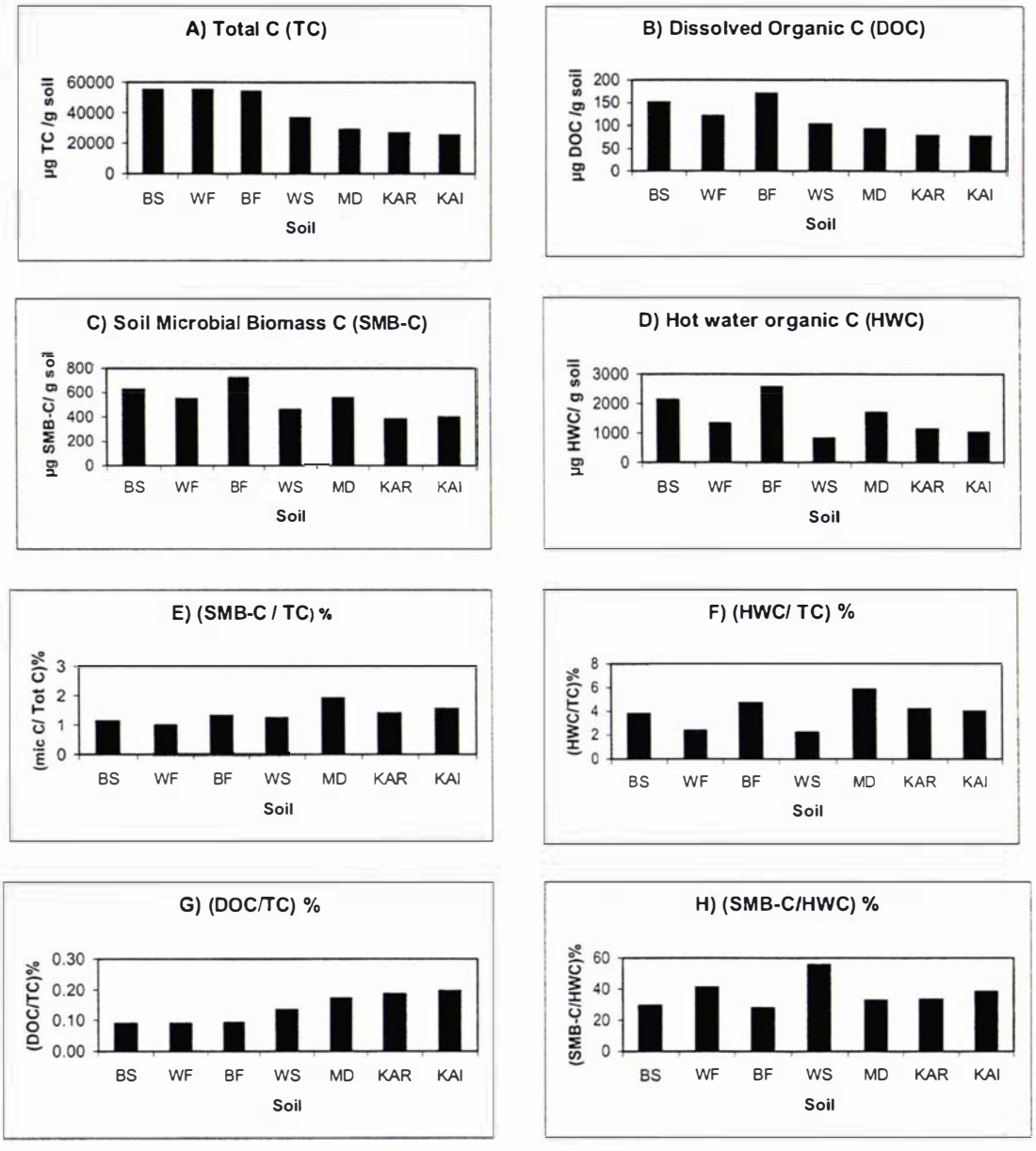


Fig. 6.1 Soil carbon related organic matter properties studied during the experiment.

Ballantrae hill country soils (BF, BS) contained higher HWC than the soil collected from Massey University's No. 1 Dairy Farm (MD). Ghani *et al.* (2000) also observed a lower level of HWC in intensively managed dairy soils compared with extensively managed sheep grazed pastures. Further, they commented that long-term N application reduced the HWC significantly. As noted above the KAR and KAI soils that were collected from experimental plots that had received large amounts of urine N over the last five years had the lowest HWC levels compared to the other soils.

When the ratio of labile organic C to TC is considered, the order of soils was opposite to the order of absolute levels of labile organic C (Fig. 6.1E, 6.1F, 6.1G). A higher proportion of the TC pool was present as labile organic C in soils collected from flatland, than in the soils collected from hill country. As noted above, this appears to be related to higher microbial activity in flatland soils than in hill soils.

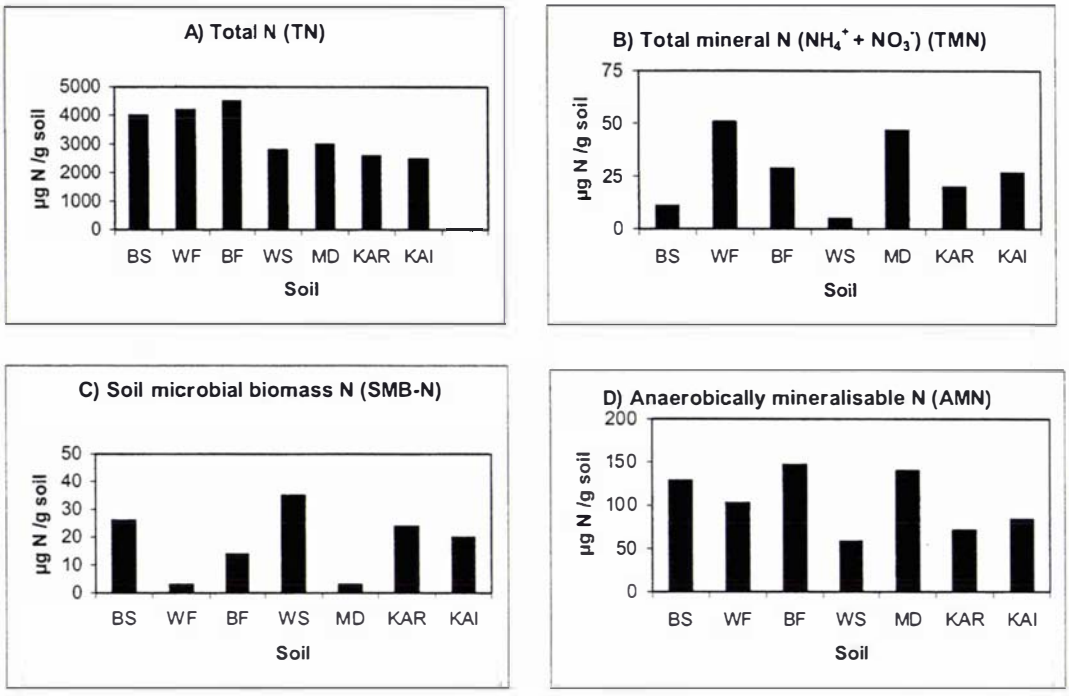


Fig. 6.2 Nitrogen related organic matter properties studied during the experiment.

The order of soils according to the TN levels (Fig. 6.2A) shows that the soils collected from hill country, except WS, contained higher levels of TN than the soils collected from flatland. The TN level of WS was similar to the TN levels of soils collected from flatlands. It might be expected that the flatland soils would have high TN levels as these soils were collected from a shelter belt area of a dairy paddock or experimental plots that had received urine N regularly over a number of years. Substantial N losses occurring through ammonia volatilisation, leaching, denitrification and plant uptake might have caused the lower levels of TN in these flatland soils. Although these losses were also observed in hill soils in previous chapters, the TN levels remain higher than the flatland soils - supporting the view, that N is conserved in hill soils more effectively (Sakadevan *et al.*, 1993).

Among the soils collected from hill country, mineral N levels were higher in flat campsites than steep sites. This was not evident in the previous field experiments described in Chapters 3 and 5, although the soils were taken from similar sites. As noted in the literature, higher soil N levels are due to N transfer to camp areas through urine and dune.

Surprisingly, the SMB-N was higher in soils collected from steep hill country (BS, WS) than from flat campsites (BF, WF) and flatland soils.

The ratio between carbon and nitrogen (C/N) has widely been used to study N availability in different soil systems. Soils collected from hill country had higher C/N ratios (12-14) than the flatland soils (10). Although the soils collected from hill country had higher TN than soils collected from flatland, the large pool of partially decomposed organic residues resulted in higher C/N ratios (Fig. 6.1) in hill soils than flat soils. Ball *et al.* (1982) reported that many top soils in the hill country of the lower North Island contain very large quantities of nitrogen, rendered largely unavailable by the relatively wide C/N ratio of the soil organic matter present.

It was clear from the literature review that hill country steep soils and hill country flat campsites are fundamentally different in how they cycle N. However, the observed soil C/N ratios do not reflect these differences. As noted in Section 5.4.9, Deluca and Keeney (1993) suggested that total soil C/N ratios do not properly reflect the status of the internal N cycle, and pointed out that the ratio of soluble C to inorganic N is a better option. Hill country steep soils (BS and WS) had markedly higher ratios of dissolved organic C to mineral N than other soils (Fig. 6.1). This indicated that there was a surplus of DOC, well above the levels of inorganic N in these soils.

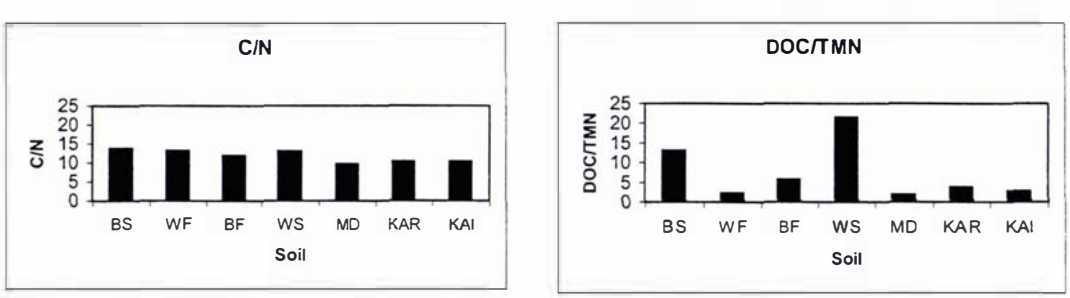


Fig. 6.3 Soil carbon to nitrogen ratios in experimental soil.

In order to identify the relationships between the various organic matter characteristics regression relationships were developed using the data in Figs. 6.1, 6.2 and 6.3. (Fig. 6.4).

The labile organic C, assessed by DOC, SMB-C and HWC was positively related to the total C (R^2 = 0.8, 0.6, 0.4. for DOC, MBC, and HWC respectively). This suggests that the total C content was a major determinant of the quantity of labile organic matter present.

There was a strong negative relationship between the ratio of SMB-C/TC and the C/N ratio (Fig 6.4 J). These two parameters could both be considered indicators of organic matter quality.

The HWC was strongly related to DOC, SMB-C and AMN (Fig. 6.4 D-F with R^2 values of approximately 0.8 in each case). Ghani *et al.* (2000) also observed strong relationships between HWC and both microbial C and mineralisable N.

Mineralisable N was positively related to the labile organic matter fractions of DOC, HWC and SMB-C (Fig. 6.4 G, F and L).

Soil microbial biomass plays a dual role in the soil, as an agent of decomposition and release of N from fresh organic residues and soil organic matter and secondly, as a pool of labile soil N. SMB-C and AMN showed a strong (R^2=0.7) positive relationship (Fig. 6.4 L) supporting the view that the microbial population plays an important role in decomposition and release of N from soil organic matter. Surprisingly, the SMB-N and AMN were negatively related, which questions the view of microbial biomass N as a labile pool of soil N.

It is interesting to note that a strong negative relationship was observed between total mineral N (TMN) and soil microbial biomass N (SMB-N) (Fig. 6.4 H).

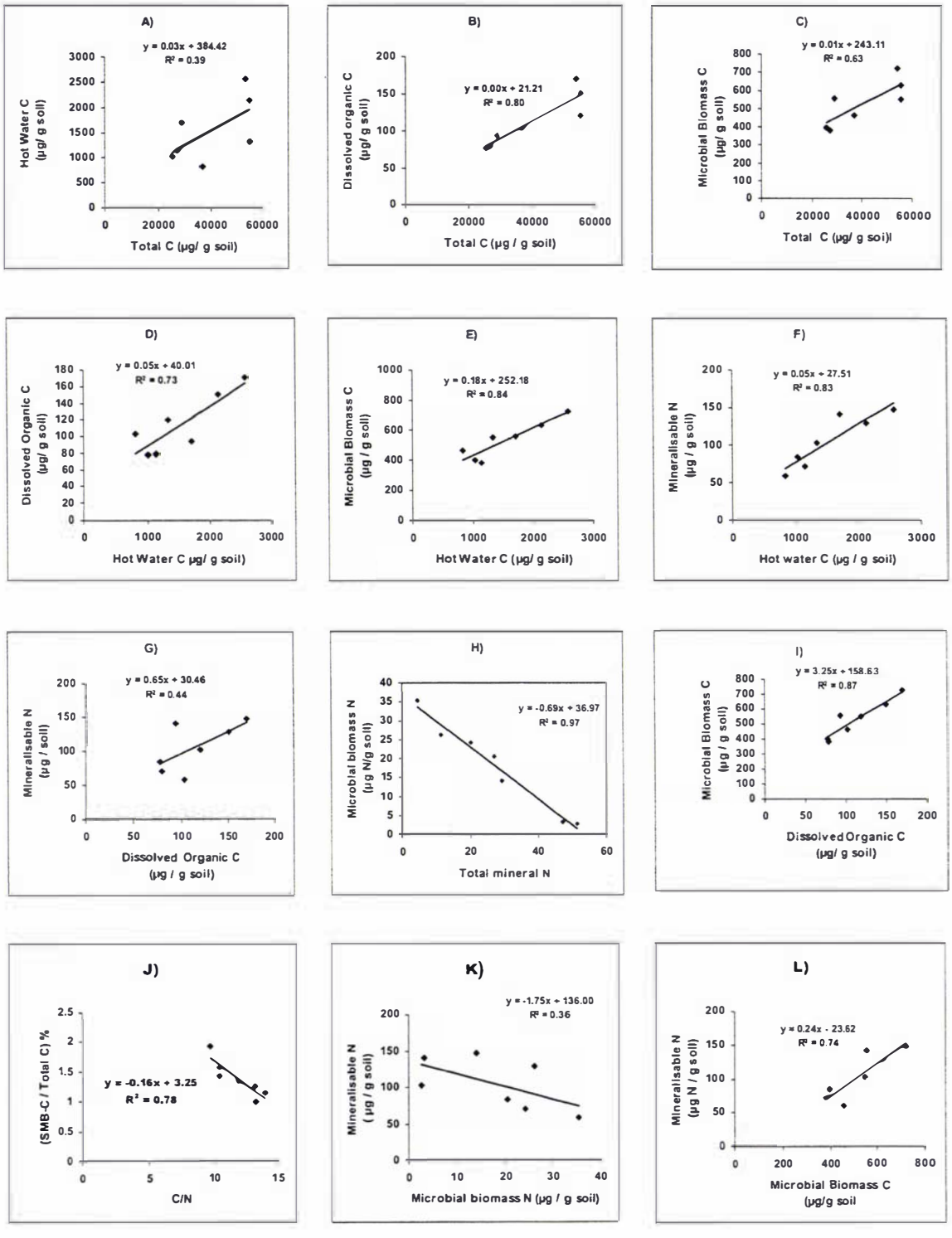


Fig. 6.4 Relationships between organic matter quality parameters.

6.3.2 Mineral N

As noted in previous chapters, mineral N comprises NH_4^+-N and NO_3^--N. The changes in the relative quantities of NH_4^+-N and NO_3^--N after urine application are discussed in this section.

Mineral N changes during the experimental period in urine treated and control pots are illustrated in Fig. 6.5 and the recovery of added urine N at the beginning and end of the experiment is illustrated in Fig. 6.6.

Not surprisingly, as seen in previous chapters, urine application significantly ($P< 0.05$) increased the mineral N levels in all soils (Fig. 6.5 & 6.6). However, the persistence of the elevated mineral N levels in urine treated soils with time was very different to the patterns observed in the field experiments described in previous chapters. In the field experiments, close to 100% of added urine N could be recovered as mineral N immediately after urine application. Thereafter, mineral N levels decreased rapidly with time.

In contrast, in the current incubation experiment, at the first sampling mineral N could only account for only 64%-81% of added urine N. Urine N present as soil mineral N at 3 DAUA was slightly higher in hill soils, ranging from 68% to 81% than in the lowland soils which ranged from 64% to 74%.

The mineral N levels of urine treated soils collected from hill country remained relatively constant from 3 DAUA until the end of the experiment at 45 DAUA (Fig. 6.5). In contrast the mineral N levels of urine treated soils collected from flatland increased significantly ($P<0.05$) from 3 to 45 DAUA (Fig. 6.5). At the last sampling (45 DAUA), mineral N levels in urine treated lowland soils had increased by 65 to 84 μg/g soil from the levels at 3 DAUA. These quantities are equivalent to 24% to 30% of the mineral N present at 3 DAUA.

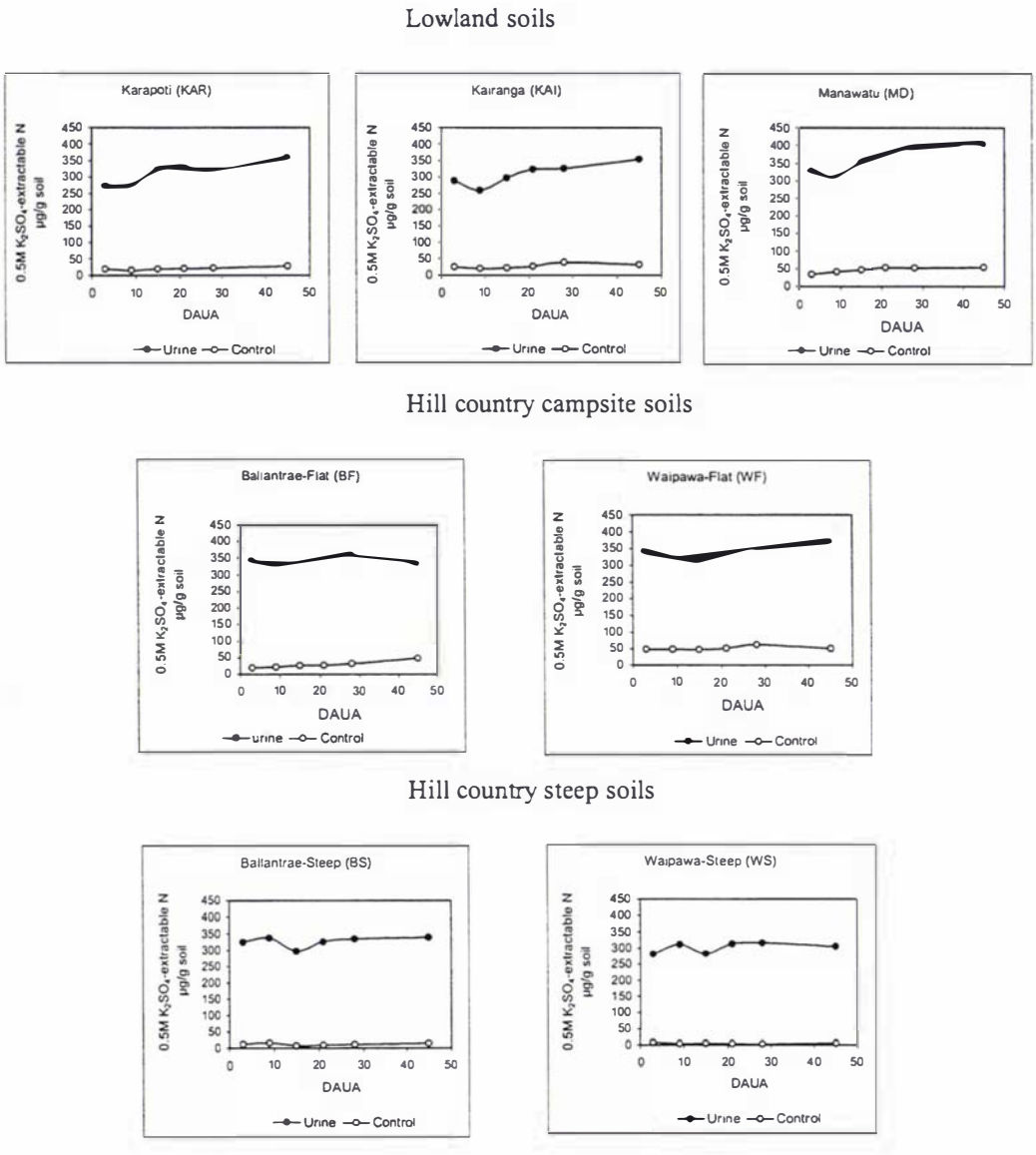


Fig. 6.5 Effect of urine application on 0.5M K_2SO_4-extractable soil mineral N. (The statistical analysis of the data in this figure is included in Appendix 3).

These trends were reinforced when the data were presented as recovery of added urine N (Fig. 6.6). At the end of the experiment (45 DAUA), the urine N recovery as soil mineral N had increased in all soils except the BF soil (Fig. 6.6). These increases were markedly higher in the lowland soils.

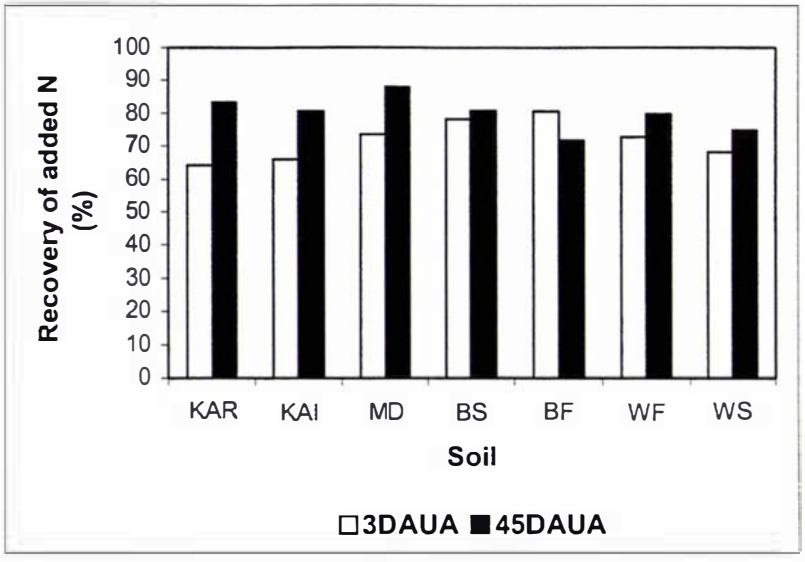


Fig. 6.6 Percentage of urine N recovered as soil mineral N at the beginning (3 DAUA) and end (45 DAUA) of the experiment.

The increase in urine N recovery as mineral N can be explained by one of two possibilities. The first possibility is the remineralisation of urine N, which was initially immobilised by microbes. The second, as discussed in previous chapters, is the release of N from resident organic matter as a result of urine addition.

6.3.3 Ammonium

Concentrations of 0.5M K_2SO_4-extractable NH_4^+-N (μg NH_4^+-N/g soil) and resin-adsorbed NH_4^+-N (μg NH_4^+-N/5 cm^2/3 days) over the duration of the experiment are presented in Fig. 6.7 and 6.8.

Urine application significantly increased the soil NH_4^+-N levels in all urine treated soils at the first sampling, 3 DAUA (Fig. 6.7 and 6.8).

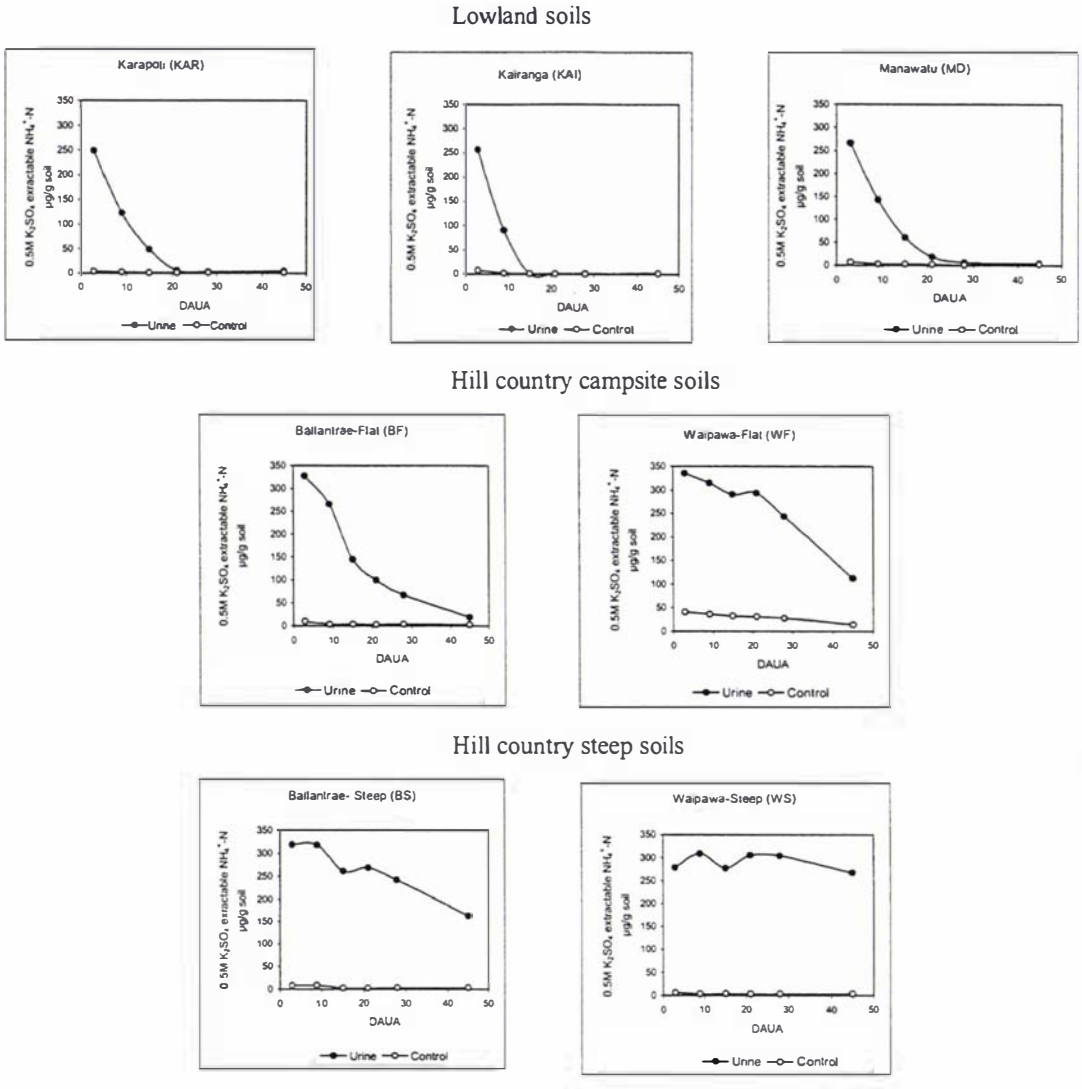


Fig. 6.7 Effect of urine application on soil 0.5M K_2SO_4-extractable NH_4^+-N. (The statistical analysis of data in this figure is included in Appendix 3).

By 3 DAUA, 245–318 μg/g soil of urine N were present as 0.5M K_2SO_4-extractable soil NH_4^+-N. These quantities are 61% to 80% of added urine N, indicating rapid urea hydrolysis after urine application. However, in lowland soils, relatively lower quantities (245-259 μg/g soil) of urine N were present as 0.5M K_2SO_4-extractable NH_4^+-N at 3 DAUA compared to the hill country soils (272-318 μg N/g soil).

As the trial progressed, the elevated levels of 0.5M K_2SO_4-extractable soil NH_4^+-N in urine treated soils decreased towards the levels of the controls in all soils except in the WS soils.

In the urine treated, lowland soils the elevated 0.5M K_2SO_4-extractable soil NH_4^+-N levels declined rapidly with time and reached the levels of the controls by 15-21 days.

In the urine treated hill country soils, the 0.5M K_2SO_4-extractable soil NH_4^+-N levels declined more slowly. The 0.5M K_2SO_4-extractable soil NH_4^+-N in the urine treated BF soils had reached control levels by 45 DAUA but in the BS and WF soils 0.5M K_2SO_4-extractable soil NH_4^+-N levels were still significantly higher than controls at 45DAUA.

The 0.5M K_2SO_4-extractable soil NH_4^+-N in the urine treated WS soil, remained at similar levels to those at 3 DAUA throughout the experiment.

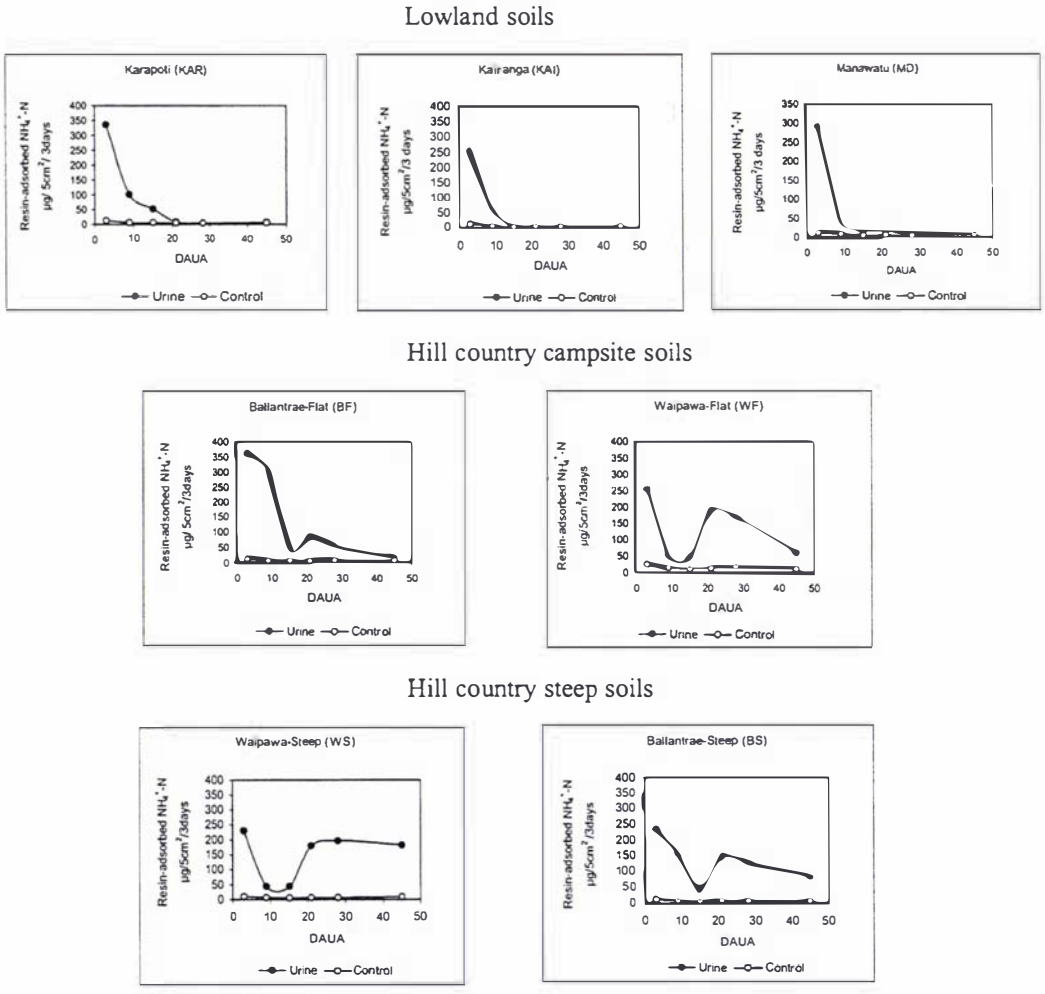


Fig. 6.8 Effect of urine application on resin-adsorbed NH_4^+-N. (The statistical analysis of data in this figure is included in Appendix 3).

At the end of the experiment, in lowland soils, <1% of applied urine N could be accounted for as 0.5M K_2SO_4-extractable soil NH_4^+-N. In hill country soils, 0.5M K_2SO_4-extractable soil NH_4^+-N accounted for 4% (BF) to 25% (WF) of applied urine in flat campsite soils and 40% (BS) to 66%(WS) in steep soils at 45 DAUA.

In most soils, resin-adsorbed NH_4^+-N (Fig. 6.8) followed similar trends to the 0.5M K_2SO_4-extractable NH_4^+-N. In hill country, urine treated soils there was a consistent pattern; resin-adsorbed NH_4^+-N at 10-15 DAUA dropped significantly and then recovered by 20 DAUA. The exact cause for this is not clear.

6.3.4 Nitrate

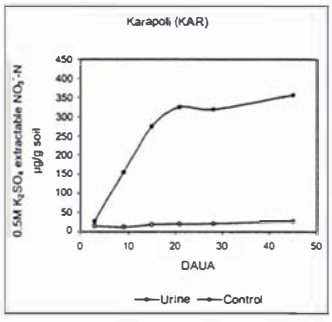
Concentrations of 0.5 M K_2SO_4-extractable NO_3^--N (μg NO_3^--N/g soil) and resin-adsorbed NO_3^--N (μg NO_3^--N/5 cm^2 resin/3 days) over the duration of the experiment are presented in Fig. 6.9 and 6.10.

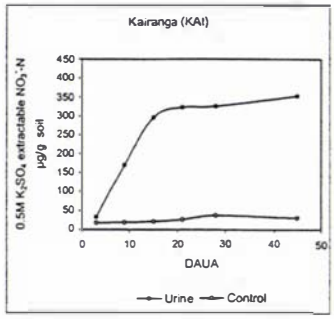
At the first sampling (3 DAUA), there were no significant differences in 0.5M K_2SO_4 -extractable NO_3^--N between the control and urine-treated soils. Soil NO_3^--N levels then built up with time in the urine-treated soils due to nitrification. However, the increase of soil NO_3^--N with time varied greatly between the tested soils, ranging from 38 to 401μg NO_3^--N /g soil at the end of the experiment.

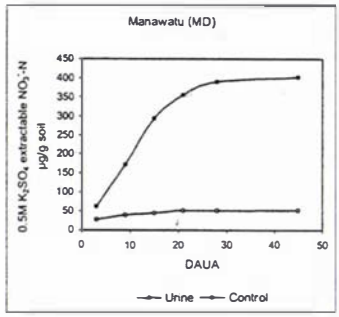
The 0.5 M K_2SO_4-extractable NO_3^--N levels in all the urine treated lowland soils increased rapidly up to 15–20 DAUA and thereafter the rate of increase of soil NO_3^--N dropped.

The changes in 0.5 M K_2SO_4-extractable NO_3^--N levels over the duration of the experiment in hill country soils varied between Waipawa and Ballantrae sites and between soils from flat and steep areas. Ballantrae soils had faster soil NO_3^--N accumulation than their Waipawa counterparts and soils from flat areas had faster nitrification than the steepland soils.

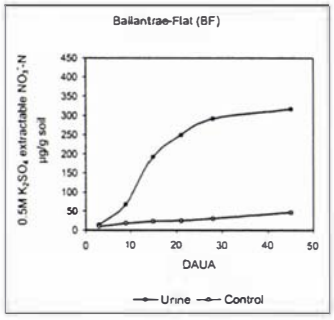
Lowland Soils

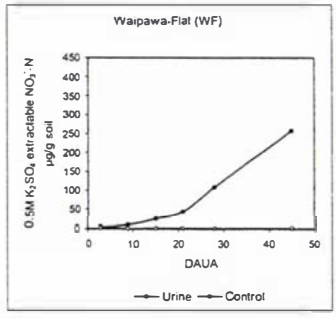




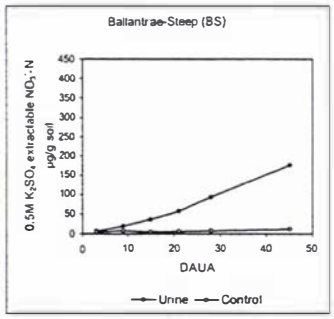


Hill country campsite soils





Hill country steep soils



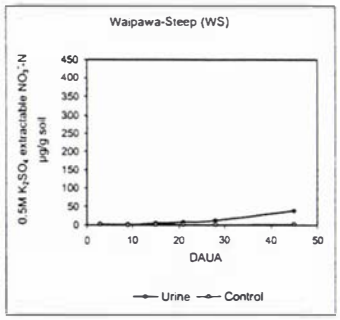


Fig. 6.9 Effect of urine application on 0.5 M K_2SO_4 -extractable soil NO_3^--N. (The statistical analysis of data in this figure is included in Appendix 3).

At the end of the experiment, in lowland soils, 81%-87% of added urine N was present as 0.5M K_2SO_4-extractable soil NO_3^--N. In hill country soils, 0.5M K_2SO_4-extractable soil NO_3^--N accounted for 55% (WF) - 68% (BF) applied urine N in flat campsite soils and 9% (WS) - 44% (BS) in steepland soils.

Resin-adsorbed NO_3^--N in all soils (Fig. 6.10) followed the same patterns as the 0.5 M K_2SO_4 -extractable NO_3^--N. However, resin-adsorbed NO_3^--N in KAR, KAI, MD and BF soils dropped somewhat in the latter part of the experiment. This could be due to loss of NO_3^--N from the soil by denitrification.

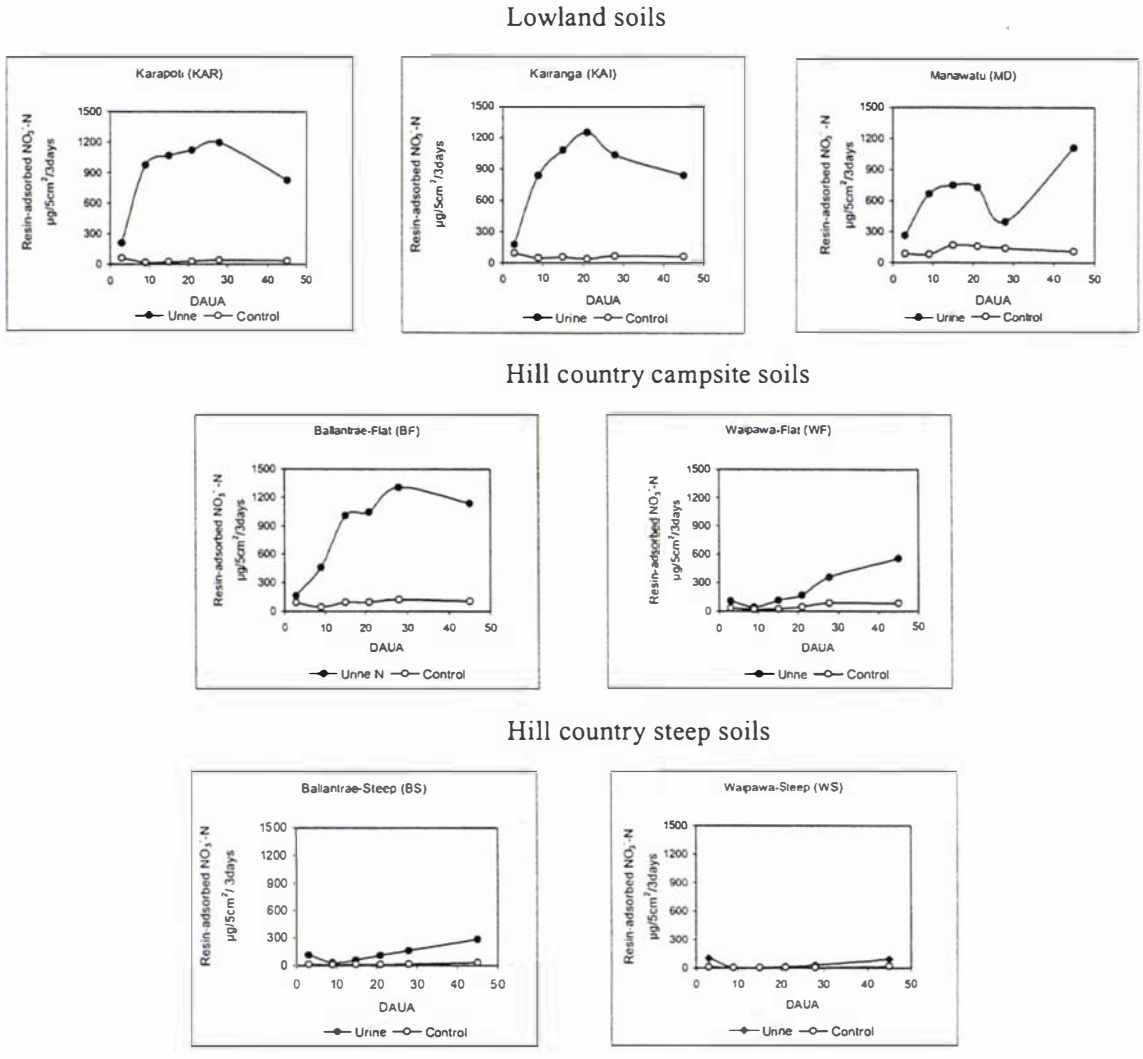


Fig. 6.10 Effect of urine application on resin-adsorbed NO_3^--N over time. (The statistical analysis of data in this figure is included in Appendix 3.)

6.3.5 Mineralisable N

The effect of urine application on readily available mineralisable N in the experimental soils is illustrated in Fig. 6.11.

Among the urine treated, lowland soils, mineralisable N levels were significantly increased compared to the control throughout most of the experiment in the KAR and Manawatu MD soils. In the KAI soil, urine application only increased mineralisable N levels at 3 DAUA.

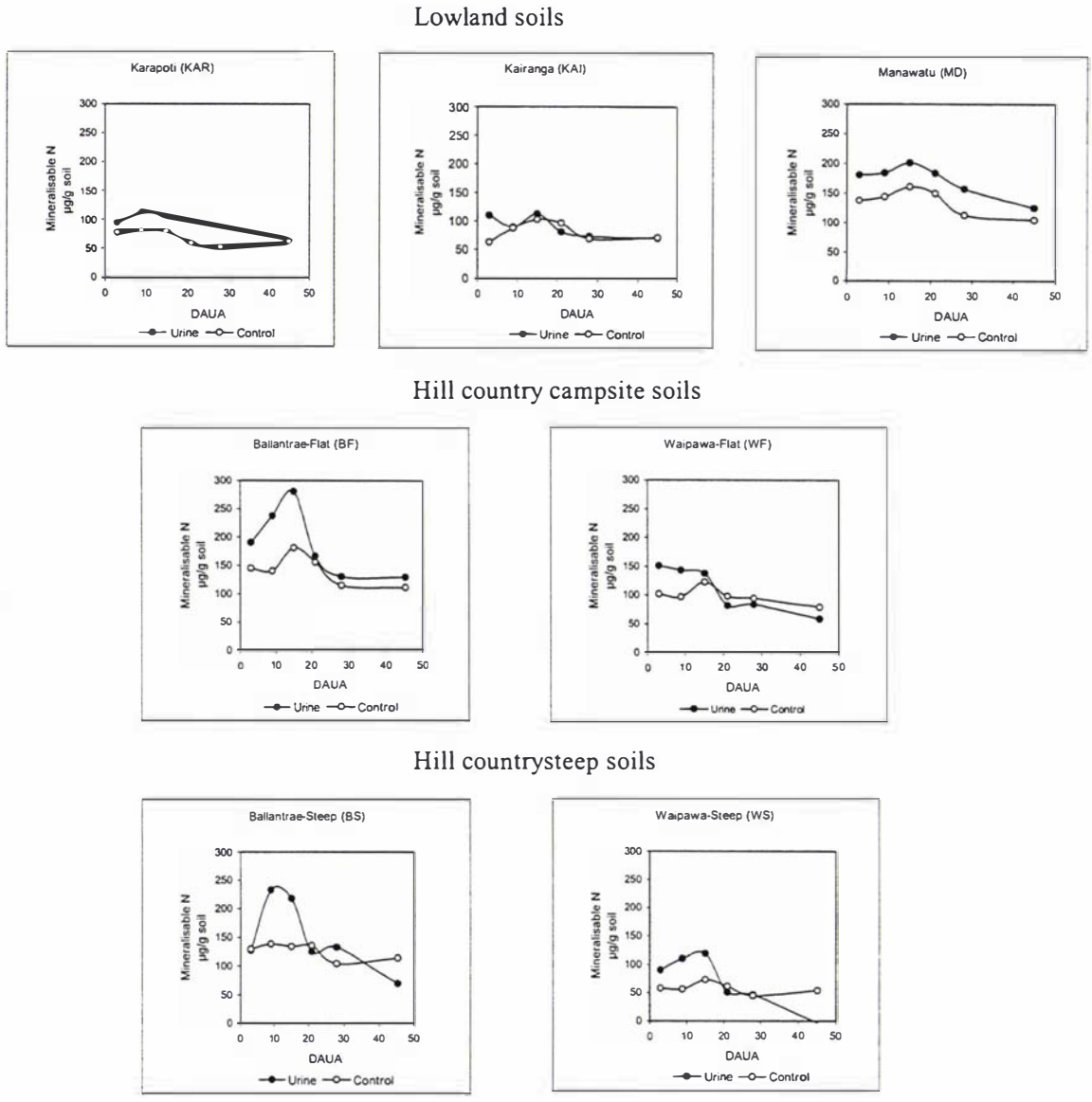


Fig. 6.11 Effect of urine application on soil mineralisable N with time. (The statistical analysis of data in this figure is included in Appendix 3).

The mineralisable N levels in urine treated KAR soils were higher than control by 17-40 µg/g soil from 3–28 DAUA. These quantities are equivalent to 4 –10% of added urine N. From 3–28 DAUA, mineralisable N in urine treated MD soils increased by 34-45 µg/g soil and these quantities were equivalent to 9-11% of added urine N.

At the beginning, 3-15 DAUA, mineralisable N levels significantly increased compared to control in all urine treated hill country soils. The increase in mineralisable N was higher in Ballantrae soils than Waipawa soils.

At 9 DAUA, mineralisable N levels were 97, 95, 47 and 53 μg/ g soil higher than the controls in BF, BS, WF, and WS soils respectively. These differences were statistically significant and were equivalent to 24%, 24%, 12% and 13% of added urine N respectively.

By 21 DAUA, the mineralisable N levels in urine treated hill soils had declined to the levels of the controls. Interestingly, at 45 DAUA the mineralisable N levels in urine treated, hill country steep soils (BS and WS) were significantly lower than the controls.

6.3.6 Dissolved organic carbon (DOC)

Previous studies have reported that solubilization of soil organic carbon occurs following urine application (Monaghan and Barraclough, 1993). It was pointed out in Section 6.3.1 that DOC is strongly related to soil microbial biomass and mineralisable N. Therefore, observing the changes in DOC are vital in the urine N cycle. The effect of urine application on soil DOC levels is illustrated in Fig. 6.12.

The DOC levels after urine application in lowland soils generally increased compared to control, suggesting solubilization of organic matter and release C to soil solution. These increases were statistically significant in the MD soils.

In contrast, the DOC levels in urine treated hill soils did not show any significant differences compared to the control.

6.3.7 Soil microbial biomass (SMB)

Haynes and Williams (1999) reported that soil microbial biomass and microbial activity are high in stock camp areas in hill pastures. This is mainly due to the transfer of nutrients and organic matter to the camp areas via dung and urine.

However, in the current experiment there was no significant difference observed in SMB-C in urine treated soils compared to control soils for any of the soils used (data not presented).

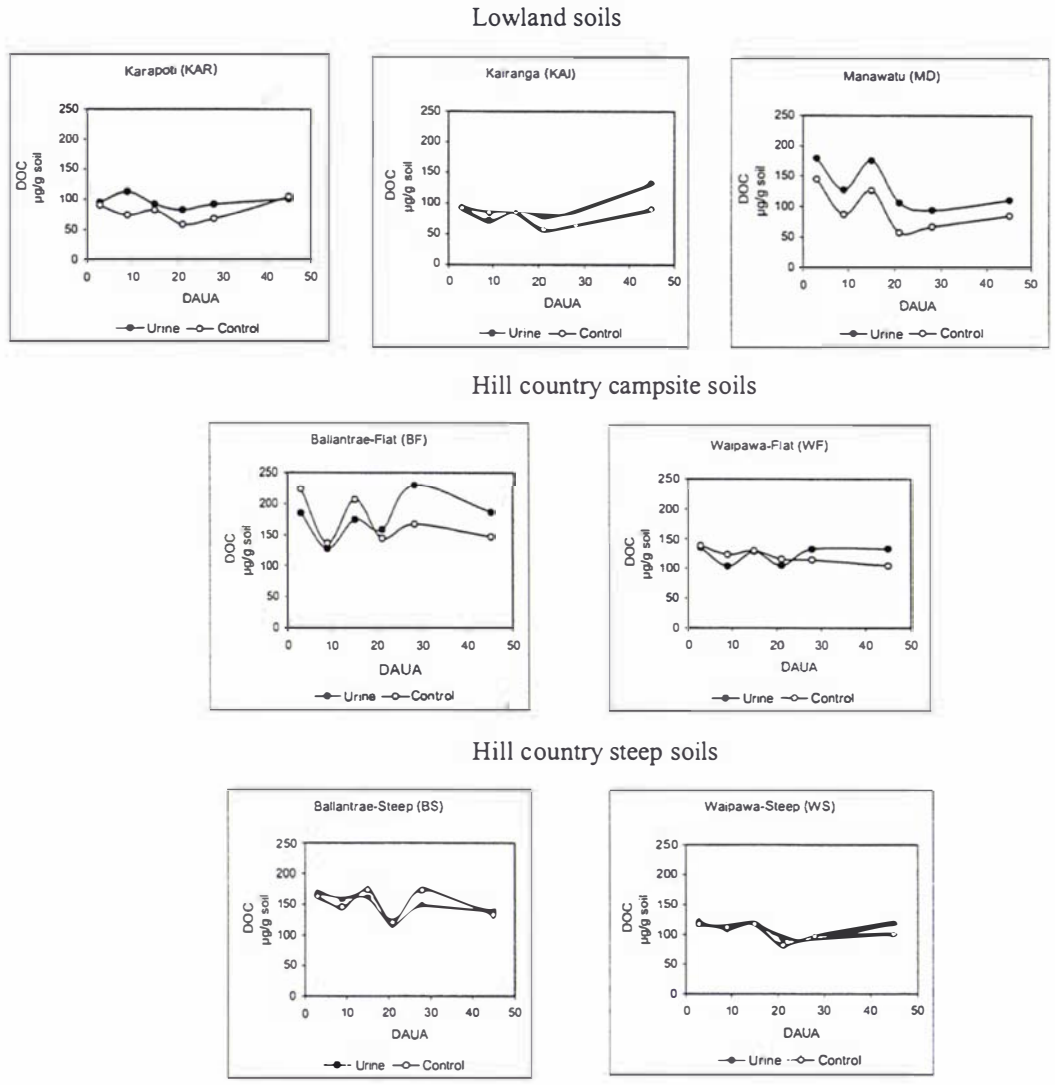


Fig. 6.12 Effect of urine application on soil DOC levels. (The statistical analysis of data in this figure is included in the Appendix 3)

It was evident from the previous sections of this chapter that microbial activities, like nitrification, were greatly increased by urine application. This suggests that microbial activity was more affected by urine application than was microbial biomass size. Lovell and Jarvis (1996) also did not observe an effect of urine addition on biomass size but did observe increased activity. They commented that substantial qualitative changes within the SMB could take place quickly and independently of any change in biomass size.

In contrast to SMB-C, SMB-N was increased after urine application (Fig. 6.13). Most of the significant increases occurred from 9-21 DAUA. The effect of urine application on SMB-N levels is illustrated in Fig. 6.13.

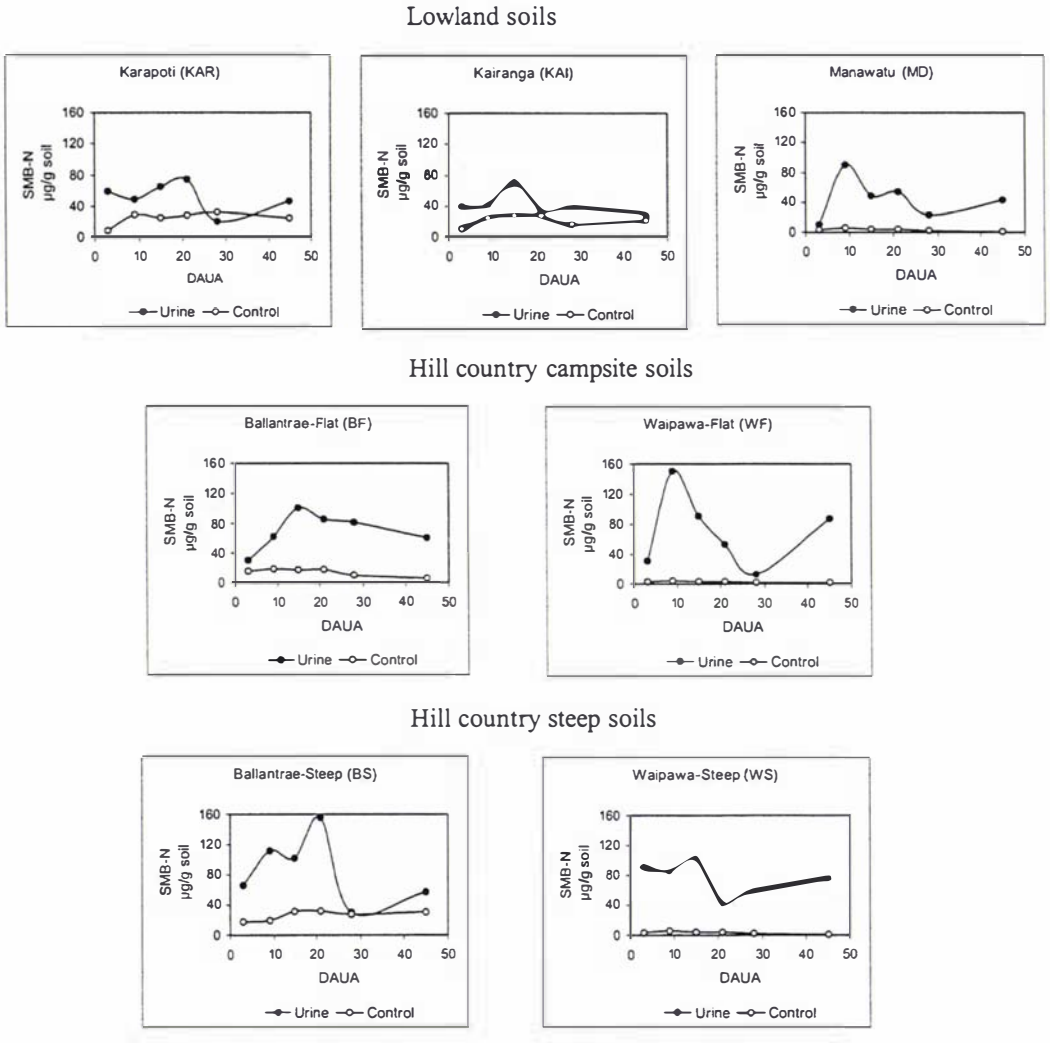


Fig. 6.13 Effect of urine application on soil microbial biomass N with time. (The statistical analysis of data in this figure is included in Appendix 3)

At 15 DAUA, all of the soils had significantly higher (P<0.05) microbial N values in urine treated pots compared to control. In lowland soils, this increase was 40 – 45 µg/g soil which was 10%-11% of added urine N. Interestingly the increased microbial N in hill country soils was approximately twice that in the lowland soils, ranging from 71-87 µg/ g soil. These quantities were 18%-22% of added urine N.

6.4 Discussion

As noted in Section 6.3.2, the proportion of added urine N recovered as soil mineral N at the beginning of the experiment was different in the current incubation experiment than in the field experiments described in Chapters 3 and 5.

In the Waipawa experiment at 1 and 6 DAUA, urine N recovery as soil (0-15 cm) mineral N was close to or >100% (Table 3.4). The urine N recovery as soil (0-30 cm) mineral N at 3 DAUA in the Ballantrae experiment was 48% - 75%. The urine N recovery as mineral N in the current incubation experiment at 3 DAUA was 68% - 73% in Waipawa soils, 78%- 81% in the Ballantrae soils and 64 %-74% in the lowland soils.

The urine N recovered at 3 DAUA is presented in Table 6.1. The total urine N accounted for at 3 DAUA was calculated using urine N recovered as soil NH_4^+-N, NO_3^--N, resin N and anaerobically mineralisable N (AMN).

Table 6.1 Apparent fate of urine N at 3 DAUA. * (rate of urine N was 400 μg N/g soil) i.e. values are treatment minus control).

Soil	Fate of urine N at 3 DAUA (μg N/g soil)					
	NH_4^+-N (A)	NO_3^--N (B)	AMN (C)	SMB- N (D)	Resin N (E)	Quantity of N unaccounted for (400*- (A+B+C+E)) (% of added urine N)
KAR	245	12	17	51	4	122 (31%)
KAI	250	15	47	29	3	85 (21%)
MD	259	35	43	7	5	58 (15%)
BS	311	3	0	48	3	83 (21%)
BF	318	4	45	15	4	29 (7%)
WS	272	1	32	69	3	92 (23%)
WF	294	0	49	28	3	54 (14%)

In this experiment, resin N was added to the other measures of mineral N when calculating recovery of urine N because the resin strips had been inserted in the pots for 3 days prior to analysis. They would therefore have adsorbed NH_4^+-N and NO_3^--N that would otherwise have been included in the mineral N. The N adsorbed to resin was from the 100 g of soil in the cup. Thus resin adsorbed N was also expressed as μg/g soil.

The percentage of urine N unaccounted for at 3 DAUA was reasonably large, ranging from 7%-31%. Some of the unaccounted for urine N could have been lost through ammonia volatilisation although the quantity of NH_3-N trapped by the volatilisation samplers was very small, ranging from 1-9 μg N/sampler. This was not surprising as the cattle urine was well mixed with soil before placement into the incubation cups.

However, there was still a possibility that some of the added urine N was volatilised and not detected by the samplers. Therefore, a simple experiment was carried out to check on the possibility of volatilisation when the same amount (6 mL) of urine was mixed with the same amount of soil (100 g). Only KAR and WS soils were used. Urine (6 mL) was well mixed with 100 g soil and placed in the same incubation cups. The soil-filled cup and a small beaker with 20 mL of 0.2 M H_2SO_4 were placed in a 15x15x 6 cm plastic container. The container was then sealed and allowed to stand for 3 days. The NH_3-N trapped in the 0.2 M H_2SO_4 was analysed. The results confirmed that the volatilisation losses were minimal, ranging from 12-15 μg N/100 g soil.

Fixation of NH_4^+-N to clay minerals is another possible sink for the unaccounted for urine N. Carran *et al.* (1982) accounted for 10% of added urine N as clay fixed N and Crush and Evans (1988) observed that fixed NH_4^+-N rose sharply and declined more slowly in plots treated with urine. Therefore, an attempt was made to check on the possibility of urine N loss through NH_4^+-N fixation by clay minerals. However, the method commonly found in the literature, described in Section 6.2.3.8 (Silva and Bremner, 1966) was time consuming and involved the use of toxic chemicals such as concentrated hydrofluoric acid (HF). Therefore, a preliminary analysis was carried out using only the KAR soil before deciding whether or not to analyse the other soils. The KAR soil was selected for two reasons. Firstly, it had the highest amount of unaccounted for urine N and secondly, Crush and Evans (1988) had reported fixed N values in Karapoti soils with and without urine addition. The decision to undertake analysis for clay fixed N was taken at the end of the experiment. Thus this analysis was done on soils from the sampling 45 DAUA.

The results suggested that the urine application had no effect on clay fixed N in the Karapoti soil. The amount of fixed NH_4^+-N in the three urine treated and three controls was approximately 260 mg N/kg soil. This value is similar to the values reported by

Crush and Evans (1988) for clay fixed NH_4^+-N in Karapoti soils sampled throughout a year, - ranging from 187-244 mg N/kg soil.

Thus, the possibility that the urine N not accounted for had been fixed into clay minerals was minimal as the differences in clay fixed N between control and urine treated pots were much less than the amounts of N not recovered in the KAR soil (122 μg/g soil).

The SMB-N was not included when accounting for urine N (Table 6.1) as it could have been double counted through the inclusion of AMN. However, the regression relationship developed between SMB-N and AMN (Fig. 6.2 K) was negative, suggesting microbial biomass N may not be included in AMN. If SMB-N was also included when accounting for urine N in Table 6.1, the unaccounted for urine N dropped to only 13% - 18% of that added in soils collected from lowland and 4 % - 9% in soils collected from hill sites.

As mentioned in Section 6.3.2, after the first sampling (3 DAUA), soil mineral N levels in urine treated lowland soils increased somewhat with time and soil mineral N levels in urine treated, hill soils remained at the same levels as at 3 DAUA throughout the experiment.

The elevated NH_4^+-N levels in urine treated lowland soils declined rapidly (Fig. 6.14). At the same time the level of NO_3^--N increased rapidly. By 15 DAUA the NO_3^--N levels in urine treated lowland soil had increased to a level approximately similar to the levels of soil NH_4^+-N at 3 DAUA (Fig. 6.14). This suggests that all the NH_4^+-N that was present at 3 DAUA may have nitrified by 15 DAUA. However, the soil NO_3^--N in urine treated lowland soils continued to increase still further indicating that some NH_4^+-N continued to be added to that present in the soil 3 DAUA.

In contrast, the NO_3^--N levels in urine treated hill soils did not increase to the same extent, with only the BF site approaching complete conversion of NH_4^+-N to NO_3^--N by the end of the experiment.

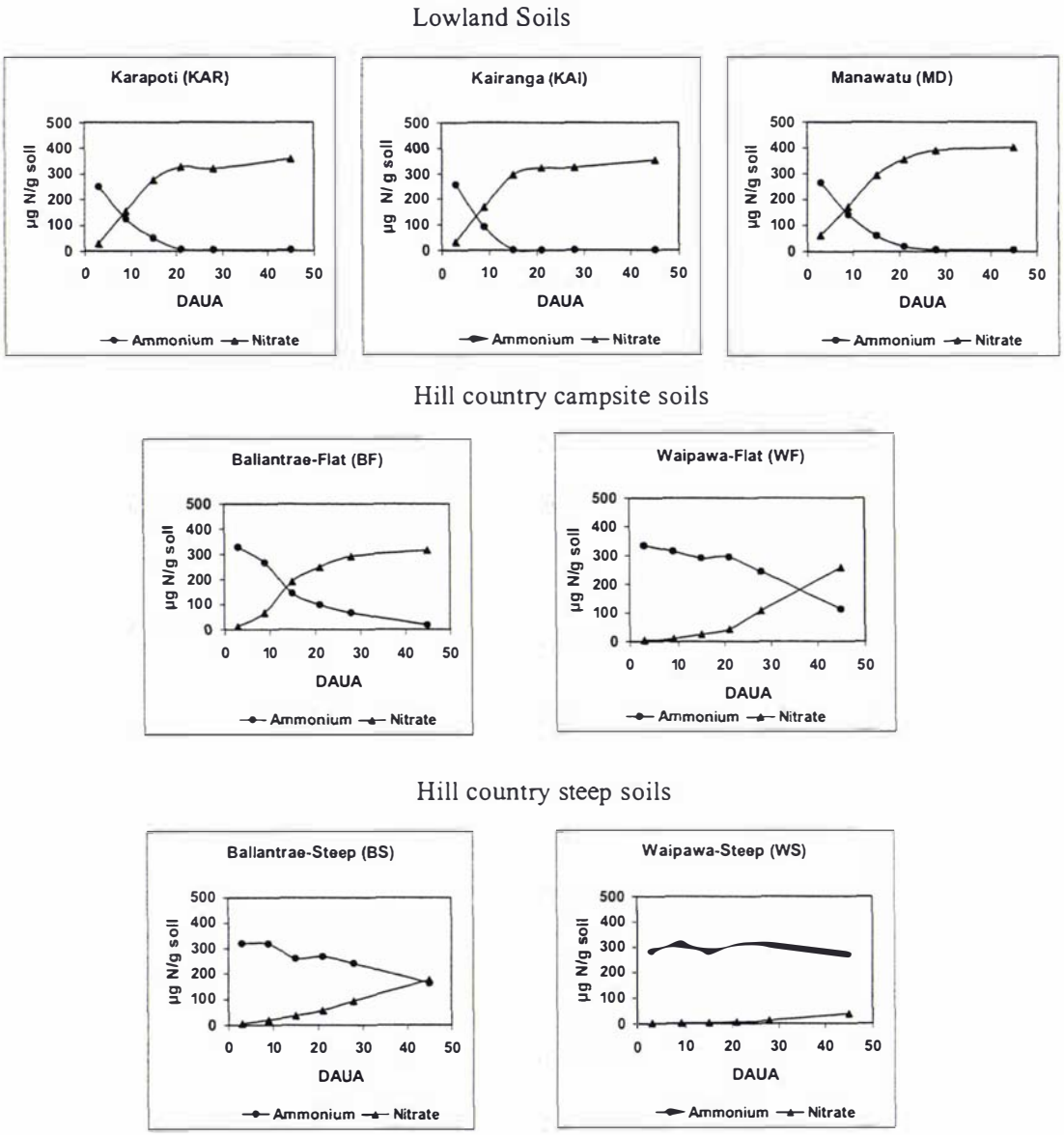


Fig. 6.14 The distribution of NH_4^+-N and NO_3^--N in urine treated soils with time after urine application.

These results demonstrate that nitrification is occurring at different rates in soils collected from lowland and hill sites. Further, there was considerable variation in the rate of nitrification between soils collected from flat campsites and steep slopes in hill country. This is discussed in more detail in Section 6.4.1.

Table 6.2 Quantitative comparison of NH_4^+-N decrease and NO_3^--N increase in urine treated soils from 3-45 DAUA. (All values are in μg N/g soil).

Soil	Decrease of NH_4^+-N from 3-45 DAUA	Increase of NO_3^--N from 3-45 DAUA	Quantity of NH_4^+-N unaccounted for as NO_3^--N
KAR	245	329	-84
KAI	255	321	-66
MD	261	339	-78
BF	309	303	6
WF	223	252	-29
BS	155	169	-14
WS	11	35	-24

Table 6.2 demonstrates that the decrease in NH_4^+-N from 3-45 DAUA was completely accounted for by the increase in soil NO_3^--N. In fact in all soils except BF, increases in NO_3^--N in urine treated soils were greater than the decreases in NH_4^+-N. The overall increase in mineral N from 3-45 DAUA was much higher in soils collected from lowland.

6.4.1 Nitrification

Nitrification is a particularly important process in grazed grassland since this is the rate limiting step in the transfer from the pool of relatively immobile NH_4^+-N, derived from animal excreta and mineralisation of soil organic N, through to the vulnerable NO_3^--N form.

As pointed out in Section 3.2.3.3, nitrification is mainly carried out by chemoautotrophic (organisms utilize the CO_2 as their sole carbon source and gain energy from oxidation of inorganic compounds) bacteria. The major factors governing chemoautotrophic nitrification are considered to be NH_4^+ substrate supply, soil temperature, soil moisture and soil pH (Section 3.2.3.3).

As discussed earlier, nitrification occurred at variable rates in the seven experimental soils after urine application. The experimental soils were ranked according to the rate of nitrification in Table 6.3. In lowland soils, nitrification was rapid up to 15 DAUA, and

then slowed as supplies of NH_4^+-N became limiting (Fig. 6.11). Therefore, soil NO_3^--N accumulation to 15 DAUA was used to calculate the daily nitrification rates in the experimental soils. As the aim was to assess the nitrification rate after urine application, the soil NO_3^--N concentrations in the controls were deducted from the NO_3^--N levels in the urine treated soils.

Soils collected from lowland sites had much higher nitrification rates than the soils collected from hill country sites. Interestingly, daily nitrification rates of soils collected from hill country showed considerable variability. BF soil had a greater nitrification rate than BS soil. Similar results were observed in the field experiment described in Chapter 5. Both soils collected from Waipawa had very low nitrification rates, supporting the results observed in the field experiment described in Chapter 3.

Table 6.3 Nitrification rates during first 15 DAUA in the experimental soils.

Soil	Nitrification rate ± SD ($\mu g\ NO_3^-$-N/g soil/day)
KAI	18.3 ± 1.51
KAR	17.1 ± 1.45
MD	16.6 ± 0.84
BF	11.3 ± 0.94
BS	2.1 ± 0.26
WF	0.6 ± 0.8
WS	0.3 ± 0.01

As discussed in the literature review (Section 3.2.3.3), high variability of nitrification rates has previously been observed in New Zealand soils (Sarathchandra, 1978; Steel *et al.*, 1980). However, the exact cause for this variation has not been clearly explained.

Watson and Mills (1998) conducted a similar incubation experiment by applying the same rate of NH_4NO_3 to different soils that had a history of fertiliser inputs of 100, 200, 300, 400 and 500 kg N/ha/yr for the past 7 years. In that experiment, the rate of nitrification was clearly influenced by previous fertiliser history and management. The nitrification rate was greater in soils with a history of high N inputs.

In the current incubation experiment, the soils collected from lowland sites had received high N inputs in previous years. The KAR and KAI soils were collected from the AgResearch experimental plots that had received large amounts of urine N for the last five years. The MD soil was collected from a sheltered area of a dairy farm where large amounts of dung and urine had accumulated. Thus, soils that had a history of high N inputs had the highest nitrification rates in this experiment, which agrees with the findings of Watson and Mills (1998).

Similarly, the soils collected from sheep campsites in hill country, where large amounts of N are transferred through urine and dune, had higher nitrification rates than soils collected from steep sites.

It is interesting to note that Jarvis and Barraclough (1991) showed evidence of "memory" effects of previous fertiliser treatments on the NH_4^+-N : NO_3^--N ratio in soils when a common rate of fertiliser was subsequently applied. Therefore, it can be assumed that previous N inputs to the current experimental soils could have resulted in the variation of nitrification rates during the incubation.

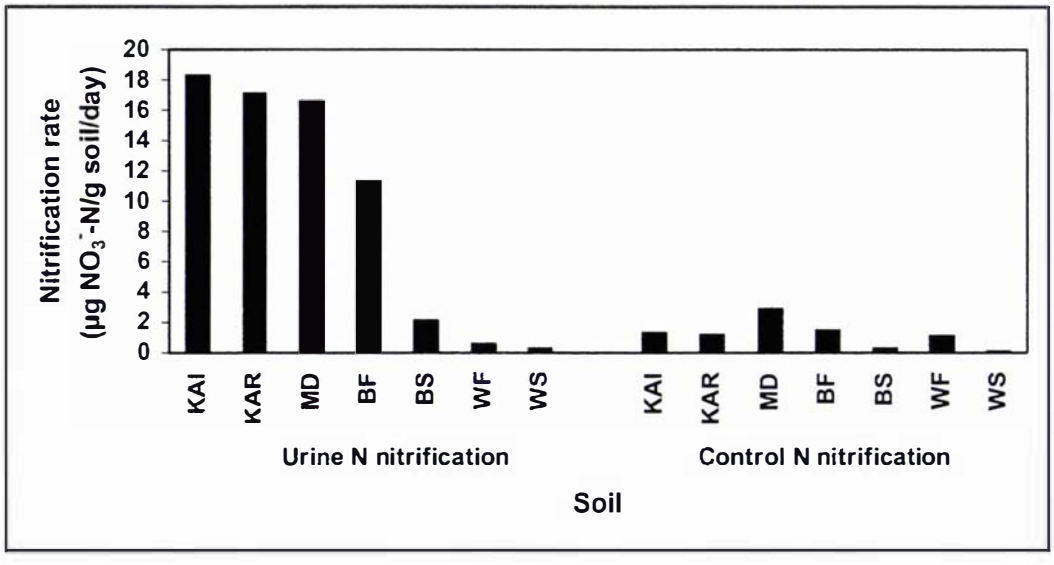


Fig. 6.15 Comparison of nitrification of urine N and control soil N.

When nitrification rates were calculated as described above for the control soils (Fig. 6.15), a similar pattern of nitrification rate was observed. In general, the KAI, KAR, MD, BF and WF soils, which had received high N inputs, had higher nitrification rates

than the low N input BS and WS hill country steep soils. However, the order of the soils based on soil nitrification rates in control pots was not exactly the same as the order after urine had been applied

Interestingly the nitrification rate in the hill country steep soils was not affected much by urine addition. As these soils had been receiving very limited mineral N inputs, mainly through organic matter mineralisation, autotrophic nitrifiers might not have been able to compete with plant and N immobilising microbes. Indeed, nitrifiers are generally poor competitors with the heterotrophic biomass for NH_4^+-N (Jansson, 1958; Jones and Richards, 1977). Hence, the autotrophic nitrifier population and *in situ* nitrifier activities might be limited.

The role of heterotrophic nitrification has been discussed by several researchers (Belser, 1979; Haynes, 1986; Bramley, 1989; Wragee *et al.*, 2001). These nitrifiers use organic carbon as a C source and for energy. Kester *et al.* (1997) reported that fungi play an important role in heterotrophic nitrification in soils with low pH.

As these hill soils contain high soluble C (Fig. 6.1), heterotrophic nitrification could be more active than autotrophic nitrification. However, no studies have obtained values for the actual amounts of heterotrophic nitrification *in situ*, and most have merely confirmed that it is occurring in their soils (Belser, 1979).

Results from a series of experiments conducted by Bardgett *et al.* (1997, 1999, and 2001) provide evidence that soil microbial communities of heavily grazed sites are dominated by bacteria, whereas in systems that are less intensively grazed, or completely unmanaged, fungi have a proportionately greater role.

Therefore, the role of heterotrophic nitrification in hill country soils would be a useful area for future research.

Jarvis *et al.* (1989) commented that the greater C/N ratio of decaying plant material and excreta in grass/clover and grass swards with low fertiliser inputs may limit nitrification.

The C/N ratio can be used as a guide to the state of decomposition, or likely ease of decomposition and mineralisation of N from organic residues (McLaren and Cameron, 1996). Soils with high C/N ratios normally contain resistant organic materials that retard decomposition and mineralisation. Previous work in hill country suggested that soils from campsites have low C/N ratios and resulting higher mineralisation of organic N than the steep soils, which normally have high C/N ratios (Ledgard *et al.*, 1982; Sakadevan, 1991).

In the present study, nitrification rates and soil C/N ratios showed a strong (R^2=0.9) negative relationship (Fig. 6.16). A similar relationship was obtained from the data of Steel *et al.* (1980) in Section 3.2.3.3.

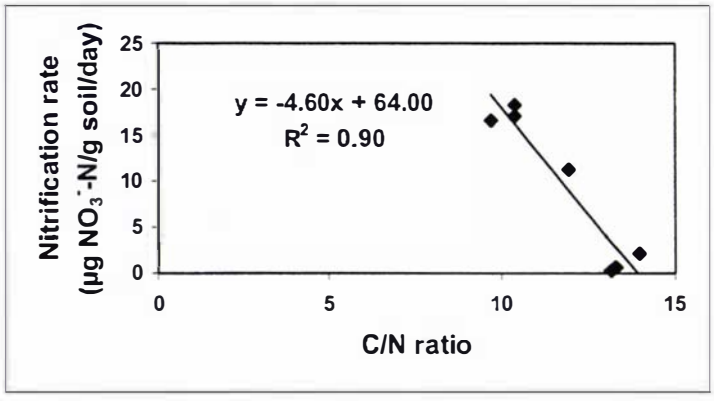


Fig. 6.16 Relationship between C/N ratio and nitrification rate.

Continuous high N inputs to lowland sites and hill campsites could lead to a narrowing of the soil C/N ratio. This leads to greater microbial activity and organic matter mineralisation and in turn will increase the availability of NH_4^+-N substrate for autotrophic nitrifiers and readily available C for heterotrophic nitrifiers.

In the hill country steep soils soil N is depleted through animal transfer (Gillingham and During, 1973). Radcliffe (1982) pointed out that herbage on flatter areas tended to decay faster than on steep slopes. Therefore, more dead plant shoot and root material accumulates in hill country, steep soils. Thus, low N inputs and high C accumulation results in higher C/N ratios in steep soils. These conditions lead to low quantities of NH_4^+-N substrate for autotrophic nitrifiers and a low nitrification rate was observed.

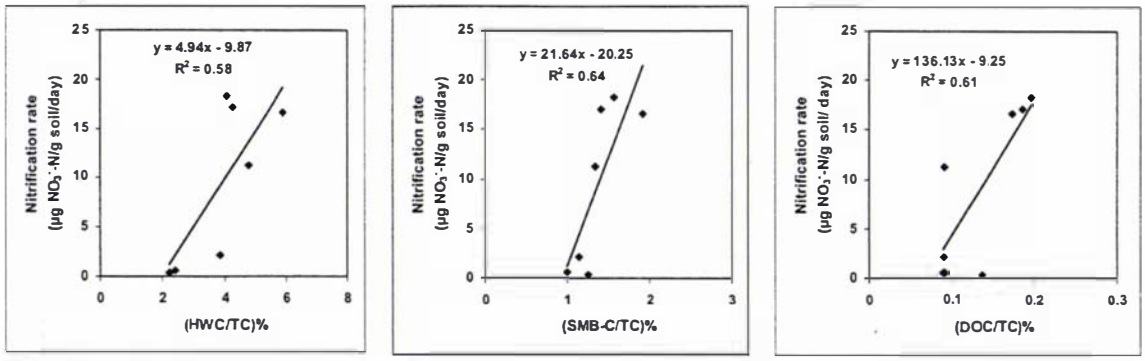


Fig. 6.17 Relationship between nitrification rate and the ratio of labile organic C to TC.

It was demonstrated in Section 6.3.1 that ratios of labile organic C to total C (SMB-C/TC, HWC/TC and DOC/TC) are higher in soils collected from lowland sites than hill country sites indicating perhaps that they are more biologically active. Therefore, greater organic matter mineralisation would be expected in these soils. The ratios of SMB-C/TC, HWC/TC and DOC/TC, expressed as a percentage of TC, were negatively related to C:N ratios (Fig. 6.2) and therefore these ratios had positive linear relationships with nitrification rate (Fig. 6.17).

Among the other factors governing nitrification, soil pH plays a major role as microbial population and enzymatic reactions are heavily dependent on soil pH. The common belief is that the nitrification activity is retarded at lower pH (Haynes, 1986a; Paul and Clark, 1988). Aluminium toxicity is suspected to be the major factor limiting nitrifier activity at low soil pH (Haynes, 1986a). However, some studies have revealed that nitrifying organisms tend to adapt to the existing soil pH (Bramley and White, 1989; Islam *et al.*, 2000). Walker and Wickramasinghe (1979) presented evidence of *Nitrosospira* mediated nitrification *in situ* in a soil with a pH as low as 4.1. Also the role of heterotrophic nitrification at lower pH cannot be ruled out (Haynes, 1986a).

The relationship between nitrification rate and soil pH in the experimental control soils is illustrated in Fig. 6.18.

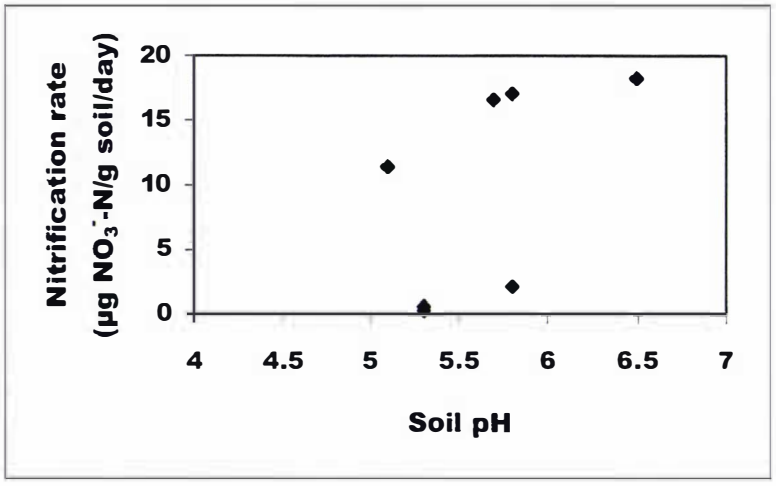


Fig. 6.18 Relationship between nitrification rate and soil pH of the experimental soils.

It can be seen that soil pH and nitrification rates are not linearly related when all the data are considered. The difference between the nitrification rates for a comparable pH was large.

In Fig. 6.18, when BF, MD, KAI and KAR soils are considered alone, there is some evidence of a linear relationship. This relationship is in agreement with the low nitrification in low pH soils. This trend is not showed by soils collected from hill country sites. The BF soil had the highest nitrification rate among the soils collected from hill country sites even though it had the lowest soil pH.

6.4.2 Relationships between resin-adsorbed N and 0.5M K_2SO_4 - extractable N

As in the field experiment described in Chapter 5, soil N was measured as resin-adsorbed N and 0.5M K_2SO_4-extractable N in the current incubation experiment. This enabled a check on the consistency of relationships developed between resin-adsorbed N and 2 M KCl -extractable N.

All the measured resin-adsorbed N and 0.5M K_2SO_4-extractable N values during the experiment were used to develop the relationships illustrated in Fig. 6.19. Thus, a total of 252 data points (7 soils x 2 treatments x 3 replicates x 6 samplings) from each method were used for the relationships.

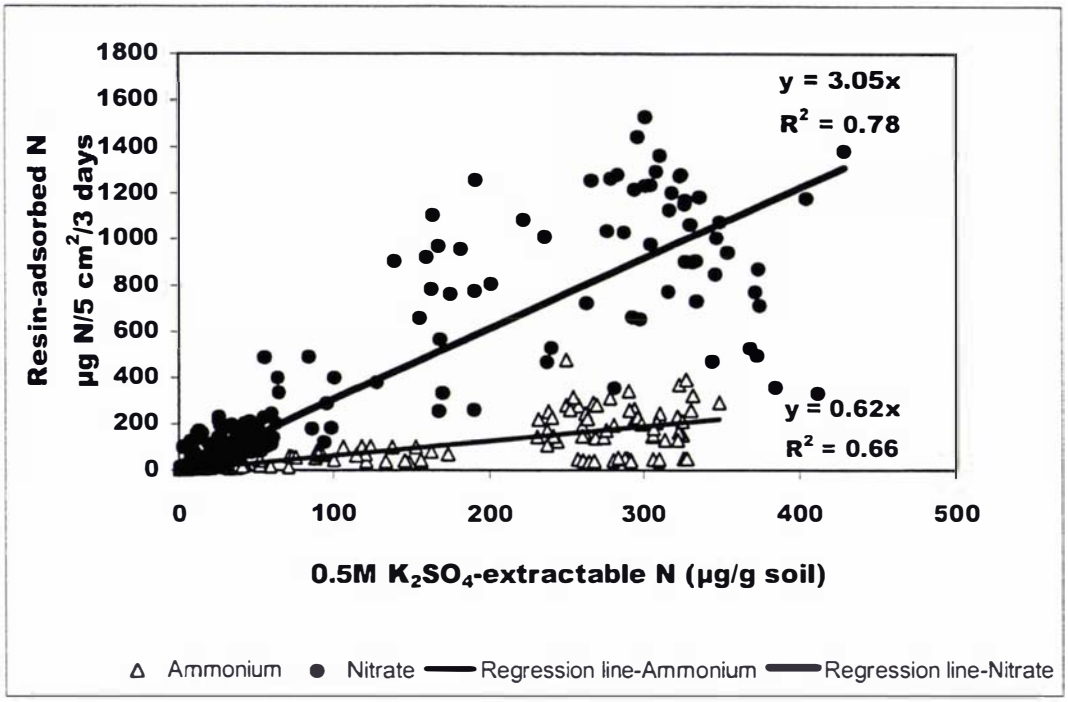


Fig. 6.19 Relationship between resin-adsorbed N and 0.5M K_2SO_4-extractable N.

As observed in Chapter 5, both NH_4^+-N and NO_3^--N showed linear relationships between resin-adsorbed N and 0.5 M K_2SO_4-extractable N. The relationships in this experiment (Fig. 6.19) were stronger than the field experiment (Fig. 5.9). This could be due to both resin-adsorbed N and 0.5M K_2SO_4-extractable N being measured from the same volume of soil in this experiment. In the field experiment, N was not measured from the same soil volume by the two methods, although both measurements were taken from the same experimental plot. In field experiment soil sampling site was spatially separated from resin sampling site to minimise soil disturbance around the resin. In addition, in the current experiment there were only two treatments and thus at some sampling times the data points were distributed at the two extreme ends of the concentration range.

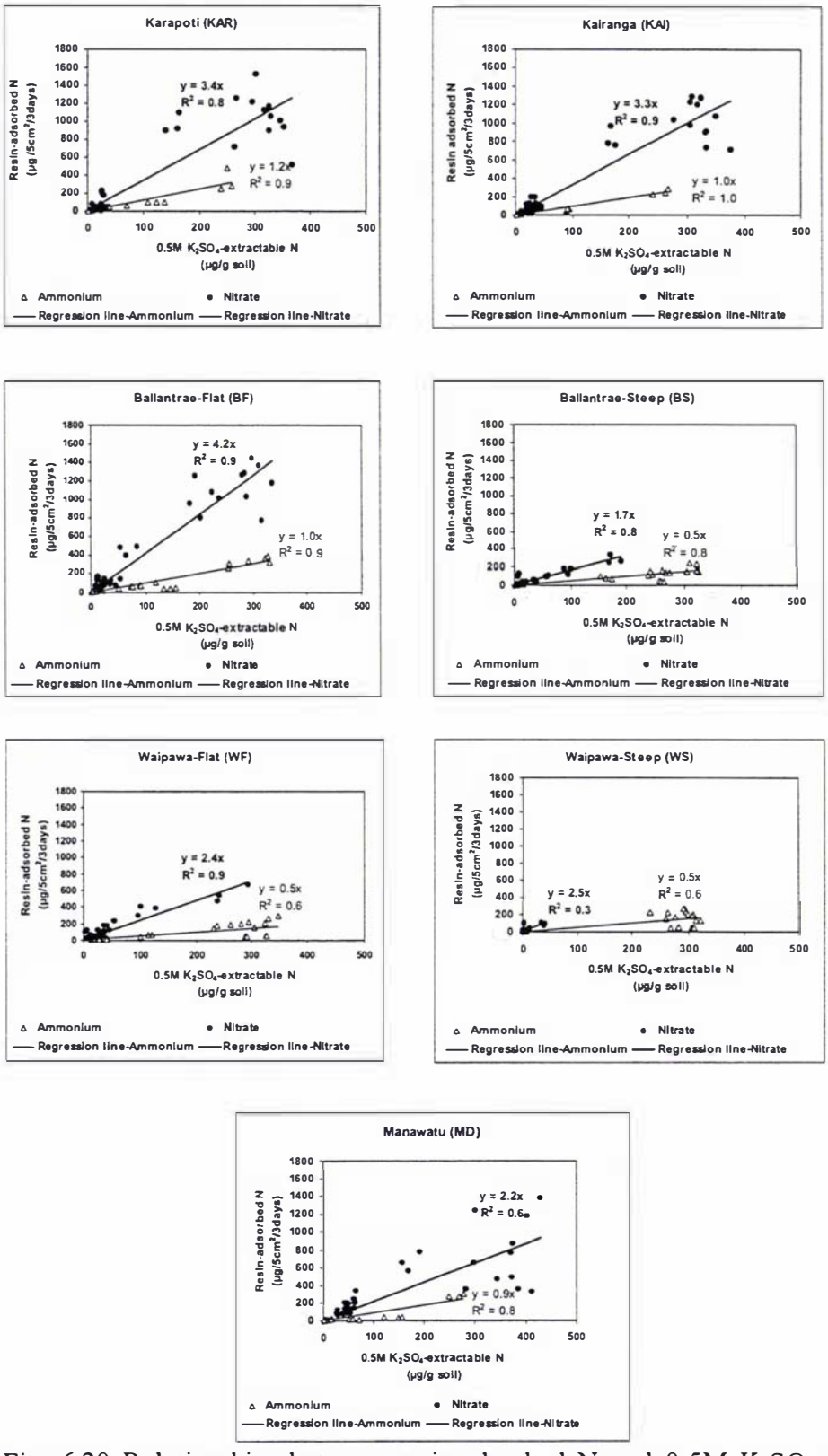


Fig. 6.20 Relationships between resin-adsorbed N and 0.5M K_2SO_4-extractable N in different soils.

The slopes of the regression lines were reasonably similar for both NH_4^+-N and NO_3^--N to the relationships developed in the field experiment described in Chapter 5. The slopes were 0.6 for NH_4^+-N and 3.1 for NO_3^--N in the current experiment compared to slopes of 1.01 for NH_4^+-N and 2.4 for NO_3^--N in the field experiment described in Chapter 5.

Similar trends were observed when the relationships were developed separately for each soil (Fig. 6.20). The relationships between resin-adsorbed NH_4^+-N and 0.5M K_2SO_4-extractable NH_4^+-N were reasonably similar between the soils with the slope of the regression line varying only from 0.5 – 1.2. However, the relationship between resin-adsorbed NO_3^--N and 0.5M K_2SO_4-extractable NO_3^--N showed greater variability between soils. The slope of the regression lines between resin-adsorbed NO_3^--N and 0.5M K_2SO_4-extractable NO_3^--N varied from 1.7 - 4.2. There was no obvious explanation for this variation.

6.5 Conclusion

Unlike in the field experiments, the mineral N recovery after urine application was less than 100%. Thus, there was no direct evidence of a priming effect after urine application. However, the quantity of mineral N in lowland soils increased with time, presumably due to a priming effect. This effect was not observed in hill country soils.

The AMN and SMB-N increased after urine application indicating immobilisation of urine N. This increase was higher in hill country soils.

The mineral N changes with time after urine application varied between the soils. This variation could be explained by the variation of nitrification rates. Soils collected from lowland sites showed greater nitrification rates than soils collected from hill country. In hill country, soils collected from campsites had higher nitrification rates than the soils collected from steep slopes. The history of N application, C/N ratio of the soil and soil organic matter quality are likely factors influencing this variation in nitrification.

Resin adsorbed N demonstrated similar patterns of mineral N change to those indicated by 0.5M K_2SO_4-extractable N. In addition, the relationships developed between resin adsorbed N and 0.5M K_2SO_4-extractable N in the current experiment were in reasonable

agreement with the relationships developed in the field experiment described in Chapter 5. However, the relationships between resin adsorbed NO_3^--N and 0.5M K_2SO_4-extractable NO_3^--N showed considerable variability between soils.

CHAPTER 7

MODELLING THE NITROGEN CYCLE IN SHEEP-GRAZED NORTH ISLAND HILL COUNTRY PASTURE

7.1 Introduction

The aim of this chapter was to apply the major research findings from the preceding chapters, and information available in the Review of Literature (Chapter 2), to study the N cycle in sheep grazed, North Island, hill country pastures.

The N cycles within landscape units of contrasting slope and aspect in hill country pasture were developed using a simple model developed in Microsoft Excel. The model was developed using the assumptions for the above ground N balance described in Section 2.3, and using the assumptions discussed in the later sections of this Chapter for the below ground components of the N cycle. The model was constructed on yearly time step.

The major purpose of the model was to develop a N balance for a hill country paddock that contained steep slopes (s), easy slopes (e) and flat campsites (c). The N cycle within each of these topographic units was developed and then these individual cycles were combined to provide an overview of the N cycle in the whole paddock.

7.2 Model inputs and development

Initially this model was developed for the notional 1 ha hill country paddocks described in Section 2.3. These notional north- and south-facing paddocks were assumed to have the same proportion of flat (campsite), easy and steep slopes as one of the paddocks investigated by Gillingham (1978) in his detailed study of P cycling in hill country. The relative areas (A) of these 3 slope categories in the paddocks were: campsites (A_c, 12.2%), easy slopes (A_e, 45.5%) and steep slopes (A_s, 42.3%).

Annual pasture production (*DM*, kg/ha/yr) on each slope and aspect was as measured by Blennerhassett (2002) at the Waipawa site (Section 2.2.1 and Table 7.1). Similarly, the percentage (%) of clover in the sward (*C*) was as measured by Blennerhassett (2002).

N fixation (kg N/ha/yr) by legumes (*NFL*) was assumed to be proportional to clover growth, although the proportionality constant varied between campsites and sloping sites (Ledgard *et al.*, 1987) (Section 2.3.2). Thus for each slope category,

$$(NFL)_c = ((DM)_c)\ ((C)_c/100)\ (0.03) \qquad (7.1)$$

$$(NFL)_e = ((DM)_e)\ ((C)_e/100)\ (0.04) \qquad (7.2)$$

$$(NFL)_s = ((DM)_s)\ ((C)_s/100)\ (0.04) \qquad (7.3)$$

where the constants (0.03 and 0.04) are as suggested by Ledgard *et al.* (1987).

The amount of N taken up (kg N/ha/yr) by pasture (*NP*) was calculated in the model from annual pasture dry matter production (*DM*) and herbage N concentration (%) (*HN*). These data for *DM* production and herbage N concentration (*HN*) were obtained from the experimental results of Blennerhassett (2002) who had measured pasture production in summer-dry hill country at the Waipawa site. Thus for campsites,

$$(NP)_c = (DM)_c\ ((HN)_c/100) \qquad (7.4)$$

Similar calculations were done for steep and easy slopes.

The measured *DM* production consisted of both grass and clover. Hence, to estimate the N uptake (kg N/ha/yr) from soil (*NS*) the amount of legume-fixed N was deducted from the plant N uptake. As an example, for campsites,

$$(NS)_c = (NP)_c - (NFL)_c \qquad (7.5)$$

The percentage pasture utilisation (*PU*) (Section 2.3.4) for each slope was as in Gillingham (1978) and was used to estimate the amount of pasture N eaten (kg N/ha/yr) by the animals (*NEA*). The plant N not utilised by animals (kg N/ha/yr) was considered to be added to the soil organic matter through the litter (*LN*). Thus for campsites,

$$(NEA)_c = (NP)_c ((PU)_c /100) \quad (7.6)$$

and,

$$(LN)_c = (NP)_c - (NEA)_c \quad (7.7)$$

As mentioned in Section 2.3.6 it was assumed that 10% of the N eaten by animals (*NEA*) was retained in animal products (*NAP*, kg N/ha/yr) and the rest was excreted (*NEX*, kg N/ha /yr). For campsites,

$$(NAP)_c = (NEA)_c (10/100) \quad (7.8)$$

$$(NEX)_c = (\mathrm{NEA})_c - (NAP)_c \quad (7.9)$$

Similar calculations were done for steep and easy slopes.

It was pointed out in Section 2.3.7 that the dung and urine distribution is uneven in hill country pasture paddocks. An example of estimating the dung and urine N deposited on each site was presented in Section 2.3.7. The same principle was used in the model to estimate dung and urine received by each site. This is explained below.

The total amount of excretal N added to the paddock (*TEN*, kg N/ha/yr) is given by

$$TEN = [(NEX)_c (A)_c/100] + [(NEX)_e (A)_e/100] + [(NEX)_s (A)_s/100] \quad (7.10)$$

Dung & Urine (*DU*) return to a particular site (e.g. kg N/ha of campsite/yr) from the total excretal N returned to the paddock (*TEN*) was calculated using the percentage excreta return to each site and the percentage land area (*A*).

As pointed out in Section 2.3.7, Gillingham (1978) measured the dung P distribution in two hill country paddocks (Section 2.3.4). His data were used to estimate the proportion of the excreta deposited on the whole paddock that were deposited on each slope category (*E*).

$$(DU)_c = [((E)_c /100) (TEN)]/ ((A)_c /100) \quad (7.11)$$

$$(DU)_e = [((E)_e /100) (TEN)]/ ((A)_e /100) \quad (7.12)$$

$$(DU)_s = [((E)_s /100) (TEN)]/ ((A)_s /100) \quad (7.13)$$

It was assumed in this model that 71% of excretal N is deposited as urine N (*UN*) and 29% as dung N (*DN*). Lambert *et al.* (1992) reported excretal N partitioning of 65%, 71% and 78% in urine for unimproved, low P fertiliser, and high P fertiliser hill country pastures respectively. The average of these values, 71% was used in these N balances. The bulk of dung N is in organic form. (Haynes & Williams, 1993). Thus, all N in dung was assumed to be incorporated into soil organic matter and released to soil slowly. The dung and urine N added to each site (kg N/ha/yr) was calculated as

$$(UN)_c = (DU)_c\ (71/100) \qquad (7.14)$$

$$(DN)_c = (DU)_c\ (29/100) \qquad (7.15)$$

with similar equations for the other slope categories.

It was evident in Chapter 3 and 5 that ammonia volatilisation was a major pathway of N loss from urine patches in hill country pastures. The losses ranged from 21% to 51% of added urine N in the two experiments. Thus, it was assumed in the model that 33% (mean of the volatilisation losses from two experiments) of added urine N is lost by ammonia volatilisation from hill pasture. It is interesting to note that these substantial losses were observed from the experiments conducted in moist winter conditions. Thus, the volatilisation estimation might be conservative, as higher volatilisation would occur in summer. The N lost through ammonia volatilisation (*VN*, kg N/ha/yr) was calculated as

$$(VN)_c = (UN)_c\ (33/100) \qquad (7.16)$$

with similar equations for the other slope categories.

Generally, leaching hasn't been considered as a major N loss mechanism in hill country pastures (Sakadevan *et al.*, 1993). This was supported by the results of Chapter 3, which indicated very low nitrification and little potential for loss of N by leaching. However, the experiment described in Chapter 5 revealed that leaching could be a major N loss mechanism in some hill country sites, especially in stock campsites. The incubation experiment described in Chapter 6 demonstrated that nitrification is variable across the tested hill country sites. Nitrification tended to be high in flat campsites. Soils collected

from Waipawa stock campsites for the incubation experiment showed nitrification after an initial lag period. Soils collected from the Waipawa steep slopes for the incubation experiment had very low nitrification rates. The soils collected from Ballantrae steep slopes however had reasonable nitrification rates. An attempt was made to discuss this variation in nitrification in Chapter 6. However, finding the exact cause for this variation is a major research area for future work.

Based on the leaching model results discussed in Chapter 5, it was assumed that 30% of added urine N to hill country campsites is leached. No leaching was considered to occur from sloping sites in hill country, based on the low nitrification rates observed in Chapter 6. Although, it was evident in Chapter 5 that some steep slopes in hill country may lose urine N through leaching, steep sites actually receive little urine and thus, even if leaching is occurring the absolute amounts would be small. The amount of N lost through leaching from campsites (*LN*, kg N/ha/yr) was calculated as

$$(LN)_c = (UN)_c\,(30/100) \qquad (7.17)$$

To calculate net mineralisation in the model it was assumed that although the size of the mineral N pool may fluctuate widely from day to day, as a result of urine addition and various loss mechanisms, on an annual basis the pool size would be low and constant. In other words, inputs would equal outputs when summed over a year. With this assumption, net mineralisation N (*NM*, kg/ha/yr) could be calculated as the difference between the other inputs to the mineral N pool (urine, atmospheric deposition) and the losses from that pool (plant uptake, volatilisation and leaching) according to the equation.

$$(NM)_c = (NS)_c - [\,[(UN)_c + (NAD)_c] - [(VN)_c + (LN)_c]\,] \qquad (7.18)$$

where *NAD* is N added by atmospheric deposition (kg N/ha/yr)

7.3 Model outputs

First, the model was used to predict the N balances for each slope category under the same conditions and assumptions described in Section 2.3. The input parameters are summarised in Table 7.1. The complete N cycles are illustrated in Fig 7.1 and 7.2.

Table 7.1 Data used to evaluate the model. **G**= measured data of Gillingham (1978), **B**= measured data of Blennerhassett (2002), **T**= Findings from this thesis.

A) North aspect

Input	Campsites	Easy slopes	Steep slopes
Land area (%) [G]	12.2	45.5	42.3
Pasture DM Production (kg/ha/yr) [B]	5543	6671	2406
N concentration in herbage (%N) [B]	2.7	2.73	2.2
Clover in herbage (% by weight of total DM) [B]	5	11	0
Pasture utilisation (%)[G]	79.2	82.8	76.2
Proportion of total excretal N deposited on slope category (%)[G]	66.6	28.6	4.8
Proportion of urine N leached (%) [T]	30	0	0
Proportion of urine N volatilised (%)[T]	33	33	33

B) South aspect

Input	Campsites	Easy slopes	Steep slopes
Land area (%)[G]	12.2	45.5	42.3
Pasture DM Production (kg/ha/yr) [B]	5543	4574	2467
N concentration in herbage (%N) [B]	2.7	2.5	2.3
Clover in herbage (% by weight of total DM) [B]	5	2	2
Pasture utilisation (%)[G]	79.2	82.8	76.2
Proportion of total excretal N deposition on slope category (%)[G]	66.6	28.6	4.8
Proportion of urine N leached (%)[T]	30	0	0
Proportion of urine N volatilised (%)[T]	33	33	33

In addition, the following inputs were unchanged in all model analyses described in this chapter.

Non symbiotic N fixation	= 13 kg N/ha/yr
Atmospheric N deposition	= 3 kg N/ ha/yr
Percentage of excretal N deposited in dung	= 29%
Percentage of excretal N deposited in urine	= 71%
Percentage of ingested N retained in animal products	= 10%

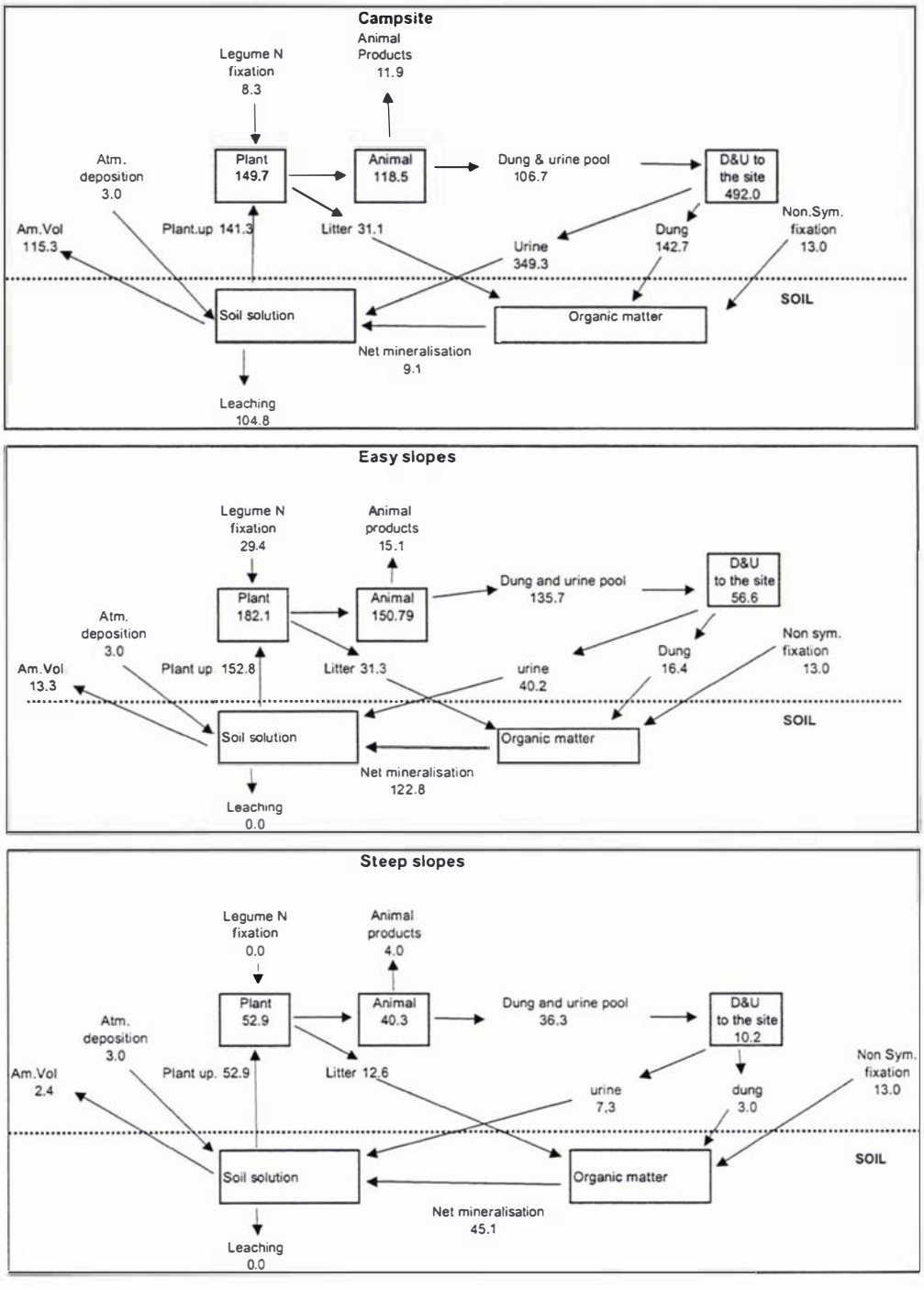


Fig. 7.1 Modelled N cycle in a hill country paddock with northerly aspect (12.2% campsite, 45.5% easy slope, 42.3% steep slope). All values kg N/ha/yr.

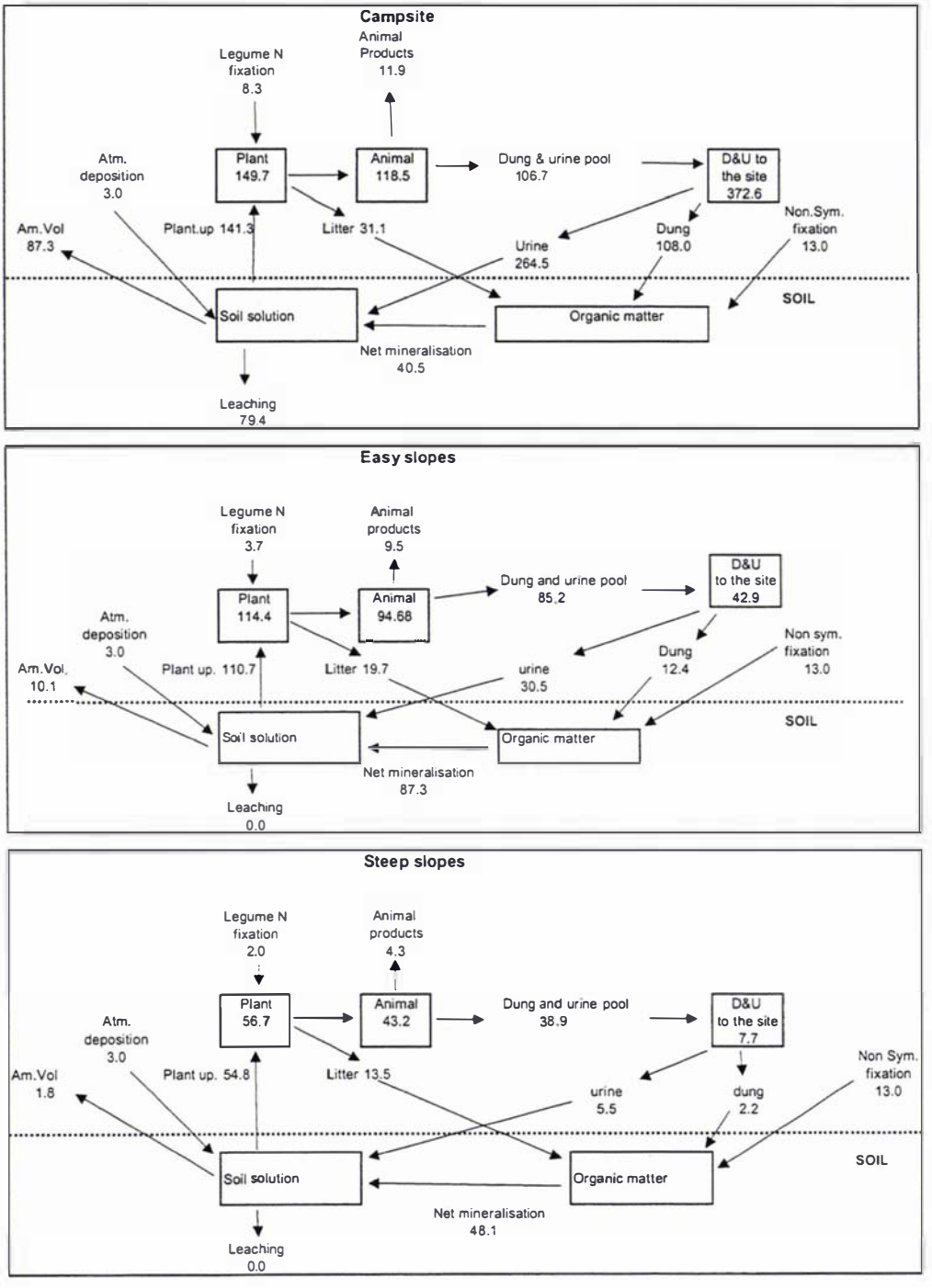


Fig. 7.2 Modelled N cycle in a hill country paddock with southerly aspect (12.2% campsite, 45.5% easy slope, 42.3% steep slope). All values are kg N/ha/yr.

Table 7.2 Modelled N balances for individual slope categories and for the overall paddocks taking into account that campsites, easy slopes and steep slopes occupy 12.2%, 45.5% and 42.3% of the paddock area respectively.

A) North aspect

INPUT (kg N/ha/yr)	**Campsite**	**Easy slopes**	**Steep slopes**
Legume N fixation	8.3	29.4	0.0
Non.Symb.fixation	13.0	13.0	13.0
Atm.deposition	3.0	3.0	3.0
Total	24.3	45.4	16.0
OUTPUT (kg N/ha/yr)			
Animal products	11.9	15.1	4.0
Animal transfer	-385.3	79.1	26.1
Ammonia volatilisation	115.3	13.3	2.4
Leaching	104.8	0.0	0.0
Total	-153.4	107.4	32.5
N surplus (Input-Output) kg N/ha/yr	177.7	-62.1	-16.5

N Balance for overall 1ha paddock

INPUT kg N/yr		**OUTPUT kg N/yr**	
Campsite	3.0	Animal products	10.0
Easy slope	20.6	Ammonia volatilisation	21.1
Steep slope	6.8	Leaching	12.8
Total	**30.4**	**Total**	**43.9**
N BALANCE (kg N/ha/yr)		**-13.5**	

B) South aspect

INPUT (kg N/ha/yr)	**Campsite**	**Easy slopes**	**Steep slopes**
Legume N fixation	8.3	3.7	2.0
Non.Symb.fixation	13.0	13.0	13.0
Atm.deposition	3.0	3.0	3.0
Total	24.3	19.7	18.0
OUTPUT (kg N/ha/yr)			
Animal products	11.9	9.5	4.3
Animal transfer	-265.9	42.3	31.2
Ammonia volatilisation	87.3	10.1	1.8
Leaching	79.4	0.0	0.0
Total	-87.4	61.8	37.3
N surplus (Input-Output) kg N/ha/yr	111.7	-42.2	-19.3

N Balance for overall 1 ha paddock

INPUT kg N/yr		**OUTPUT kg N/yr**	
Campsite	3.0	Animal products	7.6
Easy slope	8.9	Ammonia volatilisation	16.0
Steep slope	7.6	Leaching	9.7
Total	**19.5**	**Total**	**33.3**
N BALANCE (kg N/ha/yr)		**-13.7**	

The model suggests that for the notional 1 ha paddocks on both north and south aspects, there is an annual negative N balance of approximately 14 kg N/ha over the whole paddock (Table 7.2). In other words, the N losses due to retention in animal products, leaching and volatilisation were slightly greater than the N inputs by legume N fixation, non-symbiotic fixation and atmospheric deposition.

The main driving force behind these losses is N transfer from sloped areas to campsites and then high losses of N from the campsites through ammonia volatilisation and leaching.

The fact that N is transferred from sloping areas to flat campsites in hill country is well documented in the literature (Gillingham and During, 1973; Gillingham, 1978; Ledgard *et al.*, 1987; Ledgard, 2001). Nevertheless, Ledgard (2001) pointed out that these significant losses of N due to transfer of excreta are ignored in many published estimates and models of N flows and balances in grazed pastoral systems.

Ledgard (2001) tabulated a N balance for a hill country paddock that had 45% of the area as steep slopes (>20°), 40% of the area as easy slopes (10-20°) and 15% of the area as campsites. He reported an annual N input (legume + non symbiotic N fixation) of 43 kg N/ha and an annual output (animal products + transfer to farm lanes and yards) of 20 kg N/ha, resulting in a N surplus of +23 kg N/ha/yr. However, he did not consider the N losses from campsites where large amounts of urine N are deposited. Similar N surpluses were predicted in Chapter 2 when only the above ground components were considered.

It can be seen that the model predicted marked differences in N balance between slope categories in the notional paddocks (Table 7.2). In the steep slopes of north and south aspects, the model predicted annual negative N balances of 17 and 19 kg N/ha respectively. In the easy slopes of both aspects, the annual N balance was more negative than for the steep slopes. In the easy slopes, the predicted annual N balances were - 62 and - 42 kg N/ha for north and south aspects respectively. The model predicted annual N balances for campsites that were positive, indicating net N gain. The annual N balances for campsites were 178 and 112 kg N/ha for north and south aspects respectively.

The magnitude of any N deficit results from an interaction between N inputs via fixation etc, N uptake by pasture, the extent of pasture utilisation by animals and the redistribution of excreta between different slope categories. Thus in the modelled notional paddock, the greater N losses from easy slopes than steep slopes results from the greater pasture production on easy slopes as measured by Blennerhassett (2002) at the Waipawa site and the higher pasture utilisation on easy slopes as measured by Gillingham (1978). Although N fixation as estimated from the data of Blennerhassett (2002) was greater on the easy slopes, N losses due to animal transfer and volatilisation were proportionately higher on these slopes

Other works have come to similar conclusions. Ledgard *et al.* (1987) predicted that on steep slopes accumulation of N would be very slow or could be negative under high pasture utilisation. They stated that this was because on sloped sites, N was removed by grazing animals with little return in animal excreta (Fig.7.1 and 7.2). In contrast, on campsites an annual net N gain was observed due to N accumulation through animal transfer. Gillingham and During (1973) used dung distribution measurements to estimate that campsites received a net gain of 217 kg N/ha /yr, which was transferred from steeper sites.

Finally, as mentioned in Section 2.3.8, Ledgard (2001) reported a similar N balance for hill country soils. This, gave an opportunity to compare the current model predictions for sloping sites with his estimations.

The negative N balances for steep sites in the current model are 17 and 19 kg N/ha/yr for north and south aspects respectively. These prediction are in close agreement with Ledgard's estimation (-25 kg N/ha/yr) for steep sites.

However, Ledgard (2001) reported a surplus of +15 kg N/ha/yr for easy slopes while the current model is predicting a deficit of – 62 kg N/ha/yr for north easy slopes. This difference between the two models needs to be explored further.

If the N concentration in herbage was assumed to be 2.5%, the annual plant uptake of N for the reported pasture DM production of Ledgard (2001) would be 175 kg N/ha/yr for easy sites. This is similar to the current model's input of 182 kg N/ha/yr of plant N

uptake for easy slopes on the north aspect. However, there was a difference in N inputs (legume N fixation + non symbiotic fixation + atmospheric deposition) between the current model for north easy slopes (45 kg N/ha/yr) and the N input (65 kg N/ha/yr) reported by Ledgard (2001). The N removal in animal produce was 15 kg N/ha/yr in both Ledgard's estimates and in the current model. The volatilisation losses were not considered in Ledgard's balance while the current model estimated 13 kg N/ha/yr was lost through ammonia volatilisation from urine deposition on north easy slopes.

The other major difference is the amount of N transfer. The current model's prediction for N loss from easy slopes by animal transfer (79 kg N/ha/yr) is twice as high as Ledgard's estimation (35 kg N/ha/yr). N losses through animal transfer are mainly dependent on the excretal distribution and pasture utilisation on different slope categories. However, there was not sufficient information about these components in the model of Ledgard (2001) to identify where the differences in predicted N transfer between the 2 models occurred.

Comparison of the current model and that of Ledgard (2001) demonstrates that the exact level of N surplus or deficit on a particular slope category will depend on the levels of N input, pasture growth rate, pasture utilisation and excretal transfer that are assumed. What is clear from both models however, is that there are likely to be large areas of hill country where virtually all of the N added to the system by N fixation and other processes is lost and it is even likely that some areas may experience an annual N deficit. Clearly however such a situation could not persist for an extended period as soil reserves would become depleted and DM production would decrease until losses again matched inputs. The implications of this to the sustainability of hill country farming are discussed further in Chapter 8.

7.4 Sensitivity of the model to different conditions

The results summarised in Fig. 7.1 and 7.2 and Table 7.2 apply to the inputs and assumptions used in the model. It would be helpful however to check the model's sensitivity to different combinations of model inputs.

Gillingham (1978) described the P cycle for a second paddock with another combination of slope categories in hill country. This paddock included campsites (20.1%), easy slopes (55.7%) and steep slopes (24.2%). The measured pasture utilisations were 77.2%, 86.5% and 80.8% for campsites, easy slopes, and steep slopes respectively. The percentages of excreta deposited to the sites were 75%, 24% and 1% for campsites, easy slopes, and steep slopes respectively.

When these combinations were used for the model with the same model inputs for the north aspect, there wasn't any major difference in the outcome with regard to the paddock's overall N balance (Fig. 7.3). However, within the contrasting slope categories of the paddock the model indicated that when the campsite area is increased in the paddock, the annual net N surplus in campsites (expressed as kg N/ha/yr) was decreased. Similar results were reported by Gillingham (1978) for the P balance under the same two contrasting land area combinations. He observed a 119 kg P/ha/yr gain when the campsite area was 12.2% of the total area and a gain of 60.7 kg P/ha/yr in campsite areas when they made up 20.1% of the area.

7.4.1 Impact of excretal distribution

As mentioned before, the negative N balances predicted on sloping sites and in the paddock as a whole are mainly due to N transfer by animals. This is mainly governed by the proportion of the total excreta return to the paddock that is assumed to be deposited on each slope category.

In the model to date, these proportions were as measured by Gillingham (1978) in his two experimental paddocks. Thus, in the first paddock considered, 66.6% of the total excreta deposited on the paddock was assumed to be deposited on flat campsites, 28.6% on easy slopes and 4.8% on steep slopes. To check the sensitivity of the model to the pattern of excretal deposition, the model was re-run with a contrasting pattern of 10% of the total excreta deposited on flat campsites, 50% on easy slopes and 40% on steep slopes.

It is evident from Fig. 7.4 that the assumed pattern of excretal distribution plays a major role in deciding the negative or positive N balance on each slope, as well as in the whole paddock.

When the proportion of excreta deposited on campsites is very low, the N balance has changed to negative on campsites. On easy sites, when the proportion of excreta deposited was increased the negative balance was decreased by half, while on steep sites the negative balance changed to positive. When the whole paddock was considered, the negative N balance changed from -14 to -3 kg N/ha/yr.

Therefore, the model clearly demonstrates that any attempt to quantify the N balance in hill country paddocks should consider the excretal distribution pattern on the paddock or block concerned.

7.4.2 Impact of pasture utilisation

The pasture utilisation values reported by Gillingham (1978) were much higher than the pasture utilisation of 50% reported by Chapman *et al.* (1984). Ledgard *et al.* (1987) also assumed 50% pasture utilisation to estimate soil nitrogen accumulation on steep sites. Thus, it is interesting to check the model outcomes when the pasture utilisation is assumed to be at a 50% level. The model was also run to check the outcome under very low (25%) pasture utilisation.

It can be seen from Fig. 7.5, that the assumed value of pasture utilisation had a major effect on N balances in hill country. As mentioned before, when the measured (Gillingham, 1978) high pasture utilisation was used in the model, the overall paddock had a negative N balance. When a conservative pasture utilisation (50%) was assumed, the model predicted a slight accumulation of N over the whole paddock. A more substantial accumulation of N over the whole paddock occurred if a very low pasture utilisation (25%) was assumed. These results highlight the importance of pasture utilisation on the fate of N in hill country pasture, as considerable N accumulation can only occur when pasture utilisation is very low. As more pasture N cycles through the animal, there are higher losses through transfer, leaching and volatilisation.

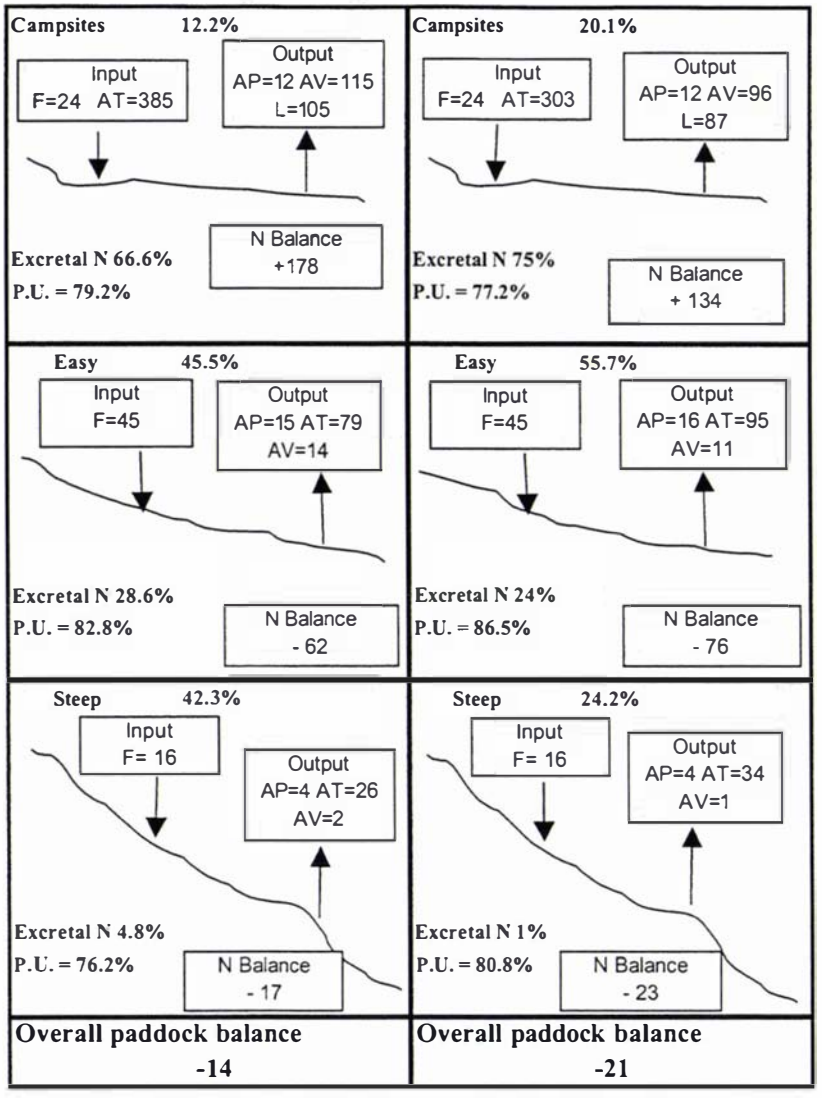


Fig. 7.3 Modelled N balance for two hill country paddocks with contrasting proportions of steep, easy and flat land. All values are kg N/ha/yr. F = N input by legume N fixation, non symbiotic fixation and atmospheric deposition, AT = Animal transfer, AP = Animal products, AV = Ammonia volatilisation, L = Leaching, P.U. = Pasture utilisation, Excretal N = Percentage of excretal N deposited on each slope category in that paddock.

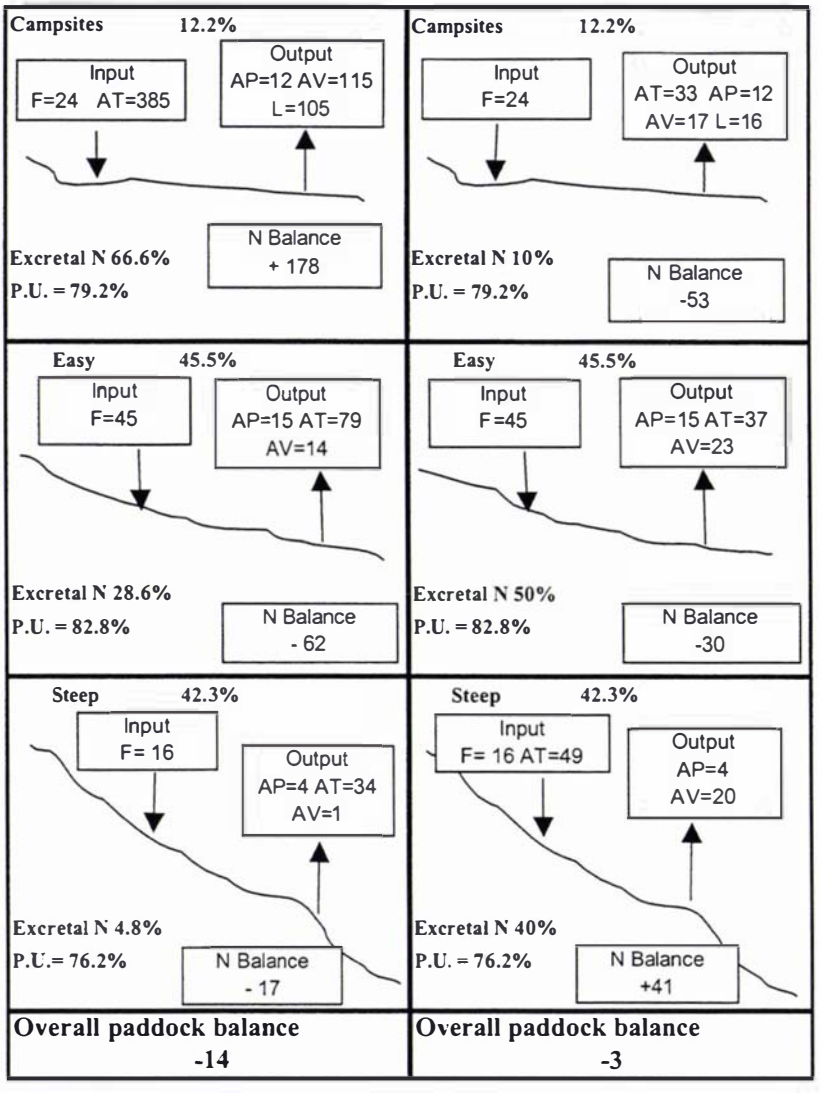


Fig. 7.4. N Balances for hill country paddocks with different excretal distributions. Values are kg N/ha/yr. Pasture DM production, proportion of clover in herbage and N concentration in herbage were as for the north aspect paddock in Table 7.1A. F = N input by legume N fixation, non symbiotic fixation and atmospheric deposition, AT= Animal transfer, AP = Animal products, AV = Ammonia volatilisation, L = Leaching, P.U. = Pasture utilisation, Excretal N = percentage of excretal N deposited on each slope category in that paddock.

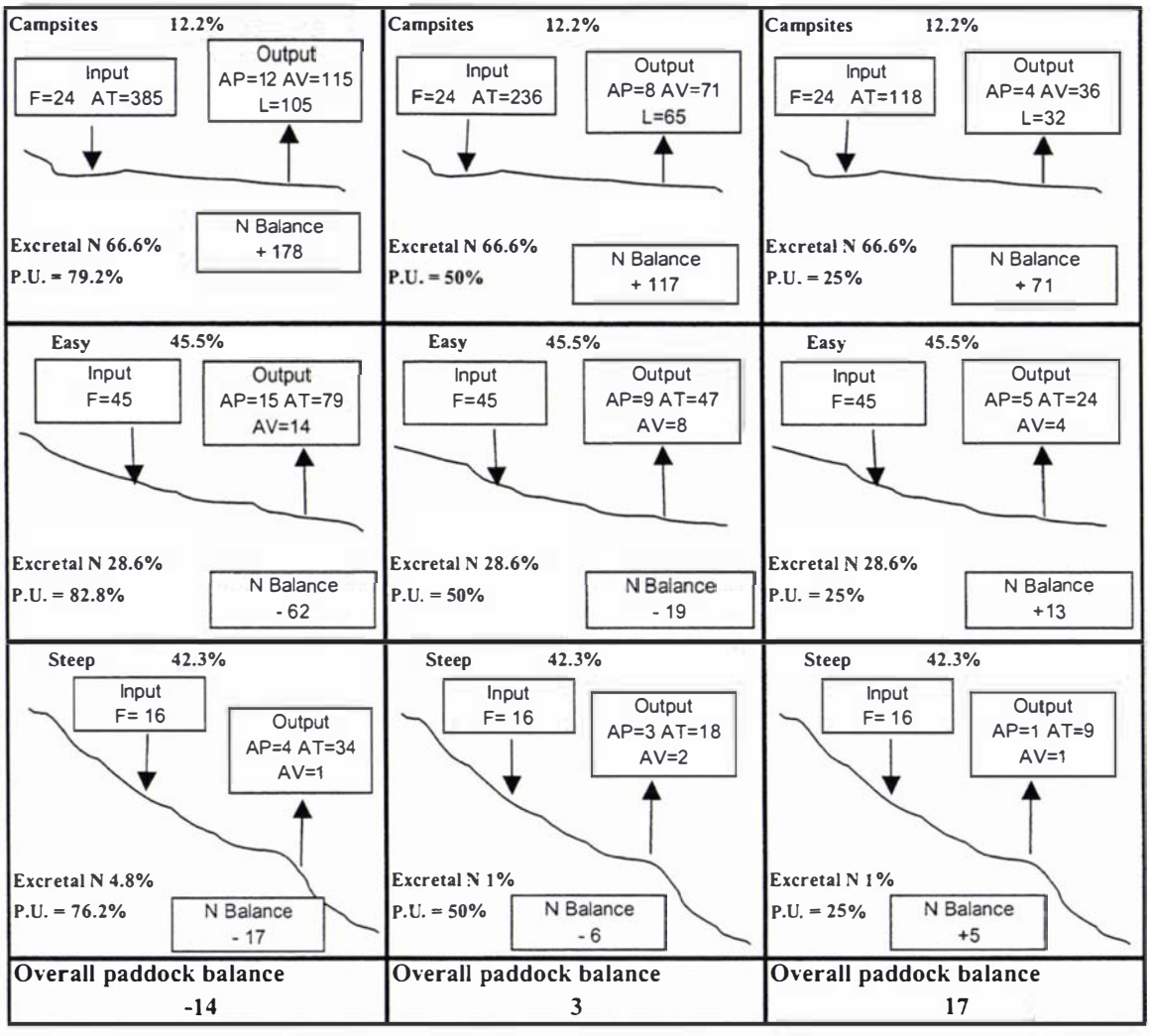


Fig.7.5 N Balances for hill country paddocks with different pasture utilisations. Values are kg N/ha/yr. Pasture DM production, proportion of clover in herbage and N concentration in herbage were as for the north aspect paddock in Table 7.1 A. F = N input by legume N fixation, non symbiotic fixation and atmospheric deposition, AT = Animal transfer, AP = Animal products, AV = Ammonia volatilisation, L = Leaching, P.U. = Pasture utilisation, Excretal N = percentage of excretal N deposited on each slope category in that paddock.

7.4.3 Impact of soil fertility, as affected by P fertiliser addition.

Blennerhassett (2002) measured pasture and clover production on different land slopes under low P as well as high soil P fertility regimes. This gave an opportunity to check the effect of high P fertiliser addition on N cycling in hill soils using the current model.

For the low P conditions the same data as in Table 7.1 were used, except that pasture utilisation was assumed to be 50% on all slope categories. The input data for the high P paddocks are listed in Table 7.3.

Table 7.3 Data used to evaluate the model on a paddock with a high level of P fertility. **G** = measured data of Gillingham (1978), **B** = measured data of (Blennerhassett (2002), **T** = Findings from this thesis.

A) North aspect

Input	Campsites	Easy slopes	Steep slopes
Land area (%)[G]	12.2	45.5	42.3
Pasture DM Production (kg/ha/yr) [B]	6078	9022	2740
N concentration in herbage (%N) [B]	3.2	2.6	1.7
Clover in herbage (% by weight of total DM) [B]	1	14	0
Pasture utilisation (%)[G]	50	50	50
Proportion of total excretal N deposited on slope category (%)[G]	66.6	28.6	4.8
Proportion of urine N leached (%)[T]	30	0	0
Proportion of urine N volatilised (%)[T]	33	33	33

B) South aspect

Input	Campsites	Easy slopes	Steep slopes
Land area (%)[G] *	12.2	45.5	42.3
Pasture DM Production (kg/ha/yr) [B]	6078	5189	3785
N concentration in herbage (%N) [B]	3.2	2.7	2.5
Clover in herbage (% by weight of total DM) [B]	1	10	7
Pasture utilisation (%)[G]	50	50	50
Proportion of total excretal N deposited on slope category (%)[G]	66.6	28.6	4.8
Proportion of urine N leached (%)[T]	30	0	0
Proportion of urine N volatilised (%)[T]	33	33	33

Blennerhassett's (2002) data revealed that at the Waipawa site, addition of high rates of P fertiliser increased pasture growth and clover production (compare Table 7.1 and 7.3). In the model, this increased clover production resulted in higher inputs through N fixation. However, the N balances illustrated in Fig 7.6 and 7.7 clearly reveal that under both the low P and high P fertiliser regimes the overall predicted N balances remain close to zero, indicating all the annual N inputs are lost from the system. Although adding P fertiliser increased N fixation, when this N goes through the animal cycle it increases N losses too.

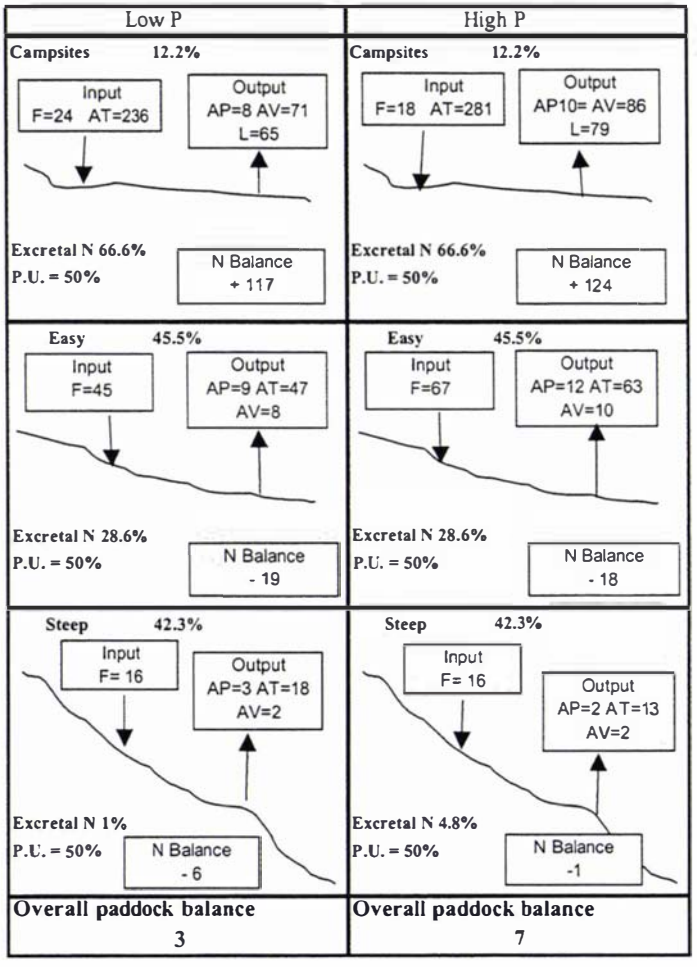


Fig. 7.6 N Balances for north aspect hill country paddocks under low P and high P conditions. Values are kg N/ha/yr. F = N input by legume N fixation, non symbiotic fixation and atmospheric deposition, AT = Animal transfer, AP = Animal products, AV = Ammonia volatilisation, L = Leaching, P.U. = Pasture utilisation, Excretal N = percentage of excretal N deposited on each slope category in that paddock

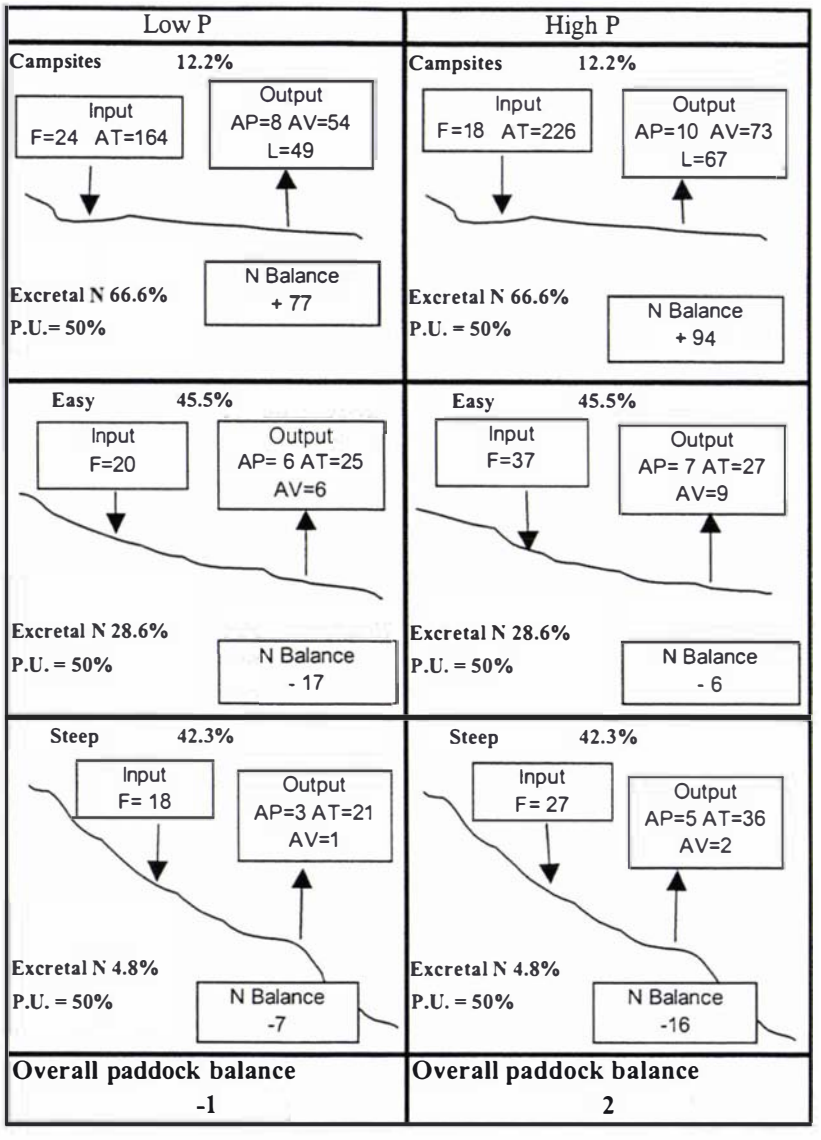


Fig. 7.7 N Balances for south aspect hill country paddocks. Values are kg N/ha/yr. F = N input by legume N fixation, non symbiotic fixation and atmospheric deposition, AT = Animal transfer, AP = Animal products, AV = Ammonia volatilisation, L = Leaching, P.U. = Pasture utilisation, Excretal N = percentage of excretal N deposited on each slope category in that paddock

These results are supported by the results of Blennerhassett (2002). He observed the N limitation in annual pasture yield (difference in pasture yield between N unlimited (potential) and N limited sites) was relatively even between low P and high P sites. He observed the highest pasture yield limitation in the HPNE (high P north easy) site,

which also showed the highest negative annual N balance in the current model (Fig. 7.4). Interestingly, his clover growth data showed that the highest annual clover growth was also recorded on the HPNE site. Thus he commented that in hill pastures, N is deficient to such an extent that even sites which have the best conditions for clover growth, are still severely restricted by N supply.

These results draw attention to a key issue with respect to N fertility in hill country pasture. In hill country, farmers apply P fertiliser to increase clover growth to overcome N deficiency by increasing the N fixation. However as mentioned above, when this increased N in herbage goes through the animal cycle it also increases the N losses. Hence, adding P fertiliser may increase annual pasture growth but residual soil N fertility remains the same. Therefore, the pasture remains highly N responsive.

Therefore, as Blennerhassett (2002) noted, the potential for N fertiliser application on hill country pasture is high and the question arises as to the value of large P fertiliser applications to overcome N deficiency through clover growth.

7.5 Improvement of efficiency of hill country N cycle

A framework for considering the efficiency of nutrient cycling is outlined below. It is based on two simple propositions.

- Sustainable management of hill country pastures requires that nutrients lost from the soil/plant/animal system in animal products, or through other loss processes, must be replaced. For some nutrients such as potassium, the nutrients may be supplied by the weathering of parent materials. For nutrients such as N however, that are not present in large quantities in soil parent materials, annual inputs are required from outside the system.

- The purpose of hill country pastoral systems is to produce animal products. Therefore a measure of the efficiency of N use might be the proportion of N inputs to the system that are converted to animal products.

Applying this concept to the modelled data in Table 7.2 for paddocks with campsites, easy slopes and steep slopes occupying 12.2%, 45.5% and 42.3% of the paddock area respectively, gave N efficiencies of 33% and 39% for north and south facing paddocks.

This calculation assumed N inputs from fixation and atmospheric deposition 30.4 and 19.5 kg N/ha/yr, for north and south facing paddocks respectively. However the data in Table 7.2 also suggested that there was a net negative N balance of 13.5 kg N/ha/yr for the north facing paddock, and 13.7 kg N/ha/yr for the south facing paddock. These notional deficits would be made up by "mining" the reserves of N in the soil organic matter, and they could therefore be considered as another input. When these inputs from soil reserves are included in the total N inputs, the estimated efficiency of N use drops to 23% for both the north and south facing paddocks.

Clearly, these efficiencies of N use are low, and theoretically at least, there is considerable room for improvement. This improvement could be achieved in a number of ways.

In the model it was assumed that only 10% of the N ingested by grazing animals was retained in animal products. This estimate was similar to those of a number of other workers (Gillingham, 1978; Lambert *et al.*, 1982a). Any processes that increase the proportion of ingested N that is retained in animal products will immediately increase the efficiency of the N cycle. The use of forages high in condensed tannins (Waghorn *et al.*, 1998) shows promise in this regard.

Efficiency of N use is also dependent on the number of times N excreted by the animal is retained in the soil for the next cycle of uptake by pasture, and ingestion by the animal. If there are no losses, other than in animal products, then eventually all the added N will be retained by the animal and the efficiency of N use will be 100%.

Losses from the system occur in two ways. Processes such as volatilisation, denitrification and leaching represent an immediate, direct loss from the system. In contrast, animal transfer to camp areas does not necessarily represent a total loss from the system, as the N could still potentially be taken up by plants. If however, the annual input of N to camp areas is larger than the maximum amount of N that could be taken

up by pasture, given the existing environment conditions, then some of this transfer to camp areas does represent an effective loss of N from the system.

In addition, it is apparent that soil conditions in camp areas, particularly nitrification activity, are such that urine N transferred to these sites is at high risk of loss by leaching.

A key therefore to improving the efficiency of N use in hill country, is to reduce transfer to camp areas. If this could be achieved the benefits would be two-fold. Firstly, a greater proportion of the paddock would receive an input of urine N to offset the chronic N deficiency of hill country pastures. Secondly, the soil conditions on slopes are likely to be less conducive to rapid nitrification and subsequent loss of the applied N.

Subdivision of paddocks and grazing management offer some potential for minimising N transfer to stock campsites. These ideas are explored further in Chapter 8.

CHAPTER 8

SUMMARY AND IMPLICATIONS FOR FUTURE RESEARCH

In New Zealand, the traditional way to build up N fertility in pasture soils has been to apply P fertiliser to provide adequate fertility for legume growth. These legumes then provided N through biological nitrogen fixation. However, studies conducted in hill country pastures (Luscombe, 1980; Ball and Field, 1982; Lambert and Clark, 1986; Clark and Lambert, 1989; Gillingham *et al.*, 1998; Blennerhassett, 2002) have revealed that these pastures are still highly N responsive. Thus, N fertiliser application to hill country pastures has been suggested as a cost effective way of boosting production.

Some scientists have gone further, suggesting precise aerial fertiliser application on hill country using GIS and GPS techniques (Gillingham *et al.*, 1999). However, to make best use of these new technologies, scientists require more detailed information on N fertility and responsiveness on contrasting topographic land units. This in turn, requires an understanding of the cycling of N in hill country paddocks, and in particular, the role of grazing animals and their excretal returns in that cycle.

The above-ground N balances developed in Chapter 2, demonstrated that N is accumulating in animal campsites that are in flat areas of the paddock, and that N is being depleted from sloped areas. When the whole paddock is considered, these above-ground balances predict that N is conserved in the system. However, whether this predicted N accumulation actually occurs depends on the below ground components of the N cycle, particularly in urine patches.

Previous studies in the literature have revealed that N transformations in urine patches vary with different environmental and soil conditions. Information on N transformations under urine patches in hill country pastures is scarce. The two field experiments and the incubation experiment described in this thesis aimed to broaden the information available on N transformations in urine patches, and to explore the implications of that information to the N cycle in hill country pastures. The major observations are summarised below.

Urine application increased the mineral N availability in soil and this increase lasted about 2 to 3 months. Immediately after urine application, soil mineral N sometimes increased by more than the amount of N added. This was due to a priming effect. The extent of the priming effect was variable across different sites, but if a priming effect is common after urine application, this may lead to accelerated losses of N from the soil organic matter, as well as from the urine N. More work is required on priming effects after urine application to identify exactly what is causing them particularly as the priming effect observed in the field could not be repeated in the laboratory incubation study.

The dominant mineral N form (NH_4^+-N or NO_3^--N) remaining in the urine patch depends on the rate of nitrification. Soil nitrification rates were highly variable across the hill country sites, but were much lower than the nitrification rates existing in more developed, flatland soils.

Within the soils from hill country sites, nitrification rates were higher in soils from flat, camp areas than in soils from steep slopes. In soils from some steep sites (eg. Waipawa), nitrification was virtually negligible. It appears that at least part of this variation can be explained by the previous history of N inputs to the soil. Numerous authors have observed higher nitrification rates in soils that have previously received high inputs of N fertiliser (Jarvis *et al.*, 1989; Jarvis and Barraclough, 1991; Watson and Mills, 1998). In the current study, soils on camp areas would have received regular inputs of urine N that is readily converted to NH_4^+. In contrast, soils on steep slopes receive few inputs of N from external sources – and even the NH_4^+-N released within the soil by mineralisation is competed for strongly by the dominant heterotrophic organisms. These factors together appear to result in inherently low nitrification activity. A significant effect of organic matter quality (C/N, ratio of soil labile organic C to total C) on nitrification was also observed. This variation of nitrification in hill pastures is an important area for future research work, as nitrification is the decisive process governing N losses from denitrification and leaching.

The variation in nitrification activity across the hill country sites led to differential potentials for leaching. The potential for N loss by leaching from campsites in hill

country is high. When the nitrification rate is high, the leaching losses might be as large as 30% of added urine N.

In this study, leaching losses were not measured directly. Rather, a simple model was used to assess the likelihood of leaching being the cause of the apparent loss of NO_3^--N from the soil in the Ballantrae field experiment, reported in Chapter 5. Although a modelling approach, such as that used in Chapter 5, provides a cost effective way of assessing the likely significance of leaching losses, validation measurements will be required at selected sites in future, to check on the reliability of the model. This is important, as it is apparent that the extent of leaching losses determines whether current farming systems are building up the N fertility of hill country pastures.

It appeared from the experiments described in this thesis that the N loss by ammonia volatilisation from urine patches in hill country is substantial, ranging from 21% to 51% of added urine N. These estimated losses were surprisingly large, as the experiments were conducted under winter conditions. However, when these estimated losses were included in the calculation of overall urine N recoveries, the resulting totals were close to 100%, suggesting that the estimated volatilisation losses were reasonable. Future studies are required to confirm whether the measurement technique used to assess the extent of NH_3 volatilisation was accurately calibrated for hill country pastures and also whether the use of synthetic rather than real urine may have affected NH_3 volatilisation.

The experiments described in this thesis confirmed the common view of pasture responsiveness to added urine N. Up to a three fold increase in pasture dry matter production could be expected in urine patches. The N concentration (%) in herbage can also increase by up to 1.7 units in pastures receiving urine, compared to controls. The urine N recoveries by pasture ranged from only 1% to 26% (mean 15%), highlighting the potential for the remaining 74-99% of added urine N to be lost from the soil.

Throughout this thesis it was assumed that urine N not accounted for by the sum of mineral and mineralisable N, together with the urine N lost from soil through plant uptake, leaching and volatilisation, was immobilised to complex organic matter in the soil. This estimated immobilisation into organic matter was large, ranging from 8-57% (mean 35%) of added urine N. The percentage immobilisation was larger from the

lower rate of urine N addition than the higher rate and larger on steep sites than flat sites.

When the above information was incorporated into a simple model of the N cycle in hill country pastures, the crucial role of urine N in determining the overall N balance was highlighted. The uneven urine N distribution within a paddock causes N transfer from sloped areas to flat campsites, resulting in a net negative N balance in sloped areas and a net N gain to campsites. As the N losses by ammonia volatilisation and leaching from campsites are substantial, the overall N outputs from hill paddocks can exceed the N inputs by N fixation.

Key factors in determining whether the overall N balance in hill country paddock is positive or negative include the level of pasture utilisation on different slopes and the actual division of excreta between campsites and the remainder of the paddock. This in turn is determined by paddock topography and aspect.

The N balances developed by this model, using the measured pasture production by Blennerhassett (2002) under low and high P fertility regimes, suggested that any increase in clover growth brought about by P fertiliser addition, had little effect on the residual N fertility of the soil. This is mainly because most N inputs are lost by animal transfer, and through volatilisation and leaching from urine patches.

Blennerhassett (2002) noted that, after climate and its interaction with topography, N availability was far and away the largest determinant of pasture production. In the absence of added N, pasture production was less than half of its potential. He commented that the mineralisable N test appeared to show some potential for estimating N availability, and thereby, pasture production. However, whilst the mineralisable N test can measure the amount of N that is potentially available to be mineralised, it cannot detect what percentage will actually be mineralised under the environmental conditions present in the field.

The *in situ* N measurement by ion exchange resin membrane spikes highlighted in this thesis is a possible alternative method to measure N availability. The N adsorption to resin spikes depends on the soil moisture, soil temperature and soil available N

concentration. Thus, resin spikes may provide a more realistic indication of N availability, under the conditions existing in different hill country aspects and slopes.

In a series of exploratory experiments, resin spikes appeared to be able to identify real differences between soils in their ability to supply N to plants – even when traditional extraction methods using 2 M KCl or 0.5 M K_2SO_4 could not differentiate between the soils. It appears that resins may be capable of detecting fluxes of N through the plant available pool, as well as measuring the size of the pool at the time of sampling. This may provide information on net mineralization of N in hill country pastures.

The resin spikes could also potentially be used to measure downward movement of N. To do this it would be necessary to design a new configuration of spike to measure resin-adsorbed N at different depths.

This thesis contributes to an understanding of the N cycle in hill country pastures in 2 ways. Firstly, it provides information on the transformations of N within urine patches. Secondly, it combines that information with other published data from a variety of sources to construct a N cycle for a notional hill country paddock.

It is apparent from this and earlier work that much of the N fixed by clovers on sloping land is transferred almost immediately to animal camp areas, where varying quantities may be lost through volatilisation and leaching. This transfer and subsequent loss of N places theoretical constraints on the quantity of pasture that can sustainably be produced on sloping land. These ideas were discussed briefly in Section 7.5 and are considered in more detail here.

Consider two extreme, hypothetical situations. In the first, N inputs through fixation are assumed to be 50 kg N/ha/yr, pasture utilisation is 100%, loss in animal product is 10% of N ingested, N concentration in herbage is 3% and excretal N is returned more or less evenly to the grazing area, with no N losses from urine patches. In such a hypothetical situation, the only N loss from the system is in animal product. The 90% of ingested N not retained in the animal is returned to the soil, and can then be used to grow more herbage.

At a herbage N concentration of 3%, the 50 kg/ha of fixed N would support an initial pasture production of 1667 kg DM/ha. In the next cycle, the 90% (45 kg/ha) of remaining N would support a further 1500 kg DM/ha of pasture production. By continuing with this approach it can be demonstrated that, under these hypothetical conditions, the input of 50 kg/ha of fixed N could produce 16,667 kg DM/ha, before all the N was lost in animal product. If environmental constraints were such that this amount of herbage could not be grown annually, then N would accumulate in the soil.
The second hypothetical situation is identical to the first, except that none of the excreted N is returned to the grazed area. In this case, as none of the N is recycled, the input of 50 kg/ha of fixed N would support only 1667 kg DM/ha of pasture production. It is unlikely that environmental constraints would restrict pasture production to below this level, and so N would not accumulate in the soil. Any pasture production in excess of 1667 kg DM/ha would involve "mining" the soil reserves, and would theoretically be unsustainable.

Clearly, any real life situation would fall between these two simplistic scenarios. However this approach may provide a conceptual framework within which the insertion of more realistic data would enable the likely sustainable maximum pasture production in the absence of N fertiliser to be estimated and the potential for N fertilisers to be assessed.

Blennerhassett (2002) assessed the relative impacts of environment and N supply on pasture production at the Waipawa site. He demonstrated clearly that N supply was insufficient to achieve potential pasture production, even at sites where that potential production was severely constrained by environmental factors, such as moisture availability and temperature.

The modelling approach of Blennerhassett (2002) provides a way of assessing potential pasture production on different slopes and aspects, in the absence of any restriction on growth from a shortage of N. If this information is combined with the N cycling approach developed in this and previous chapters, it may be possible to identify areas in hill country where potential growth is high, but the combination of low inputs in N fixation and high losses resulting from high pasture utilisation, low excretal return and

losses from urine patches, mean that N supply will always be a major limitation to pasture growth. It is these areas where N fertilisers may have their greatest application.

To illustrate this approach, data on steep and easy slopes on north and south aspects from the current study were considered within the conceptual framework outlined above. The results are presented in Table 8.1.

Pasture utilisation on all slopes was assumed to be 50% and the proportion of excreted N that was transferred off site was estimated from Fig.7.1 and 7.2. The N inputs through N fixation and deposition on each slope and aspect were as calculated in the previous models in Chapters 2 and 7.

Given these estimated N inputs and animal transfer rates, the predicted sustainable level of pasture production ranged from 1372 kg DM/ha/yr on steep northerly slopes to 6164 kg DM/ha/yr on easy northerly slopes. Sustainable production on southerly slopes was intermediate between these two extremes (Table 8.1).

To demonstrate how these numbers were generated consider the data for steep northerly slopes. At a herbage N concentration of 3% the input of 16 kg of N would support initial production of 533 kg DM. At 50% pasture utilisation with 10% of ingested N retained in animal and 72% of excreted N transferred to off site, 9.4 kg N is returned to the soil and can then be used to grow a further 315 kg DM. Similarly in the next cycle another 5.9 kg N would support another 197 kg DM. This approach was continued until the entire N input was consumed.

These sustainable (in terms of N supply) production levels are very much less than the potential yields as estimated by Blennerhassett (2002) in the absence of any N limitation. These potential yields ranged from 9,000 kg DM/ha/yr on northerly steep sites to 18,000 kg DM/ha/yr on northerly easy sites. The estimated N inputs required to maintain these potential yields on a sustainable basis range from 105 kg N/ha/yr on northerly steep slopes to 196 kg N/ha/yr on northerly easy slopes.

Table 8.1.Comparison between sustainable levels of pasture production with current N inputs and theoretical maximum pasture production in different slope categories of hill country

Slope category	Current estimated N inputs* kg N/ha	Proportion of ingested N that is transferred off site	Sustainable level of pasture production with current N inputs kg DM/ha/yr	Theoretical maximum pasture production if N is non limiting** kg DM/ha/yr	Estimated N input required to maintain theoretical maximum production kg N/ha/yr
NE	67	0.58	6164	18000	196
NS	16	0.72	1372	9000	105
SE	37	0.50	3536	12000	126
SS	27	0.80	2220	11000	134

* Values from Fig.7.6 and 7.7
** measured data of Blennerhassett (2002)

The current N inputs are clearly very much smaller than those required to sustain maximum pasture production. More work is required to quantify inputs through N fixation, to determine the extent to which optimising soil fertility for legume growth can boost N inputs towards the levels needed to enable near-maximum pasture production.

Calculations such as these, that are based on annual balances, do not take into account seasonal nutrient transformations. Thus, even if annual N fixation could be boosted to the levels indicated as being required in Table 8.1, environmental constraints (such as soil temperature) would mean that mineralisation could not provide N at a sufficient rate to allow maximum pasture growth at some times of the year.

Future research should focus on the framework for the N cycle presented in Chapters 2, 7 and 8. As has been demonstrated in this thesis, much information can be derived from related studies in the literature, but there will be a need for focussed experiments to provide information on specific issues. Of particular importance are quantitative estimates of N fixation, animal transfer and losses of excretal N.

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APPENDIX 1

1.1 Statistical significance (*P* Value) of mean comparisons for the total soil (0-15 cm) mineral N levels shown in Fig. 3.6.

Table 1.1.1 Steep site

Treatment comparison	Days after urine application				
	1	6	27	100	142
S0-S200	0.002	0.0003	0.1	0.9	0.9
S0-S400	<0.0001	<0.0001	0.001	0.9	0.9
S200-S400	0.0001	0.001	0.03	0.9	0.9

Table 1.1.2 Flat site

Treatment comparison	Days after urine application				
	1	6	27	100	142
F0-F200	0.002	0.01	0.08	0.7	0.9
F0-F400	<0.0001	<0.0001	0.001	0.9	0.8
F200-F400	<0.0001	<0.0001	0.05	0.8	0.8

1.2 Statistical significance (*P* value) of mean comparisons for soil (0-15 cm) NH_4^+-N levels shown in Fig. 3.7.

Table 1. 2.1 Steep site

Treatment comparison	Days after urine application				
	1	6	27	100	142
S0-S200	0.0003	0.0003	0.2	0.9	0.9
S0-S400	<0.0001	<0.0001	0.001	0.9	0.9
S200-S400	0.0001	0.0001	0.02	0.9	0.9

Table 1.2.2 Flat site

Treatment	Days after urine application				
	1	6	27	100	142
F0-F200	0.001	0.01	0.09	0.8	0.9
F0-F400	<0.0001	<0.0001	0.003	0.9	0.8
F200-F400	<0.0001	<0.0001	0.1	0.8	0.8

1.3 Statistical significance (*P* value) of mean comparisons for soil (0-15 cm) NO_3^--N levels shown in Fig. 3.8.

Table 1.3.1 Steep site

Treatment comparison	Days after urine application				
	1	6	27	100	142
S0-S200	0.6	0.5	0.004	0.9	0.8
S0-S400	0.6	0.5	0.2	0.9	0.9
S200-S400	0.9	0.9	0.08	0.9	0.8

Table 1.3.2 Flat site

Treatment comparison	Days after urine application				
	1	6	27	100	142
F0-F200	0.9	0.8	0.01	0.8	0.9
F0-F400	0.6	0.5	<0.0001	0.7	0.2
F200-F400	0.6	0.6	<0.0001	0.8	0.6

APPENDIX 2

2.1 Statistical significance (*P* value) of mean comparisons for the total mineral N levels shown in Fig. 5.3.

Table 2.1.1 Steep site

Treatment Comparison	Days after urine application					
	3	12	27	45	66	88
S0 – S280	< 0.0001	< 0.0001	< 0.0001	0.06	0.4	0.8
S0 – S560	< 0.0001	< 0.0001	<0.0001	<0.0001	< 0.0001	0.9
S280- S560	0.02	0.03	<0.001	< 0.0001	< 0.0001	0.8

Table 2.1.2 Flat site

Treatment comparison	Days after urine application					
	3	12	27	45	66	88
F0 – F280	0.002	< 0.0001	0.007	0.0006	0.3	0.7
F0 – F560	0.0006	< 0.0001	<0.0001	<0.0001	0.0006	0.5
F280- F560	0.6	0.26	0.0001	0.008	0.01	0.3

2.2 Statistical significance (*P* value) of mean comparisons for the 2 M KCl -extractable NH_4^+-N (0-10 cm) levels shown in Fig.5.4.

Table 2.2.1 Steep site

Treatment comparison	Days after urine application					
	3	12	27	45	66	88
S0 – S280	< 0.0001	< 0.0001	0.0002	0.4	0.07	0.6
S0 – S560	< 0.0001	< 0.0001	<0.0001	<0.0001	0.3	0.9
S280- S560	0.02	0.003	<0.0001	< 0.0001	< 0.007	0.8

Table 2.2.2 Flat site

Treatment comparison	Days after urine application					
	3	12	27	45	66	88
F0 – F280	<0.0001	< 0.0001	0.01	0.1	0.3	0.4
F0 – F560	< 0.0001	< 0.0001	<0.0001	0.0005	0.6	0.6
F280- F560	0.9	0.4	0.0006	0.02	0.6	0.2

2.3 Statistical significance (*P* value) of mean comparisons for the 2 M KCl -extractable NO_3^--N (0-10 cm) levels shown in Fig. 5.6.

Table 2.3.1 Steep site

Treatment Comparison	Days after urine application					
	3	12	27	45	66	88
S0 – S280	0.2	0.007	0.001	0.02	1	1
S0 – S560	.08	0.001	<0.0001	<0.0001	0.0006	1
S280- S560	0.5	0.3	0.01	0.001	0.0006	1

Table 2.3.2 Flat site

Treatment comparison	Days after urine application					
	3	12	27	45	66	88
F0 – F280	0.4	0.004	0.1	0.0005	1	1
F0 – F560	0.02	< 0.0001	<0.0001	0.0001	0.002	1
F280- F560	0.1	0.09	0.0002	0.002	0.002	1

2.4 Statistical significance (*P* value) of mean comparisons for the resin-adsorbed NH_4^+-N (0-10 cm) levels shown in Fig. 5.4.

Table 2.4.1 Steep site

Treatment Comparison	Days after urine application																			
	3	6	9	12	15	18	21	24	27	30	33	36	42	48	55	62	69	76	83	91	97
S0-S280	< 0001	<.007	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.001	.05	.02	.001	.4	.07	.08	.3	.1	.8	.5	.8
S0-S560	<.0001	.0008	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	.01	.09	.6	.1	.9	.5	.07	.1
S280-S560	.3	.4	.1	.04	.06	.04	.0005	.0005	.005	< .0001	.0002	.03	.1	.07	.8	.2	.5	.1	.6	.2	.1

Table 2.4.2 Flat site

Treatment comparison	Days after urine application																			
	3	6	9	12	15	18	21	24	27	30	33	36	42	48	55	62	69	76	83	91	97
S0-S280	<.0001	<.003	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	1	< 0.001	<0.001	.0007	.0001	..07	.09	..3	.004	.2	..3	.6	.7
S0-S560	<.0001	.0008	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	.0006	<.0001	<.0001	<.0001	.0002	.008	.03	.01	.2	.3	.3	.6	.9
S280-S560	.1	.3	.1	.1	.2	.02	.01	.002	.0006	<.007	.005	.08	.8	.4	.6	.1	.1	.7	.9	.9	.7

2.5 Statistical significances (P value) of mean comparisons for the resin-adsorbed NO_3^--N (0-10 cm) levels shown in Fig.5.6.

Table 2.5.1 Steep site

Treatment comparison	Days after urine application																			
	3	6	9	12	15	18	21	24	27	30	33	36	42	48	55	62	69	76	83	91	97
S0-S280	.14	.05	<.0001	<.0001	<.0001	<.0001	.0003	.0008	.0001	<0.001	<.0001	<.0001	.0005	<.0001	.07	.02	<.0001	.006	.2	.2	.5
S0-S560	.17	.3	.0005	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	.009	.009	.003
S280-S560	.8	.4	.007	.6	.5	.5	.6	.4	.05	.1	.009	.001	<.0001	.0002	.0002	<.0001	.01	<.0001	.001	.001	.0001

Table 2.5.2 Flat site

Treatment comparison	Days after urine application																			
	3	6	9	12	15	18	21	24	27	30	33	36	42	48	55	62	69	76	83	91	97
S0-S280	.2	.5	.6	.1	.02	.003	.06	.004	1	.0001	<.0001	<.0001	.001	.05	.004	.8	.7	.0001	.5	1	.04
S0-S560	.2	.9	.03	.0002	<.0001	.002	.006	<.0001	.2	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	.2	<.0001	<.0001	.01	.02	.3
S280-S560	.8	.6	.08	.02	.04	.8	.3	.1	.2	.04	.2	.2	.003	.0003	.02	.3	<.0001	.05	.003	.02	.2

2.6 Water balance for Ballantrae flat site from 09/07/00 to 10/10/00

R= Rainfall (mm); ET= Evapotranspiration (mm); W= Water depth (mm)

D = Drainage (mm)

Date	Day	R (mm)	ET(mm)	R-ET	W(mm)	D (mm)
00/7/09		0.4	0.7	-0.3	48.5	
10		0.2	0.8	-0.6	48.1	
11		0	0.9	-0.9	47.5	
12		0	1.1	-1.1	46.7	
13		0	0.1	-0.1	45.6	
14	0	0	1.0	-1.0	45.4	0.0
15	1	0	1.1	-1.1	44.4	0.0
16	2	0	0.9	-0.9	43.3	0.0
17	3	0	0.7	-0.7	**42.4**	0.0
18	4	0	1.0	-1.0	41.5	0.0
19	5	0.4	0.6	-0.2	41.3	0.0
20	6	3.2	0.1	3.2	44.4	0.0
21	7	13.2	0.2	13.1	48.0	9.5
22	8	3.4	0.3	3.1	48.0	3.1
23	9	4.4	0.5	3.9	48.0	3.9
24	10	0	1.1	-1.1	46.9	0.0
25	11	0.8	0.9	-0.1	46.8	0.0
26	12	2.6	0.6	2.0	48.0	0.8
27	13	12.2	0.6	11.6	48.0	11.6
28	14	9.4	0.2	9.2	48.0	9.2
29	15	0	1.2	-1.2	46.9	0.0
30	16	0.2	1.0	-0.8	46.0	0.0
31	17	0.4	0.7	-0.3	45.8	0.0
00/08/01	18	1.2	1.2	0.0	45.8	0.0
2	19	0	1.1	-1.1	44.7	0.0
3	20	0	1.2	-1.2	43.5	0.0
4	21	0	0.9	-0.9	42.7	0.0
5	22	0	1.5	-1.5	41.2	0.0
6	23	0	1.4	-1.4	39.8	0.0
7	24	0	1.5	-1.5	38.2	0.0
8	25	0	1.1	-1.1	37.1	0.0
9	26	1.8	0.8	1.0	38.2	0.0
10	27	0.8	0.7	0.1	38.3	0.0
11	28	20.6	0.4	20.2	48.0	10.4
12	29	3.8	0.8	3.0	48.0	3.0
13	30	0	1.2	-1.2	46.8	0.0
14	31	0	1.5	-1.5	45.3	0.0
15	32	0	1.8	-1.8	43.6	0.0
16	33	0	1.3	-1.3	42.2	0.0
17	34	0	1.9	-1.9	40.3	0.0
18	35	0.6	0.3	0.3	40.6	0.0
19	36	21.6	0.1	21.5	48.0	14.0
20	37	1.2	0.4	0.8	48.0	0.8
21	38	1	0.8	0.2	48.0	0.2
22	39	5.2	0.5	4.7	48.0	4.7
23	40	0	1.2	-1.2	46.9	0.0
24	41	0	1.2	-1.2	45.6	0.0
25	42	0.2	1.5	-1.3	44.4	0.0
26	43	5.6	0.5	5.1	48.0	1.5
27	44	0.6	1.7	-1.1	46.9	0.0
28	45	13.4	1.1	12.3	48.0	11.2
29	46	0	1.6	-1.6	46.4	0.0
30	47	1.2	0.4	0.8	47.2	0.0
31	48	8	0.6	7.5	48.0	6.7

00/09/01	49	0	1.6	-1.6	46.4	0.0
2	50	3	1.9	1.1	47.5	0.0
3	51	0.2	1.8	-1.6	45.9	0.0
4	52	0.4	2.0	-1.6	44.3	0.0
5	53	1.6	1.5	0.1	44.3	0.0
6	54	1.6	1.6	0.0	44.3	0.0
7	55	3.6	0.9	2.7	47.0	0.0
8	56	18	0.9	17.1	48.0	16.2
9	57	4.8	0.7	4.1	48.0	4.1
10	58	10.8	1.6	9.2	48.0	9.2
11	59	1.8	2.3	-0.5	47.5	0.0
12	60	0	2.4	-2.4	45.1	0.0
13	61	3.2	0.4	2.8	47.9	0.0
14	62	1.2	0.5	0.7	48.0	0.6
15	63	0.2	1.6	-1.4	46.6	0.0
16	64	0	2.5	-2.5	44.2	0.0
17	65	0	3.2	-3.2	41.0	0.0
18	66	0	2.4	-2.4	38.6	0.0
19	67	1	0.4	0.6	39.2	0.0
20	68	0.6	1.9	-1.3	37.9	0.0
21	69	0.2	1.6	-1.4	36.6	0.0
22	70	0	2.1	-2.1	34.4	0.0
23	71	0	3.5	-3.5	30.9	0.0
24	72	0.6	2.8	-2.2	28.7	0.0
25	73	7.6	0.1	7.5	36.3	0.0
26	74	0.6	1.5	-0.9	35.4	0.0
27	75	0	2.8	-2.8	32.6	0.0
28	76	0	3.5	-3.5	29.2	0.0
29	77	0.8	0.9	-0.1	29.1	0.0
30	78	16.8	0.2	16.6	45.8	0.0
00/10/01	79	11.8	0.7	11.1	48.0	8.8
2	80	27.2	0.3	26.9	48.0	26.9
3	81	5.6	3.4	2.2	48.0	2.2
4	82	9.6	1.4	8.2	48.0	8.2
5	83	0	2.1	-2.1	45.9	0.0
6	84	0.2	2.7	-2.5	43.5	0.0
7	85	9.2	0.1	9.1	48.0	4.6
8	86	0	0.9	-0.9	47.1	0.0
9	87	15	1.0	14.0	48.0	13.1
10	88	0	4.1	-4.1	43.9	0.0

2.7 Water balance for Ballantrae steep site from 09/07/00 to 10/10/00

R = Rainfall (mm); ET = Evapotranspiration (mm); W = Water depth (mm)
D = Drainage (mm)

Date	Day	R (mm)	ET(mm)	R-ET	W(mm)	D (mm)
00/7/09		0.4	0.7	-0.3	48.5	
10		0.2	0.8	-0.6	48.1	
11		0	0.9	-0.9	47.5	
12		0	1.1	-1.1	46.7	
13		0	0.1	-0.1	45.6	
14	0	0	1.0	-1.0	45.4	0.0
15	1	0	1.1	-1.1	44.4	0.0
16	2	0	0.9	-0.9	43.3	0.0
17	3	0	0.7	-0.7	**42.4**	0.0
18	4	0	1.0	-1.0	41.5	0.0
19	5	0.4	0.6	-0.2	41.3	0.0
20	6	3.2	0.1	3.2	44.4	0.0
21	7	13.2	0.2	13.1	48.0	9.5
22	8	3.4	0.3	3.1	48.0	3.1
23	9	4.4	0.5	3.9	48.0	3.9
24	10	0	1.1	-1.1	46.9	0.0
25	11	0.8	0.9	-0.1	46.8	0.0
26	12	2.6	0.6	2.0	48.0	0.8
27	13	12.2	0.6	11.6	48.0	11.6
28	14	9.4	0.2	9.2	48.0	9.2
29	15	0	1.2	-1.2	46.9	0.0
30	16	0.2	1.0	-0.8	46.0	0.0
31	17	0.4	0.7	-0.3	45.8	0.0
00/08/01	18	1.2	1.2	0.0	45.8	0.0
2	19	0	1.1	-1.1	44.7	0.0
3	20	0	1.2	-1.2	43.5	0.0
4	21	0	0.9	-0.9	42.7	0.0
5	22	0	1.5	-1.5	41.2	0.0
6	23	0	1.4	-1.4	39.8	0.0
7	24	0	1.5	-1.5	38.2	0.0
8	25	0	1.1	-1.1	37.1	0.0
9	26	1.8	0.8	1.0	38.2	0.0
10	27	0.8	0.7	0.1	38.3	0.0
11	28	20.6	0.4	20.2	48.0	10.4
12	29	3.8	0.8	3.0	48.0	3.0
13	30	0	1.2	-1.2	46.8	0.0
14	31	0	1.5	-1.5	45.3	0.0
15	32	0	1.8	-1.8	43.6	0.0
16	33	0	1.3	-1.3	42.2	0.0
17	34	0	1.9	-1.9	40.3	0.0
18	35	0.6	0.3	0.3	40.6	0.0
19	36	21.6	0.1	21.5	48.0	14.0
20	37	1.2	0.4	0.8	48.0	0.8
21	38	1	0.8	0.2	48.0	0.2
22	39	5.2	0.5	4.7	48.0	4.7
23	40	0	1.2	-1.2	46.9	0.0
24	41	0	1.2	-1.2	45.6	0.0
25	42	0.2	1.5	-1.3	44.4	0.0
26	43	5.6	0.5	5.1	48.0	1.5
27	44	0.6	1.7	-1.1	46.9	0.0
28	45	13.4	1.1	12.3	48.0	11.2
29	46	0	1.6	-1.6	46.4	0.0
30	47	1.2	0.4	0.8	47.2	0.0

31	48	8	0.6	7.5	48.0	6.7
00/09/01	49	0	1.6	-1.6	46.4	0.0
2	50	3	1.9	1.1	47.5	0.0
3	51	0.2	1.8	-1.6	45.9	0.0
4	52	0.4	2.0	-1.6	44.3	0.0
5	53	1.6	1.5	0.1	44.3	0.0
6	54	1.6	1.6	0.0	44.3	0.0
7	55	3.6	0.9	2.7	47.0	0.0
8	56	18	0.9	17.1	48.0	16.2
9	57	4.8	0.7	4.1	48.0	4.1
10	58	10.8	1.6	9.2	48.0	9.2
11	59	1.8	2.3	-0.5	47.5	0.0
12	60	0	2.4	-2.4	45.1	0.0
13	61	3.2	0.4	2.8	47.9	0.0
14	62	1.2	0.5	0.7	48.0	0.6
15	63	0.2	1.6	-1.4	46.6	0.0
16	64	0	2.5	-2.5	44.2	0.0
17	65	0	3.2	-3.2	41.0	0.0
18	66	0	2.4	-2.4	38.6	0.0
19	67	1	0.4	0.6	39.2	0.0
20	68	0.6	1.9	-1.3	37.9	0.0
21	69	0.2	1.6	-1.4	36.6	0.0
22	70	0	2.1	-2.1	34.4	0.0
23	71	0	3.5	-3.5	30.9	0.0
24	72	0.6	2.8	-2.2	28.7	0.0
25	73	7.6	0.1	7.5	36.3	0.0
26	74	0.6	1.5	-0.9	35.4	0.0
27	75	0	2.8	-2.8	32.6	0.0
28	76	0	3.5	-3.5	29.2	0.0
29	77	0.8	0.9	-0.1	29.1	0.0
30	78	16.8	0.2	16.6	45.8	0.0
00/10/01	79	11.8	0.7	11.1	48.0	8.8
2	80	27.2	0.3	26.9	48.0	26.9
3	81	5.6	3.4	2.2	48.0	2.2
4	82	9.6	1.4	8.2	48.0	8.2
5	83	0	2.1	-2.1	45.9	0.0
6	84	0.2	2.7	-2.5	43.5	0.0
7	85	9.2	0.1	9.1	48.0	4.6
8	86	0	0.9	-0.9	47.1	0.0
9	87	15	1.0	14.0	48.0	13.1
10	88	0	4.1	-4.1	43.9	0.0

APPENDIX 3

3.1 Statistical significance (*P* value) of mean comparison of soil mineral N levels between urine treated and control soils (Fig. 6.5)

Soil	Days after urine application					
	3	9	15	21	28	45
KAR	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
KAI	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
MD	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
BF	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
BS	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
WF	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
WS	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

3.2 Statistical significance (*P* value) of mean comparison of 0.5M K_2SO_4-extractable NH_4^+-N levels between urine treated and control soils (Fig. 6.7)

Soil	Days after urine application					
	3	9	15	21	28	45
KAR	<0.0001	<0.0001	<0.0001	0.4	0.7	0.6
KAI	<0.0001	<0.0001	0.9	0.9	0.9	0.9
MD	<0.0001	<0.0001	<0.0001	0.01	0.4	0.6
BF	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.06
BS	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
WF	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
WS	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

3.3 Statistical significances (*P* value) of mean comparison of resin-adsorbed NH_4^+-N levels between urine treated and control soils (Fig. 6.8)

Soil	Days after urine application					
	3	9	15	21	28	45
KAR	0.0001	0.03	0.2	0.9	0.9	0.9
KAI	<0.0001	0.0004	1	0.8	0.9	0.9
MD	<0.0001	0.0006	0.02	0.06	0.5	0.5
BF	<0.0001	<0.0001	0.01	<0.0001	0.0027	0.4
BS	<0.0001	<0.0001	0.0003	<0.0001	<0.0001	<0.0001
WF	<0.0001	0.01	0.02	<0.0001	<0.0001	0.0011
WS	<0.0001	0.1	0.09	<0.0001	<0.0001	<0.0001

3.4 Statistical significances (*P* value) of mean comparison of 0.5M K_2SO_4-extractable NO_3^--N levels between urine treated and control soils (Fig. 6.9)

Soil	Days after urine application					
	3	9	15	21	28	45
KAR	0.1	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
KAI	0.08	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
MD	0.004	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
BF	0.8	0.01	0.0002	<0.0001	<0.0001	<0.0001
BS	0.4	0.004	<0.0001	<0.0001	<0.0001	<0.0001
WF	0.7	0.8	0.3	0.04	<0.0001	<0.0001
WS	0.2	0.1	0.01	0.0008	<0.0001	<0.0001

3.5 Statistical significances (*P* value) of mean comparison of resin-adsorbed NO_3^--N levels between urine treated and controls (Fig. 6.10)

Soil	Days after urine application					
	3	9	15	21	28	45
KAR	0.2	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
KAI	0.3	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
MD	0.2	0.0007	0.0008	0.0009	0.1	<0.0001
BF	0.5	0.0014	<0.0001	<0.0001	<0.0001	<0.0001
BS	0.0001	0.2	0.02	0.0002	<0.0001	<0.0001
WF	0.06	0.5	0.03	0.007	<0.0001	<0.0001
WS	<0.0001	0.9	1	0.3	0.004	<0.0001

3.6 Statistical significances (*P* value) of mean comparison of mineralisable N levels between urine treated and control soils (Fig. 6.11)

Soil	Days after urine application					
	3	9	15	21	28	45
KAR	0.2	0.06	0.08	0.01	0.02	0.8
KAI	0.2	0.2	0.004	0.6	0.1	0.5
MD	0.009	0.01	0.01	0.03	0.007	0.1
BF	0.07	0.0006	0.0005	0.6	0.5	0.4
BS	0.9	0.0003	0.001	0.6	0.2	0.05
WF	0.002	0.0034	0.31	0.2	0.4	0.1
WS	0.09	0.009	0.02	0.5	0.9	0.006

3.7 Statistical significances (*P* value) of mean comparison of dissolved organic carbon (DOC) levels between urine treated and control soils (Fig. 6.12)

Soil	Days after urine application					
	3	9	15	21	28	45
KAR	0.8	0.06	0.5	0.2	0.2	0.8
KAI	0.9	0.2	0.8	0.07	0.06	0.001
MD	0.004	0.001	0.0002	0.0002	0.01	0.02
BF	0.02	0.5	0.05	0.4	0.0007	0.02
BS	0.7	0.3	0.3	0.8	0.1	0.6
WF	0.7	0.07	0.9	0.3	0.08	0.009
WS	0.6	0.8	0.9	0.1	0.4	0.07

3.8 Statistical significances (*P* value) of mean comparison of soil microbial biomass N (SMB-N) levels between urine treated and control soils (Fig. 6.13)

Soil	Days after urine application					
	3	9	15	21	28	45
KAR	0.002	0.2	0.01	0.006	0.4	0.1
KAI	0.2	0.2	0.004	0.6	0.1	0.5
MD	0.8	<0.0001	0.008	0.004	0.2	0.1
BF	0.7	0.09	0.003	0.01	0.01	0.04
BS	0.2	0.0003	0.0031	<0.0001	0.8	0.2
WF	0.02	<0.0001	<0.0001	<0.0001	0.08	<0.0001
WS	0.1	0.03	0.01	0.9	0.4	0.2

APPENDIX 4

Computer program (Visual Basic) for diffusion model described in Section 4.6 of Chapter 4. Darker texts are descriptions of model parameters.

```
Sub twoD()
2-D diffusion, units cm, µg, days
Dim x As Integer: Dim y As Integer
Dim M(20, 20), dM(20, 20), fy(20, 20), fx(20, 20), C(20, 20)
BD = 1.39: W = 0.26: theta = W * BD
BD= Bulk Density, W= Gravimetric water content, theta= volumetric water content
G = 192
G= Soil nitrate-N concentration (µg/g soil)
Ci = (G * BD) / theta: Cmax = (Ci / 80) * 100
Ci= Initial soil nitrate-N concentration (µg/cm^3 soil solution)
Cmax= Operational maximum nitrate-N concentration (µg/ cm^3 soil solution)
dt = 0.01: tmax = 7
dt= Time step (days)
tmax= Resin spike burial period (days)
dy = 0.25: dx = 0.25: ytot = 20: xtot = 10: L = 5
dy=Length of cell in x direction, dy= Length of cell in y direction
xtot= Number of cells in x direction
ytot=Number of cells in y direction
L= Length of resin membrane
Dl = 1.3
Dl= Diffusion coefficient of nitrate in free solution (cm^2/day)
f = 0.66 / (1 + 77.2375 * Exp(-13.9964 * theta))
f= Impedance factor
Ds = Dl * f:
Ds= Diffusion coeffient of nitrate in soil (cm^2/day)
Cumf01 = 0: Cumf02 = 0: Cumfmax = 2179 / 4
Cumf01= Nitrate N adsorbed to resin from 10,9 cell
Cumf02= Nitrate N adsorbed to resin from 10,10 cell
Cumfmax=Maximum Nitrate-N adsorption capacity of resin (µg/cm^2 resin)

For y = 1 To ytot: For x = 1 To xtot
   C(y, x) = Ci: M(y, x) = Ci * theta * dy * dx * L
M(y,x)= µg nitrate-N in each cell
C(y,x)=µg nitrate-N in cm^3 soil solution
Next x: Next y

For y = 1 To ytot
   fx(y, 0) = 0: fx(y, xtot) = 0
Next y
For x = 1 To xtot
   fy(0, x) = 0: fy(ytot, x) = 0
Next x

Do Until t >= tmax
   Worksheets("Sheet4").Cells(2, 3).Value = t
   Worksheets("Sheet4").Cells(3, 3).Value = (Cumf01 + Cumf02) * 2
   For y = 1 To ytot: For x = 1 To xtot - 1
      fx(y, x) = theta * Ds * dy * L * (C(y, x) - C(y, x + 1)) / dx
fx(y,x)=Nitrate-N flux in X direction
    Next x: Next y

   For y = 1 To ytot - 1: For x = 1 To xtot
      fy(y, x) = theta * Ds * dx * L * (C(y, x) - C(y + 1, x)) / dy
```