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**Nitrous oxide emission from soil  
under pasture as affected by grazing and  
effluent irrigation**

**A thesis presented in partial fulfilment of the  
requirements for the degree of  
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# Abstract

New Zealand's greenhouse gas inventory is dominated by the agricultural trace gases, CH<sub>4</sub> and N<sub>2</sub>O instead of CO<sub>2</sub>, which is dominant on a global scale. While the majority of the anthropogenic CH<sub>4</sub> is emitted by ruminant animals as a by-product of enteric fermentation, N<sub>2</sub>O is mainly produced by microbial processes occurring in the soil. In grazed pastoral soils, N<sub>2</sub>O is generated from N originating from dung, urine, effluent applied to land, biologically fixed N<sub>2</sub> and fertiliser. The amount of emission depends on complex interactions between soil properties, climatic factors and management practices.

Increased intensification of pastoral agriculture in New Zealand, particularly in dairying has led to an increased production of farm dairy effluent. Traditionally, direct disposal of nutrient rich farm dairy effluents (FDE) into water bodies was an acceptable practice in New Zealand, but with the introduction of the Resource Management Act (1991), discharge of effluents into surface waters is now a controlled activity and many Regional Councils encourage the land irrigation of effluents to protect surface water quality. While the impact of grazing and FDE irrigation on groundwater contamination through leaching and runoff of nutrients has been studied extensively, there has been only limited work done on the effect of these practices on air quality as affected by N<sub>2</sub>O emission.

This thesis examines the effects of various factors, such as compaction due to cattle treading, and the nature, application rate and time of effluent application on N<sub>2</sub>O emission in relation to the changes in the soil physical properties and C and N transformation from a number of small plot and field experiments. The results were then used, together with data from the literature, to predict the emissions from effluent irrigated pastures using a process-based model.

In grazed pastures, animal treading causes soil compaction, which results in decreased soil porosity and increased water filled pore space that stimulate the denitrification rate as well as influence the relative output of N<sub>2</sub>O and dinitrogen (N<sub>2</sub>) gases. A field plot study was conducted to determine N<sub>2</sub>O emission from different N sources as affected by soil compaction. The experiment comprised two main treatments (uncompacted and compacted) to which four N sources (natural cattle urine, potassium nitrate, ammonium sulphate and urea at the rate of 600kg N ha<sup>-1</sup>) and a control (water

only) were applied. Compaction was obtained through driving close parallel tracks by the wheels of the vehicle. The changes in the soils physical properties (bulk density, penetration resistance (PR), soil matric potential and oxygen diffusion rate (ODR) due to the compaction created by the wheel traction of the vehicle were compared with the changes in these properties due to the treading effect of grazing cattle, which was monitored in another field experiment. The  $\text{N}_2\text{O}$  fluxes were measured using a closed chamber technique.

The compaction at the grazing trial and at the wheel traction experimental plot caused significant changes in soil bulk density, PR, soil matric potential and ODR values. Overall, the bulk density of the compacted soil was higher than the uncompacted soil by 6.7% (end of 3 weeks) and 4.9% (end of 1 week) for the field experiment and the grazing trial, respectively. Results suggest that maximum compaction occurred in the top 0-2 cm layer. Compaction caused an increase in  $\text{N}_2\text{O}$  emission, which was more pronounced in the nitrate treatment than in the other N sources. In the case of the compacted soil, 10% of the total N applied in the form of nitrate was emitted, whereas from uncompacted soil this loss was only 0.7%.  $\text{N}_2\text{O}$  loss was found to decrease progressively from the time of application of N treatments. Total  $\text{N}_2\text{O}$  emission for the three month experimental period ranged from 2.6 to 61.7 kg  $\text{N}_2\text{O-N ha}^{-1}$  for compacted soil and 1.1 to 4.4 kg  $\text{N}_2\text{O-N ha}^{-1}$  for uncompacted soil.

In the second field plot experiment, the results of  $\text{N}_2\text{O}$  fluxes from treated farm dairy effluent (TFDE), untreated farm dairy effluent (UFDE), treated piggery farm effluent (TPFE) and treated meat effluent (TME) applied to 2m x 1m plots for 'autumn' (February-April) and 'winter' (July-September) are described. Effluent irrigation resulted in higher emissions during both the seasons indicating that the supply of C and N through effluent irrigation contributed to increased  $\text{N}_2\text{O}$  emission. The highest emissions were observed from TPFE (2.2% of the applied N) and TME (0.6% of the applied N) during the autumn and winter seasons, respectively. Emissions generated by the TFDE application were the lowest of the four effluent sources but higher than the water and control treatments. The effect of effluent irrigation on  $\text{N}_2\text{O}$  emission was higher during the autumn season than the winter season. The effect of key soil and effluent factors such as water filled pore space (WFPS), nitrate, ammonium and available C in soil and effluents on  $\text{N}_2\text{O}$  emission was examined using regression equations.

The third field plot experiment examined the effect of four TFDE application rates (25mm, 50mm, 75mm and 100mm) on  $N_2O$  emission. Treatments were added to 2m x 1m plots lined with plastic sheet to restrict the flow of effluent. The  $N_2O$  emission increased with the increasing effluent loading rate, with the emission ranging from 0.8 to 1.2% of the added N. This can be attributed to the increasing addition of N and C in the soil with the increasing application rate of the effluent. Besides, providing C and N substrates, the effluent application increased the WFPS of the soil, thereby creating conditions conducive for denitrification and  $N_2O$  emission.

A field experiment was conducted at the Massey University No 4 Dairy farm in which  $N_2O$  emission and related soil and environmental parameters were monitored for two weeks following the TFDE applications over an area of 0.16 ha in September 2003 (21mm), January 2004 (23mm) and February 2004 (16mm). Emissions were measured by a closed chamber technique with 20 chambers for each treatment, in order to cover the variability present in the field.  $N_2O$  emissions increased immediately after the application of the effluent, and subsequently dropped after about two weeks. The total  $N_2O$  emitted from the effluent application after the first, second and third irrigation was 2%, 4.9% and 2.5%, respectively of the total N added through the effluent. The higher emission observed during the second effluent irrigation event was due to high soil moisture content during the measurement period. Moreover effluent was applied immediately after a grazing event leading to more N and C input into the soil through excretal deposition. In this experiment the residual effect of effluent application on  $N_2O$  emission was also examined by monitoring emissions 12 weeks after the effluent application. The emissions from the control and effluent irrigated plots were similar, indicating that there was no residual effect of the effluent irrigation on  $N_2O$  emissions. In a separate field study,  $N_2O$  emission was monitored at the Massey University No 4 Dairy farm to examine the effect of a grazing event of moderate intensity on  $N_2O$  emission. The treatments consisted of a grazed and an ungrazed control. The fluxes from the grazed site were much higher than for the ungrazed site with the total emissions from the former site being 8 times higher than the latter site for the entire experimental period.

A modified New Zealand version of denitrification decomposition model (DNDC), a process based model, namely "NZ-DNDC", was used to simulate  $N_2O$  emission from the TFDE application in the field experiment. The model was able to simulate the emission as well as the WFPS within the range measured in the field. But

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simulated emissions from the TFDE were slightly lower than measured values. Improvements in the parameterisation for effluent irrigation are likely to further improve the N<sub>2</sub>O simulations.

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## Chapter 1

# Introduction

## 1.1 Background

The agricultural sector in New Zealand is the major contributor of ammonia ( $\text{NH}_3$ ; 55%), nitrous oxide ( $\text{N}_2\text{O}$ ; 96%) and methane ( $\text{CH}_4$ ; 87%) emissions to the atmosphere (MFE, 2005). These gases cause environmental degradation through their effects on soil acidification, eutrophication, global warming and stratospheric ozone depletion. With its strong agricultural base and relatively low level of heavy industrial activity, New Zealand is unique in having a greenhouse gas emission inventory dominated by the agricultural trace gases,  $\text{CH}_4$  and  $\text{N}_2\text{O}$ , instead of the non-agricultural source, carbon dioxide ( $\text{CO}_2$ ), which dominates in most other countries. In pastoral soils,  $\text{N}_2\text{O}$  gas is generated mainly through denitrification of nitrate ( $\text{NO}_3^-$ ) originating from the dung, urine and effluent applied to land, and biologically fixed and fertiliser nitrogen (N). The amount of the gaseous emissions depends on complex interactions between soil properties, climatic factors and agricultural practices.

With increased intensification of pastoral agriculture in New Zealand, particularly dairying, cow numbers have increased by 54% from 3.44 million in 1990 to 5.23 million in 2003 (National Inventory Report New Zealand 2004). These increased numbers of grazing animals influence the emission of  $\text{N}_2\text{O}$  through their effect on soil. For example, in grazed-pastures, animal treading is an important cause of soil compaction. Soil compaction influences the air-filled porosity of soil, oxygen exchange and therefore the denitrification rate. In New Zealand cattle are often hard grazed on pasture throughout winter and early spring. In this system, especially when the soil is wet, cattle treading causes significant soil compaction thereby creating anaerobic or micro-aerophylic conditions conducive for denitrification. Effluent application to compacted soils may exacerbate anaerobic conditions. However, greater understanding of the effect of soil compaction on  $\text{N}_2\text{O}$  emissions is also needed to devise strategies for effective effluent management. Also more information is required on the effect of

various N forms (i.e., urea, ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) on N loss through  $\text{N}_2\text{O}$  emission when applied under compacted soil conditions.

Increased intensification of the dairy industry in New Zealand has also led to increased production of the farm effluents. According to an estimate, about 70 million  $\text{m}^3$  of effluent from dairy sheds (Farm dairy effluent, FDE), 4 million  $\text{m}^3$  from piggery farms, and 50 million  $\text{m}^3$  from meat-processing plants are being generated annually (Saggar *et al.* 2004b). A large quantity of effluent is also generated from poultry-processing plants. All these effluents are often treated biologically using two-pond systems (anaerobic followed by aerobic pond) and the effluent discharging from the aerobic pond contains significant quantities of valuable nutrients that could be applied to land to improve soil fertility and increase the sustainability of farming systems. Historically, the treated effluents have been discharged into streams. Recently, the Resource Management Act, 1991 has focused attention on water quality and has led Regional Councils to strongly advocate the land application of effluents (Selvarajah 1996). Moreover, due to the high nutrient content of the effluents, recycling of these to land is considered a move towards sustainable farming. However, there have been some environmental concerns about the management of increased effluent production (Bolan *et al.* 2003a; Saggar & Bolan 2003; Bolan *et al.* 2004b; Houlbrooke *et al.* 2004; Wang *et al.* 2004).

The farm effluent irrigation to pasture lands does not consider its impact on the air quality and there have already been claims that effluent irrigation leads to increased nitrous oxide ( $\text{N}_2\text{O}$ ) and methane ( $\text{CH}_4$ ) emission. Nitrous oxide emission through effluent irrigation is one of the sources of greenhouse gases from the farming industry. Knowledge of the contribution of this effluent irrigation to temporal  $\text{N}_2\text{O}$  emission levels from soils is needed to devise strategies for effective effluent management.

Soil reaction to the effluent application is a more complex and dynamic process than that of the fertiliser-N. Although there has been extensive research on soil reaction to N fertilisers in New Zealand, little information is available on environmentally sustainable N loading rates for effluent application onto land (Selvarajah 1996). Intensive research is required to determine the suitable N loading rates for the effluent irrigation. Regional councils have come up with different loading rates for their regions, depending on the soil types and the effluent quality of the regions; the broad range of recommended annual effluent-N loading being 150–200  $\text{kg ha}^{-1}$  (Selvarajah 1996). Contamination of groundwater would not be anticipated under these conditions.

However, there are situations (e.g. short rotation forestry) where effluent applications exceed the rates recommended for grazed pastures. These situations pose a significant threat to the environment's quality. Quantitative knowledge on the  $N_2O$  emission from soils irrigated with treated farm dairy effluent (TFDE) at different loading rates needs to be obtained so that recommendations for annual effluent loading can be made, keeping in mind the  $N_2O$  emissions.

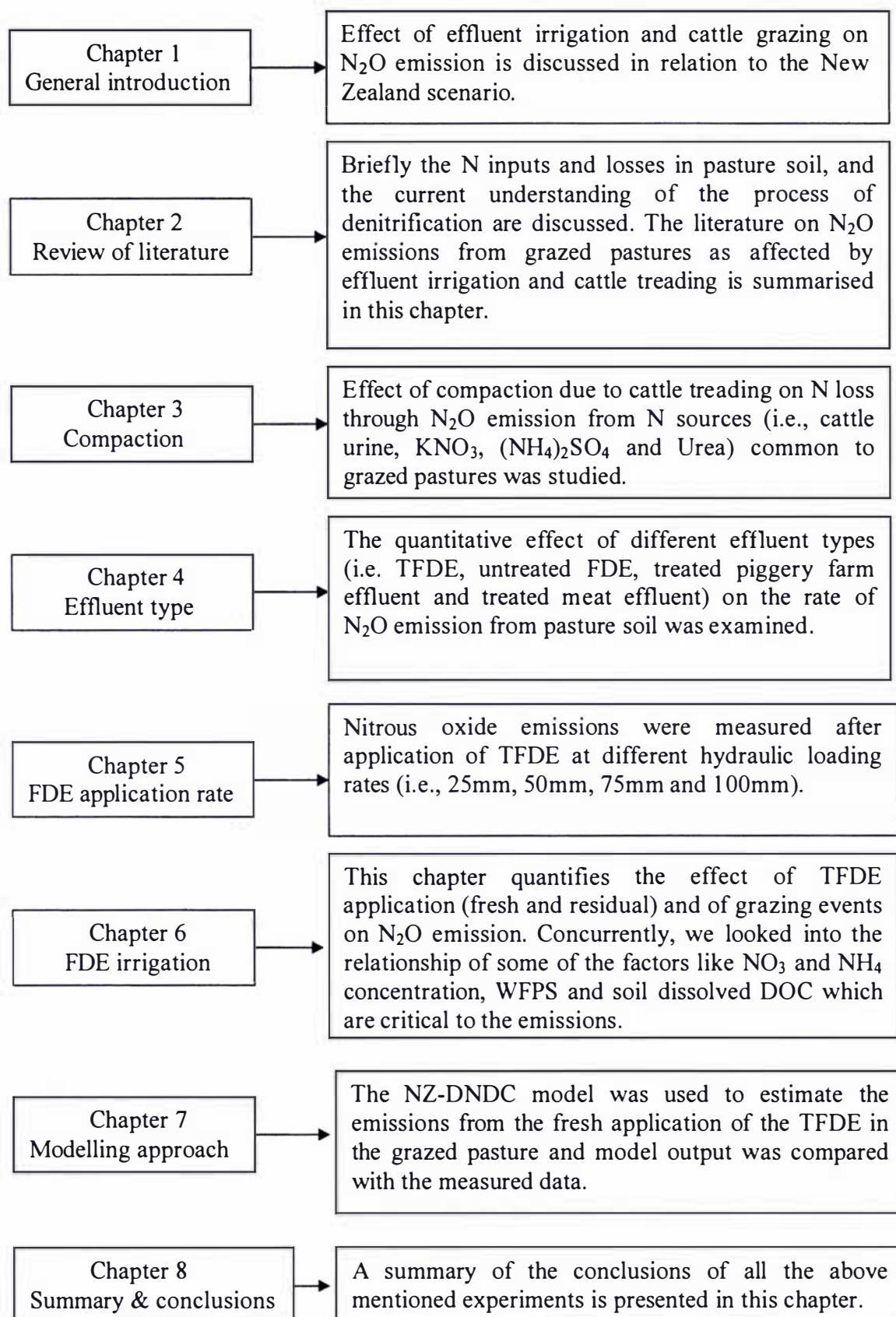
## 1.2 Thesis Objectives

The main overall objective of this thesis is:

- To quantify the contribution of effluent irrigation and animal treading to  $N_2O$  emissions from pasture.

The specific objectives are:

- To examine the effect of compaction created by animal treading and wheel tracks on the transformations of N in and  $N_2O$  emission from soil treated with different forms of N.
- Elucidation of the effect applications of different farm effluents (Treated farm dairy effluent, untreated farm dairy effluent, treated piggery farm effluent and treated meat effluent) have on  $N_2O$  emissions from pasture soils under a range of physical conditions.
- To study the loss of N as  $N_2O$  from pasture soil receiving different loading rates of TFDE.
- To examine the effect of fresh application of TFDE and the residual effect of the FDE irrigation on the  $N_2O$  emission from grazed pasture. To examine the effect of grazing on the  $N_2O$  emission.
- To assess the ability of NZ-DNDC (NZ-denitrification decomposition model) to simulate  $N_2O$  emissions from pasture irrigated with FDE.



**Figure 1.1**    **Structure of the thesis**

## 1.3 Thesis structure

The outline of the thesis is presented in Figure 1.1. **Chapter 1** gives an introduction to the effect of the intensification of dairying in New Zealand on compaction of grazed pastures and increased production of farm effluents and their potential contribution to nitrous oxide emissions. The chapter also highlights the main and the specific objectives of the thesis. **Chapter 2** provides a literature review by briefly outlining the various sources of N input to grazed pasture, the dynamics of N transformations in soil-plant systems with particular emphasis on the biochemistry and factors affecting the processes of N<sub>2</sub>O emission, and management practices to minimise N<sub>2</sub>O emission. **Chapter 3** reports the effect of the compaction caused due to cattle treading on the soil physical properties and the effect compaction has on N loss through N<sub>2</sub>O emission from various N sources (i.e., cattle urine, KNO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and Urea) common to grazed pastures. **Chapter 4** quantitatively determines the rate of N<sub>2</sub>O emission from pasture soil treated with different effluent types (i.e., TFDE, untreated FDE, treated piggery farm effluent and treated meat effluent) and its relationship to the various soil properties. **Chapter 5** quantifies the immediate and residual effects of TFDE application and also the effect of grazing on N<sub>2</sub>O emission from pasture. The relationship of N<sub>2</sub>O emissions to soil NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentrations, water filled pore space (WFPS) and soil dissolved organic carbon (DOC) are explored. **Chapter 6** examines the effect of FDE application at different loading rates (i.e., 25mm, 50mm, 75mm and 100mm of hydraulic loading of TFDE) on N<sub>2</sub>O emissions from pasture. In **Chapter 7** the NZ-DNDC model was used to estimate N<sub>2</sub>O emissions for three applications of TFDE to grazed pasture and model output was compared with the measured data. **Chapter 8** A syntheses and summary of the results from the previous chapters are presented in this chapter along with the main conclusions drawn from the research undertaken during the PhD.

The articles in scientific journals and conference proceedings that are partly or completely based on the results presented in this thesis are listed below:

Bhandral, R.; Bolan, N.S.; Saggar, S.; Hedley, M.J. 2005. Effect of compaction and nitrogen sources on nitrous oxide emissions. In: Developments in fertiliser application technologies and nutrient management, Proceedings of the 18th Annual FLRC workshop, 201-208.

- Bhandral, R., Saggar, S.; Bolan, N.S.; Hedley, M.J. 2004. Factors controlling nitrous oxide emissions from effluent application. In: Proceedings of the Workshop on the science of trace gases, 70–73.
- Bhandral, R.; Saggar, S.; Bolan, N. S.; Hedley, M. J. 2004. Nitrous oxide emissions from farm effluents. In: Supersoil 2004, the 3<sup>rd</sup> Australian New Zealand Soils Conference, [www.regional.org.au/au/asssi/supersoil2004](http://www.regional.org.au/au/asssi/supersoil2004).
- Bolan, N. S.; Saggar, S.; Luo, J.; Bhandral, R.; Singh, J. 2004. Gaseous emissions of nitrogen from grazed pastures: processes, measurements and modelling, environmental implications, and mitigation. *Advances in Agronomy*, 84: 37-120.
- Saggar, S.; Bhandral, R.; Bolan, N.S.; Luo, J. 2004. Nitrous oxide emissions from land-applied effluents. Proceedings of the 3<sup>rd</sup> International Nitrogen Conference, p 27.
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- Bhandral, R.; Saggar, S.; Bolan, N. S.; Hedley, M. J. 2003. Nitrous oxide fluxes in soil as influenced by compaction. *Proceedings of the New Zealand Grassland Association* 65: 265–271.
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- Bhandral, R.; Bolan, N.S.; Saggar, S.; Hedley, M.J. 2005. Nitrous oxide emission from grazed pasture : Effect of compaction and N sources on nitrous oxide emissions. *Soil & Tillage Research* (Submitted).



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Bhandral, R.; Bolan, N.S.; Saggar, S.; Hedley, M.J. 2005. Nitrous oxide emission from grazed pasture as affected by type and the application rate of effluent. *Journal of Environmental Quality* (Submitted).

Bhandral, R.; Bolan, N.S.; Saggar, S.; Hedley, M.J. 2005. Nitrous oxide emissions and mineral nitrogen transformations as affected by farm dairy effluent. *Journal of Environmental Quality* (Submitted).

## Chapter 2

# Review of Literature

### 2.1 Introduction

Due to the ever-increasing production of livestock and poultry products for human consumption, more and more by-products (animal wastes and excreta) from these industries have to be appropriately treated to meet environmental regulations, including safe disposal onto land. Over the last decade intensification of pastoral agriculture in New Zealand, has seen dairy cow numbers increase by 54% from 3.44 million in 1990 to 5.23 million in 2003 (National Inventory Report New Zealand 2004). On dairy farms, approximately 5% of the excreta is deposited in the milking sheds and collecting yards (MFE 2005). When the yards and milking areas are cleaned with high-pressure hoses, farm dairy effluent (FDE) is generated at approximately 50 L per cow per day (Saggar *et al.* 2004b). A number of farm and processing effluents contain significant quantities of valuable nutrients that could be applied onto land in order to improve soil fertility and increase the sustainability of farming systems (Roberts *et al.* 1992; Bolan *et al.* 2004b).

Environmental concerns have been raised about the appropriate management of such farm effluents (Saggar & Bolan 2003). In New Zealand, farm effluent management, is subject to Regional Council and dairy industry regulations. To date, most concerns associated with land application of effluents have centred on the contamination of ground and/or surface water (PCE, 2005). Many Regional Councils encourage land irrigation of effluents, which is perceived to minimize their environmental impacts on groundwater and surface water. Moreover, due to their high nutrient content, land application of effluents is considered a move towards sustainable farming. There are regulations governing land application of effluents that are generally based on total N and/or P loading (Heatley 1996; Sharpley *et al.* 1998; Cameron & Trenouth 1999). Land application loading limits have been made without due regard to its impact on the air quality. It has been reported that effluent irrigation leads to increased emission of greenhouse gases such as N<sub>2</sub>O and CH<sub>4</sub> (Saggar *et al.* 2004b).

Nitrous oxide is an important greenhouse gas and it interferes with the formation of the stratospheric ozone and also accelerates its destruction (Crutzen 1981). Increasing atmospheric concentrations of  $\text{N}_2\text{O}$  are expected to play a key role in altering the earth's climate (i.e. global warming). The majority of  $\text{N}_2\text{O}$  arises as a by-product of the processes of nitrification and denitrification in soil. The major sources of N for these processes of  $\text{N}_2\text{O}$  emission include animal excreta (urine and dung), fertilizer N and biological N fixation. Probably at least 60% of the global gross  $\text{N}_2\text{O}$  emission evolves from soils, particularly in wet tropical forest soils and cultivated soils (Prather *et al.* 1995).

This review brings together fundamental aspects of the process of  $\text{N}_2\text{O}$  emission in grazed pastures, the production and assessment of  $\text{N}_2\text{O}$  and the implications of  $\text{N}_2\text{O}$  emissions on economic loss and environmental degradation. After a brief introduction in Section 2.1 the review starts with an overview on the  $\text{N}_2\text{O}$  scenario in New Zealand (Section 2.2). Since the majority of the  $\text{N}_2\text{O}$  emission is derived from N inputs to soils, Section 2.3 outlines the various sources of N input to grazed pasture and the dynamics of N transformation in the soil. In this section special emphasis is given to the N input by farm effluents as  $\text{N}_2\text{O}$  emissions from this source form one of the major components of this thesis. Section 2.4 then discusses the biochemistry of the processes which lead to the production of  $\text{N}_2\text{O}$  from soil and the factors affecting its production. Various techniques used for measuring  $\text{N}_2\text{O}$  emission and use of process-based models to predict gaseous emissions from agricultural soils are also described. Section 2.5 explores the effect of effluent irrigation, cattle treading and excretal deposition on  $\text{N}_2\text{O}$  emission from grazed pastures. In the final section, the future research needs, mainly focusing on grazing and farm management practices to reduce gaseous emission of N in pasture soils, are briefly discussed.

## **2.2 Sources of anthropogenic $\text{N}_2\text{O}$ emissions from agriculture**

Nitrous oxide is produced both from natural and anthropogenic sources. Primary anthropogenic  $\text{N}_2\text{O}$  emissions include agricultural soil management, animal manure management, sewage treatment, and mobile and stationary combustion of fossil fuel

(National Inventory Report New Zealand, 2004). Nitrous oxide is also produced naturally from a wide variety of biological sources in soil and water through microbial transformations.

The agricultural soils are the major source of most anthropogenic N<sub>2</sub>O emissions in New Zealand and were estimated to contribute 41.83 Gg (12,969 Gg CO<sub>2</sub> equivalent) in 2002, which was 96.5% of the total N<sub>2</sub>O emissions (MFE, 2005). There has been a 27.6% increase in N<sub>2</sub>O emissions since 1990. In order to estimate the total emissions from agricultural soils, this source has been divided into 3 sub-categories:

- Direct N<sub>2</sub>O emissions from agricultural soils as a result of adding N in the form of synthetic fertilisers, animal waste (effluents and excreta), biological fixation, inputs from crop residues and sewage sludge
- Direct emissions from pasture soils in animal production systems (inputs from grazing animals)
- Indirect N<sub>2</sub>O from N lost from the field as NO<sub>x</sub> or NH<sub>3</sub>

All three of these sub-categories have been identified as key sources for the New Zealand N<sub>2</sub>O inventory (Table 2.1).

### 2.2.1 Direct N<sub>2</sub>O emission from agricultural soils

Direct N<sub>2</sub>O emissions from agricultural soils arise from synthetic N fertilizer use, application of animal waste, N fixed in soils by crops, deposition of excretal N during animal grazing and decomposition of crop residues and soil organic matter. To calculate total direct emissions, all of the N inputs are added together and an emission factor applied to it (National Inventory Report New Zealand, 2004).

There has been a five fold increase in N fertiliser use over the 12 years, from 57,541 tonnes in 1990 to 289,716 tonnes reported in 2002 (National Inventory Report New Zealand, 2004). The increased use of N fertilisers has resulted in greater quantities of N being cycled through agricultural systems, which, in turn, has increased N<sub>2</sub>O emissions from soils (Smith *et al.* 1997). These emissions do vary with the type of N fertiliser used. In general, when soil conditions favour denitrification, nitrate fertilisers cause higher emissions than urea or ammonium based fertilizers, whereas in warm, dry conditions, emissions following the application of the latter fertilisers are higher (Smith *et al.* 1997). Long term effects of fertiliser applications on N<sub>2</sub>O emissions were reported by Mosier *et al.* (1998b) who noticed that six years after fertilisation was stopped the

N<sub>2</sub>O emissions from the fertilised site were still about 50% higher than from the unfertilised site.

**Table 2.1 Summary of the agricultural N<sub>2</sub>O emission inventory for New Zealand in 2002 (National Inventory Report New Zealand 2004)**

N Source	N <sub>2</sub> O emitted (Gg yr <sup>-1</sup> )	% of total emission
Direct soil emissions from:		
Synthetic fertilisers	5.12	12.6
Animal manures	1.28	3.2
Enhanced biological N fixation	0.09	0.2
Crop residues & sewage sludge applications	0.17	0.4
Cultivated histosols	0.13	0.3
Total	6.79	16.7
Direct soil emissions from animal production	23.40	57.5
Total direct emissions	30.19	74.2
Indirect emissions from agricultural N due to:		
Atmospheric deposition	5.39	13.3
Nitrate leaching & runoff	5.12	12.6
Total indirect emissions	10.51	25.8
Total N <sub>2</sub> O emissions from agricultural soils	40.70	100

Another source of N<sub>2</sub>O emissions from the dairy industry is the application of dairy wastes such as manures and effluents to pastures, which are high in soluble carbon and hence have a potential to produce N<sub>2</sub>O when applied to soil (Watanabe *et al.* 1997; Khan 1999; Dalal *et al.* 2003). The fluxes of N<sub>2</sub>O emissions vary with waste and soil type (Saggar *et al.* 2004b). In New Zealand, large amounts of nitrogen-rich effluent are produced from the farming sector including dairy, pig, poultry farms, and associated dairy- and meat-processing plants (Hart & Speir 1992; Longhurst *et al.* 2000). When pond treated and/or applied to soils these are important sources of N<sub>2</sub>O emissions and hence will be discussed in detail in Section 2.4 of the review.

New Zealand's pastoral systems are predominantly grass/clover based, with N entering the system mainly via biological fixation. Legumes can have both a direct and indirect effect on N<sub>2</sub>O emission (Saggar *et al.* 2004b). Some legume root nodules provide favourable conditions for significant rhizobial denitrification, which is the reduction of nitrate to gaseous N by root-nodulating bacteria such as *Rhizobium* and *Bradyrhizobium* spp. (Steele *et al.* 1984). The total emissions of N via rhizobial denitrification are relatively low in New Zealand (Steele & Bonish 1987) as none of the bacterial strains associated with white clover are capable of denitrification (Daniel *et al.* 1982; Steele *et al.* 1984). Legumes could have an indirect effect on N<sub>2</sub>O emission through an increase in the soil mineral N content. But, Velthof *et al.* (1998) suggested that N<sub>2</sub>O emission from biological fixed N is probably less than from fertiliser N.

The incorporation of crop residues into soil also leads to increased emissions. Aulakh *et al.* (1991a) found that the incorporation of legume residue in the soil increased the rate of denitrification several fold with a total N loss via denitrification ranging from 51.1 to 99.5 mg N kg<sup>-1</sup> as compared to a total N loss of 14 to 18.6 mg N kg<sup>-1</sup> from soils where no residue was added. The emission rate mainly depends on the type, the stage of decomposition and the management of the residue and the measurement period.

The drainage and cultivation of organic soils enhances the mineralisation of N-rich organic matter (Mosier *et al.* 1998a), which in turn results in increased N<sub>2</sub>O emission. These emissions resulting from the mineralisation of organic N are mainly affected by groundwater level and fertiliser application (Kasimir-Klemmedtsson *et al.* 1997).

### 2.2.2 Direct emissions from animal production

A direct soil emission from animal production includes the N<sub>2</sub>O produced from the excretal deposition by the grazing animals and that from animal waste management systems (AWMS).

In New Zealand where open grazing is practiced throughout the year, excretal deposition by grazing animals contributes the most to N<sub>2</sub>O emission. Recently there have been a number of studies examining N<sub>2</sub>O emission from grazing animals (Carran & Theobald 1995; Clough *et al.* 1996; Luo *et al.* 1999b; Saggar *et al.* 2002). During grazing large quantities of N are deposited in the form of dung and urine by the grazing

animals, which can produce high  $\text{N}_2\text{O}$  emission. The range of  $\text{N}_2\text{O}$  emission factors reported for grazed pasture was 0.2% to 10% of N excreted with emissions generally being lower from pastures grazed by sheep and beef than by dairy cattle (de Klein 2001). The emissions from grazed pastures will be discussed in detail in Section 2.5 of this review.

The total  $\text{N}_2\text{O}$  emission from AWMS includes emissions from areas where animal waste is stored and treated. Farm effluent ponds are an important source in this category. Information on  $\text{N}_2\text{O}$  emission from animal waste while it is in storage is scarce because  $\text{N}_2\text{O}$  has previously been considered a small loss when compared to other gases such as  $\text{NH}_3$  and  $\text{CH}_4$ . Sibbesen & Lind (1993) measured  $\text{N}_2\text{O}$  emissions from a pig manure pile and reported a release rate of  $2.7 \text{ kg N ha}^{-1} \text{ d}^{-1}$ , which they estimated to be equivalent to 0.8% loss of total N. The analysis of the  $\text{N}_2\text{O}$  emissions from *in situ* anaerobic wastewater treatment systems of pig and dairy farms revealed average emissions of 0.002 and  $0.011 \text{ kg N}_2\text{O head}^{-1} \text{ year}^{-1}$  from pig and dairy farms, respectively (Su *et al.* 2003).

In New Zealand, where animals graze outside in the paddocks throughout the year, the AWMS-derived  $\text{N}_2\text{O}$  emission is less important. Moreover as the land application of the raw effluent increases, contributions from pond stored  $\text{N}_2\text{O}$  emissions become less significant. However, recently there has been increasing interest in the use of 'herd homes' and feedlots to overcome problems associated with animal treading, especially during wet spring and winter grazing periods (Luo *et al.* 1999b). These stand off shelters and feeding facilities are likely to result in the accumulation of manure, thereby contributing to greater  $\text{N}_2\text{O}$  emissions.

The above discussion indicates that  $\text{N}_2\text{O}$  emissions from soils are mainly dependent on the N inputs into the soil and N transformation dynamics in the soil. In the next section, I briefly discuss the various sources of N inputs into pasture soils and their transformations, and then discuss the mechanism of denitrification which is considered as the main process through which  $\text{N}_2\text{O}$  is produced in the soil. Most of this information has been published in recent reviews by Bolan *et al.* (2004b), and Saggar *et al.* (2004b) in which I contributed as a co-author.

### 2.2.3 Indirect N<sub>2</sub>O emission from N used in agriculture

A portion of the N added through fertilizers and animal excreta is emitted into the atmosphere as NH<sub>3</sub> and NO<sub>x</sub> through volatilisation, which returns to the soil during rainfall and might be then re-emitted as N<sub>2</sub>O. Mosier *et al.* (1998b) measured annual N<sub>2</sub>O emissions from a short grass steppe of about 2% of annual input estimated from wet and dry deposition, while Skiba *et al.* (1998) measured N<sub>2</sub>O emission from the atmospheric deposition of 0.2 to 15% of the N deposited, depending on the distance from the N source.

Emission factors are applied to the amounts of N that volatilise from synthetic fertilizer and waste. Relatively little is known about indirect N<sub>2</sub>O emissions from atmospheric N deposition and from leached/runoff nitrate. Both the total N inputs through atmospheric deposition and the subsequent N<sub>2</sub>O emissions from this atmospheric deposition in New Zealand are considered to be negligible. Ledgard *et al.* (1999) measured average annual N deposition rates of 2 kg N ha<sup>-1</sup> in New Zealand. However, NH<sub>3</sub> emission from urine patches is likely to be about 20% of the urine N deposited, and it is possible this NH<sub>3</sub> is being deposited downwind somewhere (de Klein *et al.* 2001).

Nitrous oxide is also emitted indirectly from N lost from agricultural soils through leaching and run-off which enters water systems and eventually the sea. Clough *et al.* (2000) have reported that the fate of N that leaches down the soil profile is uncertain though it is highly possible that it might undergo further denitrification in the subsoil. The uncertainty of the fate of leached N is reflected in the wide range of the 1996 IPCC default N<sub>2</sub>O emission values of 0.2%-12% of N leached/run-off (de Klein *et al.* 2001).



## **2.3 N dynamics in grazed pastures**

### **2.3.1 N input in pasture soil**

#### **2.3.1.1 Biological fixation**

In many countries including Australia, New Zealand and parts of North America and Europe, the use of legume-based pasture is the most common grazing management practice. In such pastures, N is derived mainly from the biological fixation of atmospheric N by a group of bacteria (known as rhizobium) living in the root nodules of the legume plants. The amount of biological N fixation depends on a number of factors including legume species, soil and climatic conditions, nutrient supply and grazing management. For example, biological N fixation rates in the range of 100–300 kg N/ha/yr are common for grass/clover pastures in New Zealand (Ledgard *et al.* 1990).

#### **2.3.1.2 Deposition of animal excreta**

In grazed pastures, a substantial amount of N is recycled through the direct deposition of animal excreta. Cattle retain up to approximately 20% of the total N intake via fodder and feeds in animal products (i.e. milk and meat). The remaining intake is excreted in urine and faeces. The proportion of total N intake excreted and its partition between urine and faeces is dependent on the type of animal, the intake of dry matter, and the N concentration of the diet (Whitehead 1970, 1986). For sheep and cattle, faecal excretion of N is usually about 8 mg N g<sup>-1</sup> of dry matter consumed, regardless of the N content of the feed (Whitehead 1995). The concentration of N in urine may vary from 1 to 20 g N l<sup>-1</sup> because of factors such as N content in the diet and the volume of water consumption, but is normally in the range of 8–15 g N l<sup>-1</sup> (Whitehead 1970). In most intensive high-producing pasture systems, where animal intake of N is high, more than half the N is excreted as urine.

Grazing animals deposit excreta unevenly across the pasture, being greatly influenced by stock type (e.g., sheep, dairy cattle, deer), stock behavior (e.g., camping of stock in small areas of the field) and stock management (e.g., winter feed pads).

### 2.3.1.3 Manure application and effluent irrigation

Confined animal production (i.e., beef and dairy cattle, poultry and swine) is the major source of manure by-products in most countries. In countries such as Australia and New Zealand, where open grazing is practiced, large amounts of manure are directly deposited onto pastureland.

Farm effluents contain a large reserve of plant nutrients (Longhurst *et al.* 2000). For example, in New Zealand, dairy and piggery effluents can supply annually N, P and K equivalents of 17,500 tonnes of urea, 12,500 tonnes of single super-phosphate, and 28,300 tonnes of potassium chloride, respectively, with a net fertilizer value worth 21.1 million dollars (Roberts *et al.* 1992; Bolan *et al.* 2003a). Application of these effluents to pasture lands has been shown to increase the dry matter yield and enhance the nutrient status of soils (Cameron *et al.* 1997).

The chemical composition of the effluent is known to vary with the type of effluent, treatment of the effluent and time (Roberts *et al.* 1992; Longhurst *et al.* 2000; Luo *et al.* 2004). Generally, only a small percentage of the total nutrient content of effluent is in a form that is readily available for plant uptake. For example, between approximately 74% and 95% of the N in dairy shed effluent is in organic form (Longhurst *et al.* 2000; Singleton *et al.* 2001), and only about 19% of the effluent N is in a readily available mineral N form (Roach *et al.* 2001). Ammonium N is the main inorganic N component, comprising 10-20% of the total N in dairy-shed effluent. So the N fractions in dairy-shed effluent have a mixture of slow- and fast-release properties, which sustains both short- and long-term pasture responses to effluent applications (Toor *et al.* 2004). The composition of some of the common farm effluents is shown in Table 2.2.

In New Zealand, the effluents (dairy and piggery farm effluents) are often treated biologically using two pond systems (Photo 2.1). In a two-pond system, the first pond is anaerobic and its waste loading is such that the oxygen in the pond is entirely consumed. The second pond, which is often termed aerobic, is usually a facultative pond, with an aerobic top layer over an anaerobic base. The aerobic pond treatment is followed by discharge of the effluent to land or stream. Biological treatment of farm effluents using the two-pond system should achieve a high degree of removal of the carbon and the suspended solids of the waste (Craggs *et al.* 2000). Only a small proportion of the nutrients such as N, P and K are removed in the two-pond systems

(Hickey *et al.* 1989; Bolan *et al.* 2003b), therefore these nutrients in farm effluents, become pollutants when discharged to streams. However, with the introduction of the Resource Management Act 1991 in New Zealand, discharge of effluents to surface waters is now a controlled or a discretionary activity, which requires resource consent.

Commonly the resource consent will require the effluent nutrient concentration to be minimised before entering the surface waters. This can be achieved by nutrient stripping of the effluent by tertiary treatment or land disposal of the effluent (Selvarajah 1996). The common method of using dairy and piggery shed wastes has been to return them directly to land. This reduces the contamination of the water bodies.



**Plate 2.1** Biological treatment of farm effluents using a pond system

Despite the general trend towards land-based application systems for treating agricultural effluents, there are still significant numbers of two-stage pond systems. For example, during 1995/96 about 40% of dairy farmers were using ponds as treatment systems (Selvarajah 1996), and during 1997 about 47% of meat-processing plants were using ponds (AgResearch unpublished data). However, recently more farmers are going for direct application of the effluent onto land. From a nutrient re-use perspective, application of effluents directly from their sources is of greater fertiliser value than using effluents from ponds. For example, the N content of effluent from meat processing is over  $200 \text{ mg N l}^{-1}$ , which can be reduced to less than  $100 \text{ mg N l}^{-1}$  at the pond discharge (Luo *et al.* 2004). Slurries obtained from ponds during de-sludging also offer a valuable nutrient source when they are applied onto land (Longhurst *et al.* 2000).

**Table 2.2** Composition and characteristics of agricultural effluents

Source	Dry matter (%)	BOD (mg l <sup>-1</sup> )	pH	Total N (mg l <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (mg l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	P (mg l <sup>-1</sup> )	K (mg l <sup>-1</sup> )
Dairy shed (yard washings)	0.04–4.96	4500	6.2–8.8	44–628	5–132	0–6	21–105	53–705
Piggery farm	0.04–2	176	NA	230–1300	170	17	65–600	162–500
Dairy-factory whey	1	4300–48000	4.5–11.9	1300–1400	NA	NA	365–880	1500–1680
Meat processing	0.02–0.22	300–3000	5.9–6.9	40–400	10–80	trace	10–30	20–150
Poultry farm-Hen manure <sup>a</sup>	40	NA	6.5	1.4–1.5	NA	NA	0.7–1.4	0.6–0.7
Poultry farm- Broiler litter <sup>a</sup>	75	NA	NA	2.5–4.4	NA	NA	1.2–1.9	0.3–1.8

<sup>a</sup> - All concentrations for poultry manure and litter expressed as percent oven-dry weight, except pH unit.

NA - Not available

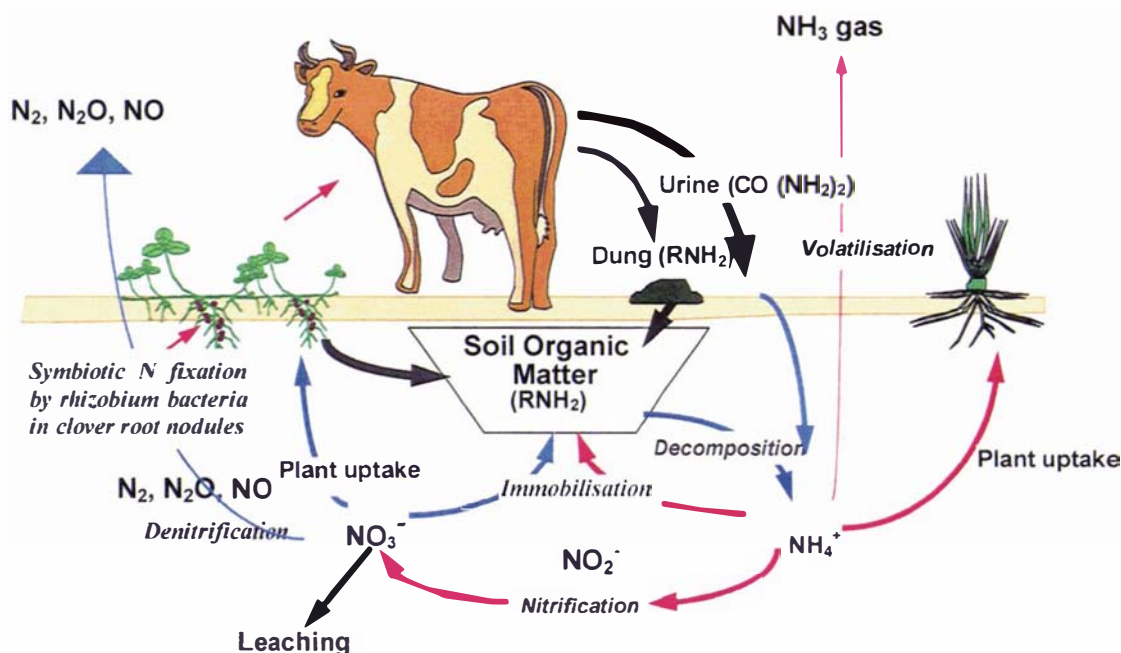
Data sources: (Hart & Speir 1992; Roberts *et al.* 1992; Carnus *et al.* 1998; Silva *et al.* 1999; Longhurst *et al.* 2000; Singleton *et al.* 2001; Di & Cameron 2002; Hawke & Summers 2003; Luo *et al.* 2004)

#### 2.3.1.4 Fertiliser input

Fertiliser applications have greatly increased pasture production on many grassland soils that are inherently deficient in nutrients. Nitrogen fertilizers are used widely in the grass-based intensive pasture production of Europe and North America. Pure grass pasture often responds linearly up to 200–400 kg N /ha/yr and application rates in this range are common (Whitehead 1995). Where pastures are cut for conservation, large quantities of nutrients are removed and the optimum N rate can be greater than that under grazed swards, where N is returned to pasture in the form of animal excreta. In legume-based pastures, a small amount of N fertiliser is traditionally added, mostly during the winter/spring period, when the rate of biological N fixation by legumes is not adequate enough to meet the demands of the pasture. The most common N fertilisers used in grazed pastures in New Zealand include urea (46% N), ammonium sulphate (21% N) and diammonium phosphate (DAP; 18% N). The form of N fertiliser used on dairy pastures depends not only on the cost per unit of N, but also on the overall efficiency of the fertiliser N. Such efficiency varies among fertilizer forms, which is attributed to the difference in the effects of fertilisers on the rate of uptake and assimilation of N, the losses of N through  $\text{NH}_3$  volatilization, denitrification and leaching, the N-induced cation/anion balance in the plants, and the acidifying effects of N (Bolan *et al.* 2004b). The effects of fertilisers on the above processes should be considered before any decision is made on the choice of N fertiliser for grazed pastures.

#### 2.3.2 N transformation in pasture soil

The transformation of N in a legume-based pasture is presented in Figure 2.1. The N transformation reactions in soils include: mineralisation, immobilisation, nitrification, denitrification,  $\text{NH}_3$  volatilization,  $\text{NH}_4^+$  fixation and  $\text{NO}_3^-$  leaching. While the first four reactions involve soil microorganisms (biotic), the last three involve only the chemical/physical processes (abiotic). It is important to understand these transformation processes in order to understand the environmental and economic implications of N cycling in soils.



**Figure 2.1** Dynamics of nitrogen transformations in legume-based pastures (189.251 Study Guide, M.J. Hedley)

### 2.3.2.1 Biotic transformations

#### *Mineralisation*

The bulk of the N in the soil and urine and faeces is in organic forms and it must first undergo microbial decomposition (mineralisation) before it is released as mineral forms. The mineralisation process involves the conversion of organic forms into inorganic forms by soil microorganisms. The process includes aminisation and ammonification reactions.

Aminisation is a microbial process in which the heterotrophic microorganisms breakdown the macromolecules of organic N compounds, such as proteins, into simple N compounds, such as amines and amino acids (Eq. 1).



The amines formed in Eq. (1) then undergo ammonification reaction, a biological process in which a group of microorganisms converts amine and amino acids into  $\text{NH}_4^+$  ions. For example, the urea N  $\text{CO}(\text{NH}_2)_2$  in urine and urea-based fertilizers undergoes an ammonification reaction, thereby releasing  $\text{NH}_4^+$  and  $\text{OH}^-$  ions (Eq. 2):



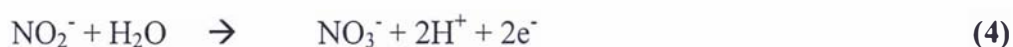


The  $NH_4^+$  ions formed through ammonification or added through ammonium fertilisers (ammonium sulphate and DAP) are subjected to several fates in the soil which include uptake by plants, conversion to nitrite ( $NO_2^-$ ) and  $NO_3^-$  (nitrification), utilization by microorganisms (immobilization), retention onto soil particles (ammonium fixation) and loss through  $NH_3$  volatilization.

The amount of N mineralised is closely related to the total N content, but N mineralisation is slower from faeces than from urine. The slow degradation of faecal material results in a slow release of other nutrients present in organic form (Whitehead 1995).

### **Nitrification**

Nitrification is defined as the biological oxidation of  $NH_3$  or  $NH_4^+$  to  $NO_2^-$  or  $NO_3^-$ . In most soil environments, nitrification is mediated primarily by autotrophic bacteria which gain energy from the oxidation of N, although heterotrophic nitrification maybe of importance in special situations (Kuenen & Robertson 1988). In autotrophic nitrification, the conversion of N takes place in two steps: the  $NH_3$  oxidising bacteria such as *Nitrosomonas* convert  $NH_3$  to  $NO_2^-$  (Eq. 3), while the  $NO_2^-$  oxidising bacteria such as *Nitrobacter* convert  $NO_2^-$  to  $NO_3^-$  (Eq. 4)



The nitrification process produces  $H^+$  ions, thereby decreasing the pH. Nitrate formed through nitrification of  $NH_4^+$  or added through  $NO_3^-$  fertilizers (e.g., calcium ammonium nitrate) is subjected to various processes, which include plant uptake, leaching losses, immobilization and denitrification.

### **Immobilisation**

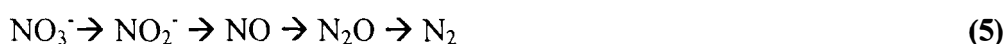
Immobilisation is a microbial process in which the plant-available  $NH_4^+$  and  $NO_3^-$  ions are converted to plant-unavailable organic N. In grazed pastures, the decomposition of senescent roots and leaves with high C:N ratios accounts for most immobilization but the addition of silage and manures promotes immobilization and reduces N availability to plants. Plant residues returned to soils need to be broken down

to release the nutrients stored in the organic matter. Soil microorganisms play a vital role in the break down (or decomposition) of plant residues; the rate of decomposition and the subsequent release of nutrients depend on the C:N ratio of the residues.

The addition of plant residues with a high C:N ratio induces immobilization of soil N by the microorganisms, thereby decreasing the amount of plant-available soil N. Conversely, plant residues with a low C:N ratio induce the mineralisation of N from the plant residues, thereby increasing the amount of plant-available soil N. It has often been observed that immobilization exceeds mineralisation when the C:N ratios are above 30 (Bolan *et al.* 2004b).

### **Denitrification**

Denitrification is one of the last steps in the soil phase of the N cycle, where the chemically or biologically fixed N is returned to the atmospheric pool of N<sub>2</sub>. Biological denitrification is defined as the dissimilatory reduction of NO<sub>3</sub><sup>-</sup> or NO<sub>2</sub><sup>-</sup> by essentially anaerobic bacteria producing molecular N<sub>2</sub> or oxides of N when oxygen is limiting (Payne 1981; Zumft 1997). Denitrification is carried out by respiratory denitrifiers that gain energy by coupling N-oxide reduction to electron transport phosphorylation (Tiedje 1988). Denitrifying bacteria can be present in nearly all soils and are generally facultative aerobes (Tiedje 1988). It is accepted that the main genera capable of denitrification in soil include *Pseudomonas*, *Bacillus*, *Alcaligenes* and *Flavobacterium* (Payne 1981; Firestone 1982; Tiedje 1988). The general pathway of the reduction of NO<sub>3</sub><sup>-</sup> during the denitrification process may be represented by Eq. (5) (Payne, 1981; Firestone, 1982).



The description of mechanisms involved in denitrification can be found in several reviews (e.g., Firestone (1982), Knowles (1982), Luo *et al.* (1999a)). The general requirements for biological denitrification include: a) the presence of bacteria possessing the metabolic capacity; b) suitable electron donors such as organic C compounds; c) anaerobic conditions or restricted O<sub>2</sub> availability; and d) N oxides, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO, or N<sub>2</sub>O as terminal electron acceptors. The process of denitrification is therefore generally promoted under anaerobic conditions, high levels of soil NO<sub>3</sub><sup>-</sup>, and a readily available source of carbon.

Although many soil bacteria seem able to denitrify, denitrifying bacteria exhibit a variety of reduction pathways. Some bacteria produce only N<sub>2</sub>, while others give a



mixture of  $\text{N}_2\text{O}$  and  $\text{N}_2$ , and some only  $\text{N}_2\text{O}$  (Stouthamer 1988). There has been some doubt whether  $\text{NO}$  is a true intermediate or a by-product (Amundson & Davidson 1990). Nitrous oxide and  $\text{N}_2$  are normally produced in soils in varying ratios, depending on the substrate, the environmental conditions, the organisms involved, and the time that has elapsed since the onset of denitrifying activity (Arah & Smith 1990). The ratio of  $\text{N}_2\text{O}:\text{N}_2$  evolved during denitrification increases as the soil becomes more aerobic (Firestone 1982).

The biological denitrification process is not solely responsible for the reduction of  $\text{NO}_3^-$  in soil. Nitrate is also subject to chemical reactions that lead to production of  $\text{N}_2$  by non-enzymatic pathways under fully aerobic conditions (Paul & Clark 1989).

Denitrification results not only in the loss of a valuable plant nutrient but also in the release of  $\text{N}_2\text{O}$  gas, which is implicated in the destruction of atmospheric ozone. The processes of  $\text{N}_2\text{O}$  emission and the factors affecting emission are discussed in detail in Section 2.4.

### 2.3.2.2 Abiotic transformation

#### *Ammonium fixation*

Ammonium ions are retained on inorganic and organic soil particles by cation exchange reactions and also fixed in the interlayers of 2:1 phyllosilicate clay minerals, such as mica, vermiculite and illite (Nommik & Vathras 1982). When other cations are added through fertilizer application, the  $\text{NH}_4^+$  ions on the cation exchange sites are released into the soil solution through cation exchange. Potassium ions, which are similar in size to  $\text{NH}_4^+$  ions (ionic radius of  $\text{K}^+ = 0.133$  nm and  $\text{NH}_4^+ = 0.143$  nm) have often been shown to replace the fixed  $\text{NH}_4^+$  ions, thereby releasing  $\text{NH}_4^+$  into the soil solution (McBride 1994). The ammonium fixation process affects N leaching and  $\text{NH}_3$  volatilization (Bolan *et al.* 2004b).

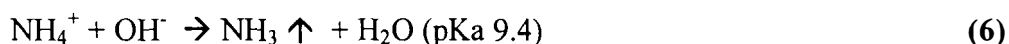
#### *Nitrate leaching*

The nitrate ion, being a non-specifically adsorbed anion, is weakly retained on the soil particles. It moves with water, and subsequent leaching not only results in the loss of a valuable nutrient but also causes ground water pollution. A high  $\text{NO}_3^-$  concentration in drinking water is toxic. The World Health Organisation has stipulated a safe upper limit of  $11.3 \text{ mg NO}_3^- \text{ l}^{-1}$  (or  $50 \text{ mg NO}_3^- \text{ l}^{-1}$ ) in drinking water.

Although leaching losses occur from both fertilizer N and urine N, a number of studies have shown that in dairy grazed pastures, urine patches are the major source of  $\text{NO}_3^-$  leaching (Di & Cameron 2002). The release of mineral N from faeces results in elevated concentrations of mineral N in the soil below the dung patch. The high concentrations of  $\text{NO}_3^-$  in dung patches (e.g., 90–130 mg N  $\text{kg}^{-1}$ ) (Ryden 1986) can also be a significant source of both  $\text{NO}_3^-$  leaching and gaseous losses of  $\text{N}_2\text{O}$  and  $\text{N}_2$  (through denitrification/nitrification) from grazed pastures.

### ***Ammonium volatilisation***

Ammonium ions in an alkaline medium dissociate into gaseous  $\text{NH}_3$ , which is subjected to volatilization losses (Eq. 6). Ammonia volatilization occurs when the soil pH is high (>7.5). In the case of urea application and urine deposition, the initial increase in soil pH through the ammonification process (Eq. (6)) is likely to result in  $\text{NH}_3$  volatilization.



In grazed pastures, biological degradation of animal excreta (dung and urine) and hydrolysis of fertilisers containing urea and  $\text{NH}_4^+$  lead to the continuous formation of  $\text{NH}_3$  in the soil, which volatilizes to the atmosphere. The rate of volatilization of  $\text{NH}_3$  is controlled by the rate of removal and dispersion of  $\text{NH}_3$  into the atmosphere (Peoples *et al.* 1995). Ammonia is lost from decomposing dung, particularly during the first week after deposition (MacDiarmid & Watkin 1972). Over the first 13 days of decomposition of cattle dung, MacDiarmid & Watkin (1972) measured a loss of 4.7% of the dung N, and Ryden *et al.* (1987) measured losses of 1.2 and 12.0% respectively for cattle and sheep dung over a 2-week period following deposition.

## **2.4 $\text{N}_2\text{O}$ emission: Production and assessment**

### **2.4.1 Process of $\text{N}_2\text{O}$ production**

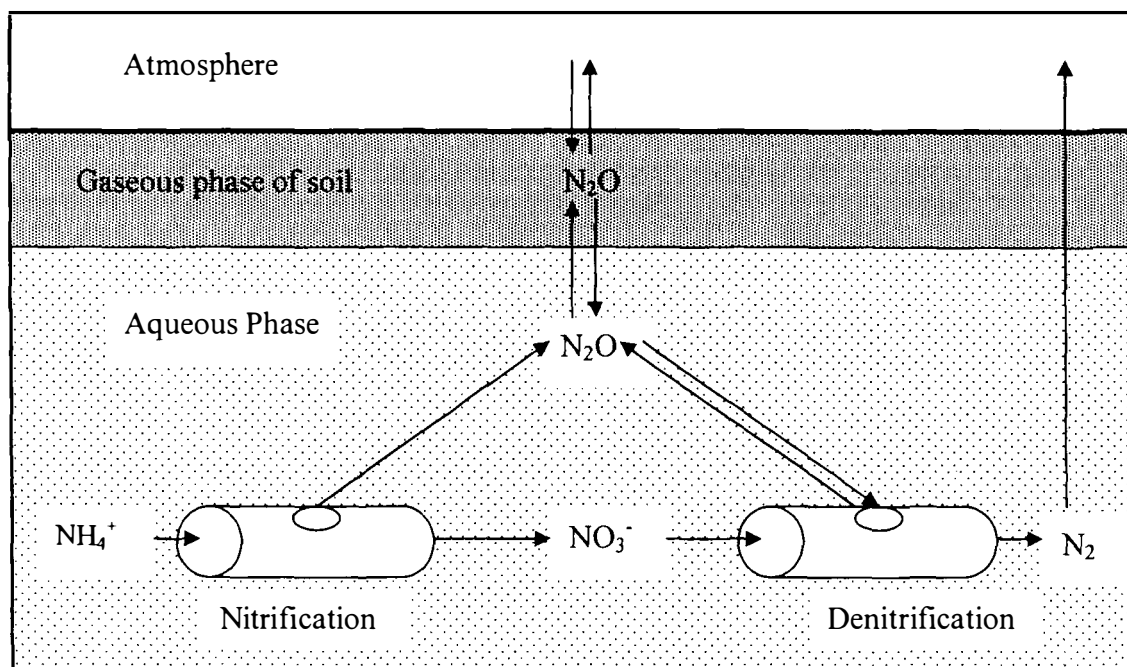
Nitrous oxide is produced in soil mainly in the course of two contrasting microbial processes: nitrification and denitrification. Both are microbially mediated mechanisms, the emission from which depends on numerous interacting factors. Nitrous oxide production by nitrifying bacteria may arise either during  $\text{NH}_4^+$  oxidation to  $\text{NO}_3^-$

or during dissimilatory  $\text{NO}_3^-$  reduction when  $\text{O}_2$  supply is limited. During denitrification,  $\text{N}_2\text{O}$  is an intermediate in the dissimilatory reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  to  $\text{N}_2$  under anaerobic conditions and may, therefore, be produced and consumed by denitrifying bacteria in soil (Robertson & Tiedje 1984).

The regulation of  $\text{N}_2\text{O}$  flux from soils by both nitrification and denitrification processes are given in Figure 2.2. The relative importance of both these processes to  $\text{N}_2\text{O}$  emission varies with the local conditions such as soil moisture status, soil temperature, and mineral N source in the soil. In wet soil, denitrification is generally the main source of  $\text{N}_2\text{O}$ , while in drier soils nitrification is the main source (Webster & Hopkins 1996; Kester *et al.* 1997). Nitrification and denitrification processes in soil often occur in close proximity so that a substantial part of the  $\text{NO}_3^-$  formed during nitrification, subsequently diffuses to the anaerobic denitrifying zone where it is reduced to  $\text{N}_2$  or gets emitted as  $\text{N}_2\text{O}$  (Nielsen *et al.* 1996).

Till recently, denitrification was considered to be the main process of  $\text{N}_2\text{O}$  emission with nitrification being of minor importance in its production (Monaghan & Barraclough 1993). Thus, most research dealing with factors influencing  $\text{N}_2\text{O}$  emissions has been centred on the process of denitrification (Haynes & Sherlock 1986). But research by Wang *et al.* (1997) and Granli & Bockman (1994) illustrated that  $\text{N}_2\text{O}$  production by nitrification process could be equally important depending on the soil conditions.

The majority of  $\text{N}_2\text{O}$  emissions in New Zealand pastoral soils are derived through denitrification (Carran & Theobald 1995; Saggar *et al.* 2004b). Furthermore, in the present study the majority of the experiments on effluent irrigation created conditions conducive for denitrification. Hence, while discussing the factors affecting the  $\text{N}_2\text{O}$  emissions, more emphasis is given to denitrification.



**Figure 2.2** A conceptual model of three levels of regulation of  $\text{N}_2\text{O}$  flux from soil: (i) the rates of nitrification and denitrification (amount of N flowing through the pipes); (ii) the ratios of end products (the size of the holes and orifices of the pipes); and (iii) diffusion and consumption of  $\text{N}_2\text{O}$  prior to escape from the soil to the atmosphere (Granli & Bockman 1994)

## 2.4.2 Factors affecting $\text{N}_2\text{O}$ emission

The emission of  $\text{N}_2\text{O}$  from soils is controlled by factors such as oxygen supply, water content, temperature, soil pH, organic matter, and N sources. In addition to these, several soil management practices such as tillage, soil compaction (Staley *et al.* 1990), irrigation and drainage (Mosier *et al.* 1986) affect the production and release of  $\text{N}_2\text{O}$  by influencing the soil's physical conditions (i.e. aeration and soil water content). The effect of individual parameters on  $\text{N}_2\text{O}$  emission is well established (Luo *et al.* 1999a; de Klein 2001). However, there is a lack of understanding of the interaction of the many factors affecting  $\text{N}_2\text{O}$  emission under various soil environments.

Environmental parameters that affect denitrification and hence the production of  $\text{N}_2\text{O}$  have been identified in laboratory studies reviewed by Payne (1981), Knowles (1982), Firestone (1982) and Bolan *et al.* (2004b) and the relative importance of these

parameters has been investigated in a number of field studies (e.g., (Ryden 1983; Rolston *et al.* 1984; Davidson & Swank 1986; Aulakh *et al.* 1991a; Luo *et al.* 2000).

In general,  $N_2O$  production appears to proceed in soils under a much broader range of conditions than would be predicted on the basis of the biochemistry of the process and the physiology of nitrifiers and denitrifiers.

### 2.4.2.1 Soil factors

#### *Soil water and aeration*

Soil water content together with the rate of oxygen consumption (respiration) determines the oxygen availability (Tiedje 1988). Oxygen availability is one of the most important factors affecting  $N_2O$  emission from soil. Dobbie & Smith (2003) found that large  $N_2O$  fluxes in grassland soils occurred when soil water filled pore space (WFPS) was >60%. Both, nitrification and denitrification processes are strongly controlled by WFPS (Davidson *et al.* 1991).

Field studies have shown that an increase in denitrification rate is associated with restricted soil aeration when high soil water content is present in pasture systems (de Klein & van Logtestijn 1994b; Ledgard *et al.* 1999; Luo *et al.* 2000). A number of studies showed the existence of a threshold of soil water content above which denitrification rates increased sharply (de Klein & van Logtestijn 1994b; Ruz-jerez *et al.* 1994). Below this critical threshold value, denitrification rates appeared to be unrelated to soil water content. de Klein & van Logtestijn (1996) suggested the soil water threshold for many soils is equivalent to field capacity or above. In general, threshold water content decreased when soil texture became finer with clay soils maintaining a higher WFPS for a longer period of time than rapidly draining sandy soils.  $N_2O$  can escape more easily from coarse-textured soil types (Granli & Bockman 1994). It is also suggested that low soil oxygen content resulting from soil compaction through animal treading, particularly when soils have high water content, could increase denitrification rates in grazed pastures (Luo *et al.* 1999a; Menneer *et al.* 2005).

Nitrification is an aerobic process, but when the supply of  $O_2$  is limited the nitrifying bacteria can use  $NO_2^-$  as an electron acceptor and reduce it to  $N_2O$  (Bollmann & Conrad 1998).

The  $N_2O:N_2$  ratio has often been found to decrease with increasing soil water content (Colbourn & Dowdell 1984; Rudaz *et al.* 1999). Under conditions of relatively

inactive denitrification during summer and early autumn, Ruz-jerez *et al.* (1994) noticed that the  $\text{N}_2\text{O}:\text{N}_2$  ratio was at its highest ( $\geq 1$ ) when most of the  $\text{N}_2\text{O}$  was possibly arising from nitrification. However,  $\text{N}_2\text{O}$  emissions from denitrification are mainly determined by the denitrification rate and not by the  $\text{N}_2\text{O}:\text{N}_2$  ratio as long as the soil is not so wet that the escape of gases from soil is hindered and most of the  $\text{N}_2\text{O}$  is reduced to  $\text{N}_2$  (Granli & Bockman 1994). Reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  is favoured in soils with very high clay content. Such soils can show low  $\text{N}_2\text{O}$  emission rates compared to coarser soils (Arah *et al.* 1991).

### **Soil mineral N**

Availability of the mineral N ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) to bacteria is an important controlling factor for the microbial processes that produce  $\text{N}_2\text{O}$ . The rates of denitrification and  $\text{N}_2\text{O}$  emission both increase with increasing soil  $\text{NO}_3^-$  concentration, whereas production of  $\text{N}_2\text{O}$  by nitrification is enhanced as the soil  $\text{NH}_4^+$  increases. Hence, application of N through fertilizers, manures or effluents that are high in mineral N contents is usually followed by an increase in  $\text{N}_2\text{O}$  emissions (Luo *et al.* 1999a; de Klein *et al.* 2001; Dalal *et al.* 2003; Eckard *et al.* 2004; Saggar *et al.* 2004b).

The availability of  $\text{NO}_3^-$  for denitrifying bacteria is the first step in biological denitrification, and the denitrification rate would therefore be expected to depend on  $\text{NO}_3^-$  concentration. The denitrification rate usually increases after the addition of  $\text{NO}_3^-$  in the field (Ryden 1983; Corre *et al.* 1990; Jarvis *et al.* 1991; de Klein & van Logtestijn 1994b; Ledgard *et al.* 1999; Saggar *et al.* 2002; Saggar & Bolan 2003), provided other factors are not limiting (McCarty & Bremner 1992; Luo *et al.* 1999b).

Nitrate concentrations have also been observed to influence the  $\text{N}_2\text{O}:\text{N}_2$  ratio in the gaseous products of denitrification. Nitrate usually inhibits  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$  (Bremner & Blackmer 1978). Therefore, at low  $\text{NO}_3^-$  concentrations,  $\text{N}_2$  is the predominant product and at high  $\text{NO}_3^-$  concentrations,  $\text{N}_2\text{O}$  often predominates (Arah & Smith 1990).

Mostly, oxidation of  $\text{NH}_4^+$  (i.e. nitrification) proceeds more rapidly than formation of  $\text{NH}_4^+$  through mineralisation (i.e. ammonification), so the nitrification process is usually  $\text{NH}_4^+$  limited (Granli & Bockman 1994). McTaggart and Tsuruta (2003) found greater  $\text{N}_2\text{O}$  emissions from  $\text{NH}_4^+$  fertiliser than from  $\text{NO}_3^-$  fertiliser even at WFPS of 85%, indicating that soil conditions were predominantly aerobic and that nitrification was the main source of  $\text{N}_2\text{O}$  emission. Inubushi *et al.* (1996) reported that nitrification



was the predominant source of emissions of  $\text{N}_2\text{O}$  from an andosol, incubated at 60% and 80% water-holding capacity, regardless of fertiliser presence or type.

Cai *et al.* (2002) observed that  $\text{N}_2\text{O}$  emission was in the range of 0.3 to 1.9% of N applied and observed that it was not a significant pathway of N loss from the N fertiliser applied to maize and wheat crop. Chen *et al.* (1998) observed similar result from  $^{15}\text{NH}_4^+$ -N application to the rice crop on alkaline soil where more applied N was lost through  $\text{NH}_3$  volatilisation (15-25% of applied  $^{15}\text{NH}_4^+$ -N) than through denitrification (<5% of applied  $^{15}\text{NH}_4^+$ -N).

Paramasivam *et al.* (1998) observed that the form in which N fertiliser is added in the soil influences the gaseous loss of N by denitrification. They observed a 1.9 to 2.3 fold higher cumulative  $\text{N}_2\text{O}$  production when ammonium nitrate (@ 200 mg N  $\text{Kg}^{-1}$  soil) was applied in the liquid form rather than the dry granular form and attributed to the easy availability of the N in the soil to micro organisms.

### **Carbon availability**

The supply of readily decomposable organic matter in soil is also critical in controlling the rate of denitrification (Payne 1981; Reddy *et al.* 1982; Robertson & Tiedje 1984; Beauchamp *et al.* 1989). Permanent pastures develop surface layers rich in organic material with potential for denitrification when fertilized by urine and dung, deposited during grazing (Ryden 1986). The presence of ample C substrate can also result in rapid  $\text{O}_2$  consumption and possible  $\text{O}_2$  depletion, which may then also indirectly enhance the potential for denitrification (Petersen 1999). It has been suggested that the decomposition of plant litter, animal faeces, and root exudates from the perennial plant cover, maintain moderate to high levels of available carbon in grazed pasture soils for denitrification (Carran *et al.* 1995).

Land application of farm effluents increases the soil C availability thereby enhancing the  $\text{N}_2\text{O}$  emissions (Barton & Schipper 2001). Other researchers have also attributed increased  $\text{N}_2\text{O}$  emissions to the C content of animal slurries (Petersen 1999; Chadwick *et al.* 2000).

The dependence of C availability results in higher denitrification potentials generally found in surface soils than in subsoils (Khan & Moore 1968). Organic C content decreases with depth in most mineral soils thus acting as a limiting factor for denitrification activity in subsoils (Weier & Doran 1987; Luo *et al.* 1996; Luo *et al.* 1998). Myrold & Tiedje (1985) showed that the diffusion rate of organic compounds in some soils limited the denitrification rate. Carbon availability can also influence the

proportions of  $\text{N}_2\text{O}$  and  $\text{N}_2$  produced. With increasing availability of C there is complete reduction of  $\text{NO}_3^-$  and therefore less  $\text{N}_2\text{O}$  production in relation to that of  $\text{N}_2$  (Smith & Tiedje 1979; Arah & Smith 1990; Dendooven *et al.* 1998).

Organic carbon input stimulates the microbial activity in an aerobic environment as well, which creates  $\text{O}_2$  limitation and thus reduces autotrophic nitrification (Granli & Bockman 1994).

### **Soil pH**

Soil pH has been called the master variable of the soil, since it influences many physical, chemical and biological properties and processes in the soil (Brady & Weil 1999). It has been reported that the rates of both denitrification and nitrification increase with pH from acidic conditions (pH 3 to 5) to neutral or slightly alkaline conditions with optimal pH being 7-8 (Focht 1974; Haynes & Sherlock 1986).

Denitrification declines if soil acidity shifts towards lower pH (Bremner & Shaw 1958; Bryan 1981; Nagele & Conrad 1990; Ellis *et al.* 1998a). However, Simek *et al.* (2000), found no significant relationship between soil pH and denitrifying enzyme activity, though denitrification potential was significantly correlated with soil pH. The degree of soil acidity also influences the ratio of the gaseous products of denitrification ( $\text{N}_2\text{O}:\text{N}_2$  ratio). It has been observed that the proportion of  $\text{N}_2\text{O}$  increases as pH decreases, with  $\text{N}_2\text{O}$  frequently appearing as the dominant product in acid soil (Christensen 1985; Parkin *et al.* 1985). For example, Rochester (2003) derived a negative exponential function between  $\text{N}_2\text{O}/\text{N}_2$  mole fraction and soil pH from a number of laboratory and field studies involving a range of soil types. A greater proportion of  $\text{N}_2\text{O}$  relative to  $\text{N}_2$  was emitted from acid soils; approximately equivalent amounts of these two gases were emitted from soil of pH 6.0 and for alkaline grey clays (pH 8.3–8.5) the  $\text{N}_2\text{O}/\text{N}_2$  mole fraction was about 0.024. Because the reduction of  $\text{N}_2\text{O}$  is inhibited more than the reduction of  $\text{NO}_3^-$  by acidic conditions,  $\text{N}_2\text{O}$  production is enhanced and becomes more dominant at low pH conditions (Koskinen & Keeney 1982).

In soils where nitrification is the main source of  $\text{N}_2\text{O}$ , emissions tend to increase with increasing pH, at least in the range of pH 6 to 8, though there seems to be no trend in the product ratio of nitrification ( $\text{N}_2\text{O}:\text{NO}_3^-$ ) with changing pH (Granli & Bockman 1994).



### ***Soil compaction***

Soil compaction is regarded as the most serious environmental problem caused by conventional agriculture (Hansen 1996), especially in moist temperate climates (Douglas & Crawford 1993). Overuse of machinery, intensive cropping, short crop rotations, intensive grazing and inappropriate soil management lead to compaction (Hamza & Anderson 2005). Soil compaction can occur in a wide range of soils and climatic conditions and is intensified by the use of tillage or grazing on soils high in moisture content and low in organic matter.

Soil compaction adversely affects soil physical fertility, particularly the storage and supply of water and nutrients, through increasing bulk density and soil strength, and decreasing soil porosity, soil water infiltration, and water holding capacity. These adverse effects reduce fertilizer efficiency and pasture yield, increase water logging, and runoff and soil erosion with undesirable environmental pollution problems (Hamza & Anderson 2005). Soil compaction decreases the proportion of coarse pores (O'Sullivan & Ball 1993), air permeability and gas diffusion (Ball *et al.* 1997) and thus potentially increases the abundance of anaerobic microsites (Sitaula *et al.* 2000).

The production, consumption and transport of  $N_2O$  in soil are strongly influenced by the changes in soil structural quality and in water content associated with compaction (Ball *et al.* 1997). Reduced or no tillage systems increase  $N_2O$  emission (Aulakh *et al.* 1984) because of increase in compaction. Soil compaction by tractor wheels can also increase  $N_2O$  emission compared to zero traffic levels (Douglas & Crawford 1993). In grazed-pastures, animal treading is an important cause of soil compaction and can have a significant adverse effect on soil properties and plant growth. The effect of cattle treading on soil compaction and on  $N_2O$  emission will be discussed in detail in Section 2.5.2 of this Chapter.

#### **2.4.2.2 Climate factors**

##### ***Soil temperature***

The rate of  $N_2O$  emission exhibits temperature dependence, as is the case with all other biological processes. Denitrification and nitrification rates increase with temperature. However, while the denitrification product ratio ( $N_2O:N_2$ ) falls with increasing temperature (Maag & Vinther 1996; Castaldi 2000), the nitrification product ratio ( $N_2O:NO_3^-$ ) tends to rise (Goodroad & Keeney 1984). The combined effect is that

N<sub>2</sub>O emission rates increase with temperature. The minimum temperature for emissions is generally associated with the occurrence of free water, whereas the maximum temperature is approximately that value limiting biological activity in the soil. The range of temperature correlation factors ( $Q_{10}$ ) for N<sub>2</sub>O emission is very wide. Smith *et al.* (1998) compiled a list of previously reported  $Q_{10}$  values, and found that the values ranged from less than 2 to more than 20. Dobbie and Smith (2003) observed that the temperature response of the N<sub>2</sub>O emissions was greater over the lower range of temperature than the higher range, with  $Q_{10}$  of 3.7 and 2.3 for 5-12°C and 12-18°C temperature ranges, respectively. The overall increase in the rate of N<sub>2</sub>O production in soil with an increase in temperature is due to the combined effect of increases in O<sub>2</sub> gradients in soil due to increased respiration (Craswell 1978), and its effects on a range of biological processes such as mineralisation, nitrification and soil denitrification.

Temperature is thought to be one of the main factors causing temporal fluctuations in denitrification (Ryden 1983). Studies by Powlson *et al.* (1988) and Malhi & Osullivan (1990) indicate denitrifying bacteria can adapt to soil temperature conditions, so the optimum temperature for denitrification could differ in different regions. Several researchers have found that denitrification losses during the winter period are limited by the soil temperature (Ryden 1986; Jarvis *et al.* 1991; de Klein & van Logtestijn 1994b), although rapid losses of N by denitrification have been reported after the addition of mineral fertilizers and organic manure at low soil temperatures (Egginton & Smith 1986b; Thompson *et al.* 1987; Schwarz *et al.* 1994).

The temperature range between 25 and 35°C is considered optimum for nitrification to take place (Haynes & Sherlock 1986). However like denitrifying bacteria, the indigenous nitrifiers have temperature optima adapted to their climatic regions (Granli & Bockman 1994).

### ***Rainfall***

Enhanced N<sub>2</sub>O efflux following rainfall has been commonly reported for agro ecosystems and is generally attributed to the dual effects of bringing applied substrate into contact with soil microbial biomass and reducing soil O<sub>2</sub> levels (Ellis *et al.* 1998b). However, sometimes a decrease in emissions might be observed after an initial burst because of the downward movement of N with the wetting front following water application (Paramasivam *et al.* 2002). The moisture status of the soil at any place depends on the water supply by rainfall and irrigation, water removal by drainage and evapo-transpiration and the soil's water storage capacity. Peak N<sub>2</sub>O emission or

denitrification rates are generally found following rainfall or irrigation events (Velthof *et al.* 1996a; de Klein *et al.* 1999).

Nitrous oxide emissions from denitrification are greatly elevated with increased rainfall intensity and rainfall is thus a potential suitable parameter in a predictive model for N<sub>2</sub>O emissions (Corre *et al.* 1990). However, sometimes there might be little evidence to relate precipitation events directly to N<sub>2</sub>O flux peaks though the highest emission rates do coincide with the period of highest precipitation (Cates & Keeney 1987).

Nitrous oxide emissions are usually found to occur in bursts following high rainfall events; emissions returning to background levels within 24-48 h after rainfall (Corre *et al.* 1990). These bursts in emissions are shorter lived for light textured soils than heavy textured soils (12 h in a sandy loam soil and 48 h in a clay loam soil) (Sexstone *et al.* 1985). This short-term episodic response of N<sub>2</sub>O emission to rainfall can be an important factor for deriving a meaningful temporal sampling scheme (Corre *et al.* 1990).

The topography of the area also plays an important role in influencing the effect of rainfall on the N<sub>2</sub>O emission rate. A better correlation was observed between rainfall levels and emission rates at the foot of a slope (0.73) than from a flat area (0.57) (Corre *et al.* 1990). Also the time taken for emissions to return to background levels was higher (48h) from the foot of a slope than from the flat area (24h).

As discussed earlier, the deposition of urine and faeces of farm animals (either during grazing or through effluent application) forms the major pathway by which N is cycled in pastures (Parsons *et al.* 1991). During dry conditions, the soil dries rapidly after urine/dung addition and severely limits the nitrification process. But after a rainfall event when the soil moisture reaches its optimum level the stored N in soil undergoes nitrification and increased emission is observed. For example, Bronson *et al.* (1999) did not observe any significant change in N<sub>2</sub>O emissions from the soil where sheep urine was added until a rainfall event occurred 14 days after the treatment addition, after which the emissions from urine treated soils were significantly higher than the water treated soil.

On average, the annual precipitation in New Zealand ranges between 800-1500mm and is fairly evenly distributed throughout the year (Alaric 1992). The seasonal variation in rainfall pattern differs from place to place, though the main feature for the North Island is a broad precipitation maximum in winter and early spring with a

minimum during the summer months (Salinger *et al.* 2003). This creates conditions conducive for the denitrification to occur during the winter season.

### 2.4.3 Measuring techniques

Despite the importance of N<sub>2</sub>O as a greenhouse gas and its role in destroying the stratospheric ozone, its global budget remains poorly understood at present (Prather *et al.* 1995). The most important reason is the difficulties in measuring the fluxes and then correctly extrapolating them to the global scale. The atmospheric lifetime of N<sub>2</sub>O is about 130 years (Granli & Bockman 1994), therefore the small fraction of the annual emission over the high background concentrations makes the precise flux measurement difficult. High spatial and temporal variability hinders further the efforts to accurately measure N<sub>2</sub>O fluxes (Dalal *et al.* 2003). In the past, except for the acetylene inhibition method, none of the techniques have been extensively used to measure N<sub>2</sub>O flux under field conditions, because analytical methods that respond rapidly enough, or are sensitive enough to quantify N<sub>2</sub>O were not available. But the equipment necessary for extensive field studies of N<sub>2</sub>O emissions are now available. In the last three decades the measurement techniques and instrumentation for quantifying gaseous N fluxes have been improved considerably. However, the uncertainties in the regional budgets have not yet been reduced due to large spatial heterogeneity and the temporal variability of the factors that control N fluxes in ecosystems.

Nitrous oxide flux is measured mainly in two ways:

- Chamber method, and
- Micrometeorological approach

Smith *et al.* (1994) summarised the N<sub>2</sub>O fluxes measured by the chamber method and micrometeorological techniques over six consecutive days and observed that mean fluxes from the chamber methods, using Gas Chromatography (GC), Fourier-Transform Infrared spectrometers (FTIR), and long-path infrared spectroscopy to detect N<sub>2</sub>O, were larger than those from the micrometeorological method.

Emission of N<sub>2</sub>O gas from soil should preferably be measured without any disturbance either of the soil or of the processes that form or remove N<sub>2</sub>O. At present chamber methods are considered the reference methods as they combine good detection sensitivity with practical simplicity. But they are known to disturb the soil and emission process during their installation in the soil. For example, (Matthias *et al.* 1980) noticed

that the insertion of a metal cylinder into the soil to a depth of 5 cm leads to a 250% increase in the rate of emission of  $\text{N}_2\text{O}$ .

### ***Chamber method***

The  $\text{N}_2\text{O}$  emissions from terrestrial ecosystems have been measured using chambers for a considerable time. This method has been described in detail by many researchers (Mosier 1989; Hutchinson & Livingston 1993; Holland *et al.* 1999; Meyer *et al.* 2001). A chamber consists of an open bottom cylinder which has a detachable lid. The chamber is placed on the soil surface for a specific period of time, during which the gas emitted from the soil accumulates into the headspace of the chamber. Gas samples are collected periodically and analysed for  $\text{N}_2\text{O}$  concentration. Gas chromatography (GC) using electron capture detector (ECD) is the most commonly used method for gas analysis and permits convenient analysis of  $\text{N}_2\text{O}$ . The major characteristic of the electron capture detector (ECD) is its great selectivity based on the electron absorption coefficients of the compounds, which pass through the detector. Nitrous oxide has been shown to have a high electron absorption coefficient at temperatures around  $300^\circ\text{C}$  (Kaspar & Tiedje 1980). The gas chromatography system can provide a linear response to a large  $\text{N}_2\text{O}$  concentration range.

There are two types of chambers used under field conditions to monitor  $\text{N}_2\text{O}$  emission known as closed chambers and open chambers.

### ***Closed chambers***

Nitrous oxide in these chambers is directly quantified by measuring the short term build up or decrease in concentration in a sealed enclosure placed over the land surface. They are usually easy to construct from a variety of readily available materials which are inert for  $\text{N}_2\text{O}$  (IAEA, 1992). Closed chambers can be further divided into two types:

- Fixed base type chambers are constructed with separate collars which are inserted into the soil for the duration of the experiment, and a gas tight chamber is attached for a short period (Ambus & Christensen 1994). The main advantage of the static chambers is that these are easy to use and inexpensive. But they are highly labour intensive and a large number of chambers are required to cover the high spatial and temporal variability in  $\text{N}_2\text{O}$  emission under field conditions. Long time placement of these chambers in the field is known to affect the soil microclimate and thus  $\text{N}_2\text{O}$  gas flux.

- Removable chambers are constructed as a single unit which are installed in the soil for each sampling time and then removed until the next measurement period (Mosier & Hutchinson 1981). These chambers enable the randomisation of chamber positions, thereby covering spatial variability present in the field without interfering with field operations. But they are labour intensive and cause more soil disturbance every time they are inserted in the soil.

#### *Open chambers*

Open chambers are coupled to the atmosphere via an air inlet through which outside air is continuously drawn into the chamber and forced to flow over the enclosed soil surface. The gas flux from the soil is calculated from concentration difference, flow rate, and the area covered by the chamber (IAEA, 1992). The effects of N<sub>2</sub>O accumulation are reduced in open chambers which allow a longer period of measurements. However, open types are sensitive to pressure deficits inside the chamber due to induced air flow and may cause artificially high fluxes.

To reduce the labour and time required in measuring N<sub>2</sub>O emissions via chamber methods, automated chambers have been developed. Automated chambers provide continuous flux measurement without being labour intensive (Brumme & Beese 1992; Wang *et al.* 1997; Ambus & Robertson 1998). These have been especially useful in measuring small changes in N<sub>2</sub>O fluxes in the field. However, their main limitation is that they are very expensive to maintain. Moreover, they are not able to cover the spatial variability present in the field as they measure flux from a small area. A large number of chambers are required at a time to cover the within site variability of N<sub>2</sub>O flux. Often temporal variability is dominated by sudden change in factors affecting the N<sub>2</sub>O emission events (Meyer *et al.* 2001). The quantification of temporal and spatial variability is thus important to accurately measure fluxes on a large scale (Laville *et al.* 1999).

#### ***Micrometeorological approach***

Micrometeorological approaches are based on measurements of moving air masses over the ecosystems and have an advantage over chamber techniques of achieving spatial and temporal integration of N<sub>2</sub>O flux under field conditions. Fluxes are measured over large areas (1km<sup>2</sup> to several million ha) (Fowler 1999). Micrometeorological methods measure gas emissions from the field without disturbing the gas exchange between the atmosphere and the soil. Sensors mounted on towers detect the movement and gas content of air above and within the plant canopy; the rate



and direction of flux can be determined from gas concentrations, gradients and turbulence (Fowler *et al.* 1995). Four different approaches used in the micrometeorological method of measurement are: eddy correlation, flux gradient, mass balance calculations and nocturnal boundary approach. Although the technique is not as sensitive as the chamber approach, it appears to be promising for quantifying annual flux measurements for entire landscape units (Griffith *et al.* 2002). It's only at very few places that micrometeorological systems are being used for N<sub>2</sub>O estimation but where they have been deployed, the results are in agreement with those obtained from chamber measurements (Christensen *et al.* 1996; Mosier *et al.* 1996).

Measurement of N<sub>2</sub>O emissions by the micrometeorological method is difficult because of small concentrations of N<sub>2</sub>O and a need for appropriate weather conditions as turbulent conditions can alter the results. Another major limitation is the high cost of the instrumentation. The major advantages include long term monitoring of the N<sub>2</sub>O emissions on a landscape scale and field measurements to integrate spatial and temporal heterogeneity of N<sub>2</sub>O emissions, and the concurrent measurement of other trace gas fluxes to assist in interpreting field measurements (Fowler 1999; Laville *et al.* 1999).

In future, combinations of chamber and micrometeorological approaches might prove appropriate. While chamber techniques will help to measure low fluxes and to make comparisons among different land management strategies, micrometeorological methods will help to measure spatially integrated fluxes (Dalal *et al.* 2003).

#### 2.4.4 Modelling N<sub>2</sub>O emissions

The major difficulty in quantifying annual N<sub>2</sub>O fluxes at the field scale is the high degree of spatial and temporal variability. Few field measurements are available for both natural and managed ecosystems, and most do not cover long enough periods to capture seasonal variations. The Intergovernmental Panel on Climate Change (IPCC) default methodology has been used to estimate global agricultural N<sub>2</sub>O emissions (Mosier *et al.* 1998a). Based on a review of field studies by Bouwman (1996), IPCC methodology uses a fixed N<sub>2</sub>O emission rate of 1.25% for the N applied through fertiliser, manure, green manure or fixed by leguminous crops. New Zealand currently uses a modified animal IPCC methodology to produce an annual emission inventory for N<sub>2</sub>O. The emission factor used is 0.01 kg N<sub>2</sub>O-N kg<sup>-1</sup> excreted N, which is based on two New Zealand studies of representative pastures (Carran *et al.* 1995; Muller *et al.* 1995).

The highly empirical IPCC default methodology remains an approximation of unknown accuracy because of i) uncertainty in emission factors, ii) uncertainty in indirect emissions, iii) limited data on the type and amount of N excreted by grazing animals, and iv) the spatial and temporal variability of N<sub>2</sub>O emission. Also, the IPCC methodology is not sufficiently flexible to allow mitigation options to be assessed. International experience in deriving emission factors from field measurements at sites with different soil types, climate and crops (IPCC, 1997) shows that these emission factors have a large range, which leads to a large uncertainty in emission estimates (Brown *et al.* 2001a; Saggar *et al.* 2004a).

Mathematical models are important in simulating complex phenomena involved in N<sub>2</sub>O emission. The models can then be used at different scales to extrapolate measured data to wider temporal and spatial scales.

Accordingly, a more robust, process-based approach is required that is internationally acceptable and quantifies N<sub>2</sub>O emissions at the field level more accurately than the IPCC methodology. Such an approach is needed to develop regional and national scale inventories with known levels of uncertainties. Improved assessment of N<sub>2</sub>O emission also requires techniques to reduce random variation within farm units, and knowledge of factors that result in systematic variation among different farms and across seasons. Therefore, all the process-based models of N gas emissions must consider the ecosystem N cycle and the interaction of the N cycle with the C cycle, and the environmental and other biophysical conditions that result in systematic variations. In the past 20 years, considerable progress has been made on the development of accurate emission estimates for N<sub>2</sub>O. Several detailed biochemical process-based models of N gas emissions have been developed over the last several years. About 60 process-based models are available from internet sites, such as:

<http://yacorba.res.bbsrc.ac.uk/cgi-bin/somnet> & <http://eco.wiz.uni-assel.de/ecobas.html>

Of these models, a modified version of Denitrification and Decomposition (DNDC) model (Li *et al.* 1992) named “NZ-DNDC” has been used in New Zealand to provide site-specific and regional estimate N<sub>2</sub>O emissions from soils in recent years, and is described here.



#### 2.4.4.1 DNDC

The Denitrification and Decomposition (DNDC) model (Li *et al.* 1992) has reasonable data requirements and has produced robust regional estimates for the US (Li *et al.* 1996), China (Li *et al.* 2001) and the UK (Brown *et al.* 2001b; Brown *et al.* 2002). In New Zealand a modified 'NZ-DNDC' model simulated effectively most of the WFPS and N<sub>2</sub>O emission pulses and trends from ungrazed and grazed dairy pastures and fairly reproduced the real variability in underlying processes regulating N<sub>2</sub>O emissions (Saggar *et al.* 2002; 2003; 2004a).

The DNDC model consists of four submodels: thermal-hydraulic, crop-growth, decomposition, and denitrification. The model is based on the kinetic processes of N<sub>2</sub>O production where denitrification is activated by a rainfall/irrigation event that saturates the soil. Soil temperature and moisture are the key factors controlling both decomposition and denitrification. The thermal-hydraulic submodel uses basic climate data to simulate soil moisture conditions and to capture anaerobic microsite formation and sequential substrate reduction. The crop growth submodel simulates growth of various crops from sowing to harvest. Biomass is accumulated based on daily N and water uptake, and thermal degree-days. Yield and N content of above and below-ground plant components are modelled. The decomposition submodel has four soil carbon pools: litter, microbial, labile and passive. Each pool has a fixed C: N ratio and decomposition rate influenced by soil texture (clay content), and soil moisture and temperature. The decomposition submodel provides initial NO<sub>3</sub><sup>-</sup> and soluble C pools for the initiation of denitrification, which is also activated by rainfall and increased WFPS. An increase in the WFPS by rain or irrigation events decreases soil oxygen availability. The denitrification submodel predicts N<sub>2</sub>O emission based on WFPS, soluble C, soil temperature, soil pH, available N and denitrifier biomass (Frolking *et al.* 1998).

The DNDC model is designed in such a way that soil moisture has a large influence on N<sub>2</sub>O fluxes through its impact on the volume of soil in which denitrification occurs and the duration of denitrifying conditions. Water infiltration also causes NO<sub>3</sub><sup>-</sup> leaching. Therefore, successful simulation of N<sub>2</sub>O emissions will depend on the successful simulation of soil moisture conditions. The original version of DNDC has default parameters for soil-water content at field capacity and wilting point as a function of soil texture. The model uses a multi-layered soil for simulating soil water conditions.

Numerous international researchers from Canada, the U.K., Germany, the Netherlands, Italy, Finland, Australia, New Zealand, China, Japan, Thailand and the Philippines have made significant contributions to the development of the model and its applications.

Saggar *et al.* (2002; 2003; 2004a) recently modified DNDC to better represent New Zealand's grazed pasture systems and the modified model 'NZ-DNDC' was then used to simulate N<sub>2</sub>O emissions from pastures grazed by dairy cattle. Overall, the NZ-DNDC was found to predict effectively the annual measured emission from both the grazed and ungrazed farms; annual emission estimates for both farms were within 10% of the measured values, and within the uncertainty range of the measured values. The modified model fairly reproduced some of the variability in underlying processes regulating N<sub>2</sub>O emissions. However, estimates based on the NZ refined IPCC methodology (New Zealand Greenhouse Gas Inventory 2004) were about 25 to 60% lower than for the measured values. The NZ-DNDC model was, therefore, better at predicting N<sub>2</sub>O emissions than the refined IPCC methodology.

Saggar *et al.* (2002; 2003) suggested that to achieve more reliable field-scale estimates of N<sub>2</sub>O emissions for grazed pastoral systems, further model refinement is needed to account for slow winter pasture growth and N uptake and the flush of spring pasture growth. NZ-DNDC appears to capture the key processes controlling N<sub>2</sub>O emissions, and offers a robust platform for future achievement of this goal (Saggar *et al.* 2002). Current research on N<sub>2</sub>O abatement in New Zealand (Saggar *et al.* 2003) focuses also on using NZ-DNDC to simulate the efficacy of mitigating fertiliser- and urine-induced N<sub>2</sub>O emissions from grazed pasture systems, using nitrification inhibitors, and on developing best management practices for efficient effluent application to reduce N<sub>2</sub>O emissions.

## 2.5 N<sub>2</sub>O emission from grazed pasture

In New Zealand, where open grazing is practiced, large amounts of animal excreta are directly deposited onto pastureland. New Zealand's approximately 5.3 million dairy cows and 4.5 million beef cattle excrete daily around 80 million m<sup>3</sup> of excreta (Saggar *et al.* 2003; Saggar & Bolan 2003; Saggar *et al.* 2004a; 2004b). Moreover, the intensification of the dairying industry in New Zealand over the last decade (New Zealand Greenhouse Gas Inventory 2004) has elevated these figures

further. New Zealand's 39.5 million sheep also make a significant contribution. The N in urine could provide a major source for  $\text{N}_2\text{O}$  emissions, and the anaerobic decomposition of dung results in the emission of  $\text{CH}_4$ .

Also in dairy farms some faecal excretions are deposited in the milking shed, generating large volumes of dairy-shed effluent. Faecal material from non-ruminant animals, primarily pigs, poultry and horses, also decomposes anaerobically and is a further source of emissions when applied to land. It is estimated that annually in New Zealand about 70 million  $\text{m}^3$  of effluent are being generated from dairy sheds, 4 million  $\text{m}^3$  from piggery farms, and 50 million  $\text{m}^3$  from meat-processing plants (Saggar *et al.* 2004b). All these effluents and manure contain significant quantities of valuable nutrients that could be applied onto land to improve soil fertility and increase the sustainability of farming systems. However, there have been some environmental concerns about the management of increased waste production (Bolan *et al.* 2003a).

### 2.5.1 Emission from land application of effluent

Nitrous oxide emissions are highly dynamic and vary with time after manure application, type of application and supplemental water additions (Sommer *et al.* 1996). Although ratios of  $\text{N}_2\text{O}$  emissions to total denitrification are extremely variable, past studies have indicated that  $\text{N}_2:\text{N}_2\text{O}$  ratios after manure slurry additions range from nearly 1 to 3 (Jarvis *et al.* 1994; Jarvis & Pain 1994). Comfort *et al.* (1990) found that  $\text{N}_2\text{O}$  loss was greatest shortly after liquid manure injection and was followed by a shift to  $\text{N}_2$  emissions. Thus, in soils where FDE is repeatedly applied, frequent shifts between  $\text{N}_2\text{O}$  and  $\text{N}_2$  production could be observed.

Nitrous oxide evolution from the pasture soils treated with liquid dairy-manure application was often greater than the total denitrification from row crops on similar soils fertilized with inorganic fertilizer (Lowrance & Smittle 1988; Lowrance 1992). Barton & Schipper (2001) suggested that higher  $\text{N}_2\text{O}$  emissions from DFE (50 kg N  $\text{ha}^{-1}$ ) than from inorganic N fertiliser ( $\text{NH}_4\text{Cl}$  @ 50 kg N  $\text{ha}^{-1}$ ) was due to enhanced denitrification activity resulting from the readily oxidizable C in the FDE creating a high BOD. Barton & Schipper (2001) further noticed that denitrification rates increased immediately after DFE irrigation, peaked at 24h, and then decreased to pre-irrigation rates after 3 days. Very low  $\text{N}_2\text{O}$ -emission (0.03% of the added N) was observed in a recent measurement, following an application of dairy-shed effluent to a very dry soil in

autumn in the Waikato region (J. Luo pers comm.). On the other hand Clough & Kelliher (2005) observed overall lack of any enhanced  $\text{N}_2\text{O}$  production following raw DFE application to the soil ( $2\text{--}4 \text{ kg inorganic N ha}^{-1}$ ) as compared to the control and attributed it to the insignificant hydraulic loading resulting in the low moisture status of the soil and the low input of C & N into the soil. These results further corroborate the importance of WFPS in  $\text{N}_2\text{O}$  emissions.

Nitrous oxide emission is found to vary with the nature of the effluent applied. For example, Khan (1999) measured 1.9% and 0.1–0.3% of the applied N as  $\text{N}_2\text{O}$  emissions from piggery effluent and dairy factory effluent, respectively and attributed the low  $\text{N}_2\text{O}$  emissions from DFE to its application by flood irrigation. Saturated soil water conditions can reduce  $\text{N}_2\text{O}$  emission by enhancing the complete reduction of N oxides to  $\text{N}_2$  gas (Kester *et al.* 1997). Chadwick *et al.* (2000) found that dairy cow slurry increased soil  $\text{N}_2\text{O}$  emissions more than pig slurry mainly because of the greater C addition in the former.

Liquid-waste injections have been shown to create an anaerobic environment abundant in inorganic N and readily oxidizable C (Comfort *et al.* 1988). Following surface application or injection to a grassland soil in winter Thompson *et al.* (1987) found denitrification losses were 12% and 21%, respectively of the total N applied. Denitrification rates in the upper 30 cm of a sandy grassland soil increased up to  $400 \text{ g N ha}^{-1} \text{ d}^{-1}$  following slurry injection, and  $13.7 \text{ kg N ha}^{-1}$  was estimated to be lost during the 18-week experimental period (de Klein *et al.* 1996). The increased denitrification rates after slurry injection can be attributed to the presence of large quantities of inorganic N together with high organic C levels and increased soil water content (Rice *et al.* 1988). Chadwick (1997) observed that the proportion of N input emitted as  $\text{N}_2\text{O}$  increased with increasing time after effluent application, and was higher in the soil with surface-applied effluent than with injected effluent after 89 and 117 day measurement periods; however, during the initial 72 days, a reverse trend was observed. Similarly, Comfort *et al.* (1990) found that the largest emission of  $\text{N}_2\text{O}$  occurred shortly after the injection of liquid dairy-cattle manure, and was followed by a shift to  $\text{N}_2$ . Maximum loss occurred 5 days after injection and corresponded with the maximum  $\text{CO}_2$  concentrations in the soil atmosphere.

The results of the above studies suggest that the rate of denitrification in the injected zone is mainly controlled by the availability of C. Environmental factors that

accelerate the mineralisation of the organic C in the injection zone may in part explain the seasonal emissions of  $\text{N}_2\text{O}$  observed by others in the field (Thompson *et al.* 1987).

The  $\text{N}_2\text{O}$  emission rates vary with the season. Rochette *et al.* (2004) found that cumulative  $\text{N}_2\text{O}$  emissions were 1.74 and 2.73% of the added N ( $200 \text{ kg N ha}^{-1}$ ) in the fall and spring seasons, respectively. The greater emissions in spring were associated with warmer and more well aerated soil causing faster nitrification of the slurry added  $\text{NH}_4^+$ . Watanabe *et al.* (1997) noticed that, in an autumn experiment, fluxes began to increase within a few days after the application of excreta, with  $\text{N}_2\text{O}$  flux reaching the maximum after 16 days. The flux then decreased gradually and reached the background level in 60 days. In the winter experiment,  $\text{N}_2\text{O}$  fluxes began to increase 45 days after the application and reached a maximum after 80 days. The differences were considered to be caused by the differences of soil temperature between autumn and winter. Soil temperature of more than  $5^\circ\text{C}$  is required for a significant denitrification rate (Aulakh *et al.* 1983).

Nitrous oxide emission from land application of manure and effluent has been affected by the level of hydraulic and N loadings. For example when liquid dairy manure was applied at four N rates (246, 427, 643 and  $802 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) denitrification was found to increase with  $\text{N}_2\text{O}$  evolution rates reaching 14, 14, 22 and  $16 \text{ kg N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$ , respectively (Lowrance *et al.* 1998). Nitrous oxide emissions accounted for about 29% of total denitrification.

Nitrous oxide is mainly produced during the aerobic storage and treatment of animal excreta, as well as after land spreading. The New Zealand Meat Industry Research Institute has researched land application of meat-processing effluents under New Zealand conditions and recommended pasture-loading rates under different management practices (Russell & Cooper 1987). These effluents are characterized by high COD ( $1200\text{--}3000 \text{ mg l}^{-1}$ ) and high protein N levels ( $40\text{--}200 \text{ mg l}^{-1}$ ), with the bulk of the organic N being soluble (Cooper *et al.* 1979). Nutrient-loading rates of  $150\text{--}200 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  are recommended for irrigation schemes where the irrigated area is grazed (Houlbrooke *et al.* 2004). However, application of these wastes to land in excess of plant requirements results in elevated emissions of greenhouse gasses. Russell *et al.* (1991) measured denitrification losses as high as  $200 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  at sites receiving  $1000 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  of irrigated effluent.

Russell *et al.* (1991) reported different denitrification rates and  $\text{N}_2\text{O}:\text{N}_2\text{O}+\text{N}_2$  ratios under forestry and pasture following meat-effluent irrigation. The forest soil lost

about 27%, and the pasture soil lost only 4% as  $\text{N}_2\text{O}$  of the total applied N per irrigation. The  $\text{N}_2\text{O}:\text{N}_2\text{O}+\text{N}_2$  ratio was close to 1 in the forest soil and was between 0.51 and 0.75 in the pasture soil. They further obtained higher peak emission rates at pasture sites with primary-treated effluent ( $1\text{--}137\text{g N}_2\text{O-N ha}^{-1}\text{ d}^{-1}$ ) than pasture sites with anaerobic effluent ( $1\text{--}62\text{g N}_2\text{O-N ha}^{-1}\text{ d}^{-1}$ ). The higher emission with the primary-treated effluent was attributed to the higher C concentration. Meat-processing wastewaters contain high concentrations of N. Immediately following an irrigation event, the  $\text{N}_2\text{O}$  production rate increased rapidly and reached a peak (Russell & Cooper 1987). As aerobic conditions re-established, the  $\text{N}_2\text{O}$  emissions rate fell again to background levels.

Thompson & Pain (1991) observed similar daily emission rates for swine effluent and cattle slurry. The emissions did not peak until 30 hrs after the first effluent application but emission peaks were observed much earlier (8 hrs) during second and third applications. Other studies have shown highly variable courses for peak response following animal waste application. Sharpe & Harper (2002) and Whalen *et al.* (2000) reported maximum responses within several hours of swine-effluent applications. Studies with cow manure have shown peak emissions from 1 to 7 days after application (Cabrera *et al.* 1994) and with meat effluent within 10 hrs of application (Russell *et al.* 1991).

Swine-management systems often concentrate animals into relatively small areas, which can result in waste disposal problems. It is estimated that 20–30% of this waste is stored in lagoons with subsequent application of the effluent onto soil (Hatfield *et al.* 1993). Several studies with swine effluents have shown that application of these wastes increases  $\text{N}_2\text{O}$  emissions (Stevens & Cornfort 1974; Egginton & Smith 1986a; Cabrera *et al.* 1994). A 10-fold increase in  $\text{N}_2\text{O}$  emission was observed from a south-eastern US wheat field fertilized with swine effluent having total N and  $\text{NH}_4^+$  concentrations of 660 and 600  $\text{mg l}^{-1}$ , respectively, and 0.05% of the total added N was emitted during an 8-day measurement period (Whalen 2000). The increased emissions resulted from the interactive effects of increases in soil moisture and N and organic C.

Sharpe & Harper (1997) reported very high emissions from swine effluent application, where three applications of this effluent to oats emitted 13% of the total N during the measurement period. However, when the effluent was applied to a soybean crop,  $\text{N}_2\text{O}$  emission was about 1.5% of the total N applied (Sharpe & Harper 2002). Rochette *et al.* (2000) noticed that  $\text{N}_2\text{O}$  emission increased with an increasing manure



loading rate and the total N<sub>2</sub>O emissions were 0.62, 1.23 and 1.65% of the total N applied in control, 60 Mg ha<sup>-1</sup> and 120 Mg ha<sup>-1</sup> levels, respectively; this may be attributed to the increased availability of NO<sub>3</sub><sup>-</sup> for the denitrification process. The effect of slurry was observed for only 30 days, after which the emissions more or less reached the background level from a loamy soil with 19 consecutive years of pig-slurry application, suggesting that the effect of effluents on N<sub>2</sub>O emission is short-lived.

### **2.5.2 Emission from compaction caused by cattle treading**

In grazed-pastures, animal treading is an important cause of soil compaction and can have a significant adverse effect on soil properties and plant growth. There is a growing concern about the long term impact that treading damage may be having on soils and their ability to sustain pasture production under increasing intensification

As cattle exert greater static loadings (up to 400 kPa) than sheep (50-125 kPa) (Willatt & Pullar 1984; Thomas *et al.* 1990), it is the management of cattle, especially during the wetter months that represents the major challenge. Moreover the dynamic loading from moving animals can be more than double those of stationary animals, and on wet or loose soils bearing capacities may be less than 100 kPa (Chancellor *et al.* 1962).

Several soil management practices such as tillage, soil compaction (Staley *et al.* 1990; Hansen *et al.* 1993), irrigation and drainage (Mosier *et al.* 1986) affect the production and release of N<sub>2</sub>O by influencing the soil's physical conditions (i.e. aeration and soil water content). Soil compaction caused due to cattle treading alters soil N transformation rates and processes, especially mineralisation and denitrification, which leads to reduced N uptake by plants. The production, consumption and transport of N<sub>2</sub>O are strongly influenced by the changes in soil structural quality and in water content associated with compaction. Soil compaction doubled the N<sub>2</sub>O emission from an imperfectly drained clay loam (McTaggart *et al.* 1997) and by 36% from a sandy loam soil (Hansen *et al.* 1993).

Bakken *et al.* (1987) observed a 2-6 fold difference in the measured denitrification rate between the compacted and the uncompacted soils, and this difference showed little dependence on the average activity level on each date of measurement. Accumulated values for measured denitrification during 75 days were 3-5

kg N ha<sup>-1</sup> in uncompacted soil and 15-20 kg N ha<sup>-1</sup> in compacted soil. Hansen *et al.* (1993) in a field trial found that soil compaction resulted in increased N<sub>2</sub>O emission and this compaction effect was more pronounced in soil that was fertilised (with 140 kg NH<sub>4</sub>NO<sub>3</sub>-N). They further observed that the accumulated N<sub>2</sub>O emissions from NPK-fertilised treatment were 5.3% and 3.9% of the total N added in compacted and uncompacted soils respectively, as compared to the 2.7% and 3.1% of the total added N from compacted and uncompacted soils, respectively where cattle slurry was added.

Ball *et al.* (1999) concluded that the influence of compaction on N<sub>2</sub>O emissions appeared to act mainly through increased topsoil wetness, resulting in greater anaerobic conditions associated with reduced gas diffusivity. They suggested that manipulation of topsoil compaction status, such that compaction is light and confined to near the soil surface, may help in mitigating both surface fluxes of N<sub>2</sub>O and losses to the subsoil. They further observed that heavy compaction treatment gave a greater N<sub>2</sub>O emission response to rainfall than zero compaction treatment.

### 2.5.3 Emission from excretal deposition

The N excreted by sheep and cattle onto grazed pastures provides high localised concentrations of available N and C in soils, and is the main source of anthropogenic N<sub>2</sub>O emissions from New Zealand, contributing about 85% of the total (Cameron *et al.* 2000).

The large spatial and temporal variability in N<sub>2</sub>O fluxes has to be assessed if accurate estimates of N<sub>2</sub>O losses are to be derived for grazed grasslands. Spatial variability of fluxes is large, with coefficients of variation ranging from 21 to 286% found by Williams *et al.* (1999). Saggar *et al.* (2002; 2003) observed large spatial and temporal variations in N<sub>2</sub>O fluxes from two dairy-grazed pastures, with large fluxes measured after each grazing and rainfall event, followed by a decline. The N<sub>2</sub>O fluxes from the grazed sites were much higher than those from the ungrazed sites. The spatial variations in N<sub>2</sub>O fluxes observed for the grazed sites throughout the year were also large, with a coefficient of variation values ranging between 56 and 262%. Spatial variability in N<sub>2</sub>O emissions is naturally large in most soils because of soil heterogeneity and the episodic nature of N<sub>2</sub>O emissions. Variability is likely to increase as a result of animal grazing and the uneven distribution of excretal returns. The fluxes are often more during the autumn-winter period than during the spring-summer period



(Allen *et al.* 1996). This seasonal pattern of  $\text{N}_2\text{O}$  fluxes is consistent with the data of Ruz-jerez *et al.* (1994) and Carran *et al.* (1995). In addition to the heterogeneous distribution of biological hotspots resulting from the uneven distribution of excreta, grazing also introduces additional spatial variability to denitrification rates because of the animal treading effect on soil (Saggar *et al.* 2002; 2003).

Sherlock and Goh (1983) measured greater losses of  $\text{N}_2\text{O}$  when simulated urine was added to the soil than when aqueous urea was applied. Also, peak emissions were observed 24 to 48 hrs after urea application, whereas high emissions were observed immediately after the urine application. They proposed that the initial stimulation of  $\text{N}_2\text{O}$  emission on urine application could be explained by either chemodenitrification or by anaerobiosis in microsites as a result of  $\text{CO}_2$  generated from rapid hydrolysis of urea. There was an immediate increase in  $\text{N}_2\text{O}$  emission after urine application, with rates reaching a peak of  $89 \text{ mg N m}^{-2} \text{ d}^{-1}$  within 6 hr; with an estimated 7% of the applied urine-N was lost as  $\text{N}_2\text{O}$  over 42 days. Increases in  $\text{N}_2\text{O}$  emission within 24 hr of urine application were also observed by de Klein & van Logtestijn (1994a) and Koops *et al.* (1997b).

When cattle urine (natural and synthetic) was applied to 5 pastoral soils of different drainage class, the  $\text{N}_2\text{O}$  emissions varied greatly for the first 4 months and ranged from 0.3 to 2.5% of the urine-N applied (de Klein *et al.* 2003). Application of synthetic urine at 4 different rates (100, 250, 500 and  $1000 \text{ kg N ha}^{-1}$ ) to a pasture soil under controlled laboratory conditions resulted in 6.4, 2.4, 3.2 and 0.5% loss as  $\text{N}_2\text{O}$ -N of the urine-N was applied (Clough *et al.* 2003b). In another study where emissions were measured from urine-affected grassland soil, de Klein & van Logtestijn (1994a) found that 16% and 8% of the urine-N applied was lost as  $\text{N}_2\text{O}$ -N during the two measurement periods.

Yamulki *et al.* (1998) noticed application of livestock excreta increased  $\text{N}_2\text{O}$  emissions significantly compared to the control (untreated) plots. Although the total average  $\text{N}_2\text{O}$ -N emissions from the dung ( $9.9 \text{ mg N}_2\text{O-N patch}^{-1}$ ) were equal to those from the urine ( $9.5 \text{ mg N}_2\text{O-N patch}^{-1}$ ), the average loss from the urine (0.56%) was much higher than from the dung (0.19%). The fact that three times more N was added with dung than with urine on an area basis indicates that losses were related more to the readily available form of N and C in urine rather than to total content. Allen *et al.* (1996) also observed similar effects during winter, but their results indicated a higher percentage loss from dung application than from urine during spring and summer

application. This could be caused by more anaerobic conditions, different trends in mineralisation-immobilization in the dung or a lower rate of N uptake by the growing grass and consequent increased availability of N for soil microbial processes.

The large amounts of  $\text{NH}_4^+$  typically nitrified in the urine patch make it likely the nitrification process would contribute significantly to  $\text{N}_2\text{O}$  losses from grazed pastures (Monaghan & Barraclough 1992). Although Monaghan & Barraclough (1993) found low  $\text{N}_2\text{O}$  emission from nitrification and the major N loss as  $\text{N}_2$  under controlled conditions, they suggested these findings might not be applicable to field conditions where higher  $\text{N}_2\text{O}$  and lower  $\text{N}_2$  losses were expected. de Klein & van Logtestijn (1994a), while measuring denitrification and  $\text{N}_2\text{O}$  emissions from urine application to grasslands, found denitrification was the main source of  $\text{N}_2\text{O}$  immediately after urine application. It was 14 days after application, when soil water content dropped to 15% (v/v), before nitrification became a major source of  $\text{N}_2\text{O}$ . Overall, urine significantly increased  $\text{N}_2\text{O}$  emissions up to 14 days after application, with rates amounting to  $6 \text{ kg N ha}^{-1} \text{ d}^{-1}$ . Lovell & Jarvis (1996) also reported substantial emissions of  $\text{N}_2\text{O}$  following urine application ( $417 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ ). Within the urine patch,  $\text{N}_2\text{O}$  production was the largest in the centre of the patch ( $15.3 \text{ mg N m}^{-2} \text{ d}^{-1}$ ) and decreased slowly towards the edge. Maximum  $\text{N}_2\text{O}$  production was about  $50 \text{ mg N m}^{-2} \text{ d}^{-1}$ . In another field study, the amount of N lost as  $\text{N}_2\text{O}$  through denitrification was negligible, and all  $\text{N}_2\text{O}$  produced must have thus originated from nitrification (Koops *et al.* 1997b).

## 2.6 Conclusions and future research needs

The significance of the processes of gaseous emission in N use efficiency in agricultural, grassland, and forest systems and their implications for environmental quality are well recognized. Gaseous emission of N occurs through  $\text{NH}_3$  volatilisation and denitrification releasing  $\text{N}_2\text{O}$  &  $\text{N}_2$ . One of the products from the denitrification process,  $\text{N}_2\text{O}$ , has been implicated in both global warming and stratospheric ozone depletion. Ironically, denitrification has also been used as a means to improve the efficiency of N removal from wastewaters and to protect water quality when the end product is  $\text{N}_2$ .

The emission of  $\text{N}_2\text{O}$  from soils is controlled by factors such as oxygen supply, water content, temperature, soil pH, organic matter, and N sources. In addition to these, several soil management practices such as tillage, soil compaction (Staley *et al.* 1990; Hansen *et al.* 1993), irrigation and drainage (Mosier *et al.* 1986) affect the production and release of  $\text{N}_2\text{O}$  by influencing the soil's physical conditions (i.e. aeration and soil water content). Soil surface conditions can have a major impact on denitrification through its direct effect on soil aeration and an indirect effect on N transformations (Arah *et al.* 1991). The effect of individual parameters on  $\text{N}_2\text{O}$  emission is well established. However, there is a lack of understanding of the interaction of the many factors affecting  $\text{N}_2\text{O}$  emission under various soil environments.

There has been a substantial development in methodology and instrumentation for quantification of  $\text{N}_2\text{O}$  emissions in recent years, and various methods of measurement are now available. These techniques have been widely applied in the field using chambers and intact soil cores, and give acceptable results. High temporal and spatial variation confound the measurement of gaseous emission in the field, especially in grazed pasture, and reliable quantification of emission rates remains a goal to be achieved.

The rates of gaseous emission in grazed pasture soils obtained from a limited number of measurements are often found to vary significantly. In addition to uneven distribution of animal excreta, which are the major sources of gaseous emission, the pasture soils have year-round root activity and hence  $\text{O}_2$  demand, and the presence of active roots also stimulates soil microorganisms through exudation of C compounds. This favours denitrification, as does the presence of animals with their consequent effects on soil structure and localised high concentrations of available N.

Under the Kyoto Protocol, which came into effect from 16<sup>th</sup> February 2005, New Zealand is legally committed to limit its greenhouse gas emissions to the 1990 levels or else take responsibility for not being able to do so. Agricultural scientists are therefore helping the New Zealand government by providing farmers with tools to reduce these emissions.

The ultimate goal is to be able to estimate emissions accurately on a regional and national scale based on available climatic data, soil types, and grazing animals and their excretal N inputs. However, the IPCC methodology used to estimate  $\text{N}_2\text{O}$  emission has a number of limitations because it treats all agricultural systems as being the same under all climates, in all soils, in all crops and in all management systems, and ignores

all site-specific controls. The process-based modelling approaches offer a solid beginning to this goal and a base for future development. The strength of these approaches is in their capacity to link N gas fluxes to soil, plant and animal processes of grazed pasture ecosystems, particularly those controlling N dynamics. Future testing of these mechanistic models at regional and national scales is essential in elucidating variations on a scale relevant to global change.

To reduce the risk of environmental contamination through effluent irrigation, it is prudent land application guidelines be developed that consider the impact of effluents on terrestrial, aquatic and atmospheric environments. While technologies developed to manage effluents acceptably may not show a short-term economic return on capital outlay, they improve the long-term marketability of export dairy products. Such products are sold to consumers in countries that are placing increasing emphasis on the environment and the sustainability of the dairy industry. Hence, managing effluents should address the safe, hygienic, economic and practical aspects.

Knowledge about the conditions that influence N<sub>2</sub>O emissions from soil is considerable, but much work needs to be done to transform this basic knowledge into guidelines for good agricultural practice for low N<sub>2</sub>O emissions. I consider the following research areas should be pursued:

1. Currently there are inadequacies in our understanding of the effect soil compaction, induced due to cattle grazing, has on N<sub>2</sub>O emission in the field. More information about the causes of variability in the denitrification process under field conditions is required to enable better estimates of gaseous emission rates on grazed pastures. Also the effect of compaction on N<sub>2</sub>O emission as influenced by the various forms of N inputs to pasture soils needs to be investigated.
2. Major sources and factors controlling N<sub>2</sub>O emission from effluent irrigation are qualitatively well known, but quantitatively there are large gaps in our knowledge. Quantifying and reducing N<sub>2</sub>O emissions from effluent irrigation is clearly a pressing need which will help to identify the best management practices to reduce gaseous emissions and will also allow farmers to develop good practices for efficient effluent irrigation to mitigate greenhouse gas emissions.
3. One area of particular interest is the effect that the type of farm effluent has on N<sub>2</sub>O emission. Different farm effluents have different characteristics in terms of

the nutrient concentration and carbon levels. The varying effect of these farm effluents on  $\text{N}_2\text{O}$  emission need to be investigated.

4. Research on the relationship between  $\text{N}_2\text{O}$  emission and N loading rates through effluent irrigation is desirable to reduce N loss through gaseous emission. Information is needed to set up a maximum N loading limit through effluent irrigation in terms of  $\text{N}_2\text{O}$  emission.
5. Testing of empirical models to account for the emissions following effluent irrigation and their mitigation strategies.

## Chapter 3

# Effect of compaction and nitrogen sources on nitrous oxide emission

### 3.1 Introduction

Soil compaction, as a consequence of the intensive farming of crops and animals, is an important problem that modern mechanised agriculture is facing (Poesse 1992; De Neve & Hofman 2000). It occurs mainly due to the use of heavy machinery, intensive land use and inappropriate soil management practices and is one of the major sources of the physical degradation of agricultural soils (Flowers & Lal 1998; Hakansson & Lipiec 2000; Wiermann *et al.* 2000). Soil compaction can occur in a wide range of soil types and climatic conditions (Hamza & Anderson 2005).

Soil compaction due to animal trampling is one of the factors responsible for the degradation of the physical quality of the soils under grazed pastures. Cattle exert static loadings up to 400 kPa (Willatt & Pullar 1984; Thomas *et al.* 1990) and the bearing capacities of soil, especially when wet, may be less than 100 kPa (Chancellor *et al.* 1962) thus increasing the risk of damage to soils. Compaction disrupts the soil's physical integrity by modifying porosity and impeding gas, water and nutrient movement and root elongation in the soil profile (Greacen & Sands 1980), often leading to a decline in plant growth. Compaction also affects the mineralization of soil organic C and N (De Neve & Hofman 2000) thus affecting plant nutrient availability. In countries like New Zealand, where dairy farming with open grazing systems is the major land use practice, cattle treading causes significant soil compaction.

Soil compaction can have a major impact on denitrification and N<sub>2</sub>O emission through its direct effect on soil aeration and an indirect effect on N and C transformations (Carran *et al.* 1995; Clayton *et al.* 1997; Anger *et al.* 2003). Soil compaction reduces soil pore diameter, increases water filled pore space (WFPS) which in turn restricts oxygen diffusion within the soil and leads to increased N<sub>2</sub>O production rates (McTaggart *et al.* 1997; Ruser *et al.* 1998; van Groenigen *et al.* 2005).

The effect of the chemical form of N input on N<sub>2</sub>O emission from soils has been widely reviewed (Eichner 1990; Granli & Bockman 1994; Bouwman 1996; Clayton *et al.* 1997; Baggs *et al.* 2003; Pinto *et al.* 2004). It has been reported that the form of N fertiliser applied along with the tillage practices and soil type can significantly affect N<sub>2</sub>O emission from soils (Eichner 1990; Granli & Bockman 1994; Clayton *et al.* 1997). However, very little experimental data is available to quantify the combined effects of compaction and form of N input to grazed pasture on the total N<sub>2</sub>O emissions. Greater understanding of the effect of soil compaction on N<sub>2</sub>O emission in relation to other soil properties is needed to devise strategies for reducing these emissions.

The present study was, therefore, undertaken to determine interactive effects of soil compaction and form of N sources on the loss of N through N<sub>2</sub>O emission from soil under grazed pasture. The effect of compaction on N<sub>2</sub>O emission was examined in relation to its effect on some of the soil physical properties. To eliminate the variability induced due to the non-uniform excretal deposition by the grazing cattle while measuring the treading effect on N<sub>2</sub>O emission, compaction was created using vehicle wheels. The changes induced by cattle treading on soil physical properties were recorded in a separate grazing trial reported in section 3.3.1 of this chapter and the grazing effect on the N<sub>2</sub>O emission will be discussed in chapter 6.

The specific objectives of the study reported in this chapter include:

- To examine the effect of animal treading and wheel tracks on compaction as measured by various soil physical properties.
- To examine the transformation of different forms of N in compacted and uncompacted soils and to study the effect of these transformations on N<sub>2</sub>O emission.
- To examine the effect of compaction and N form on soil chemical properties.
- To establish predictive regression relationships between various soil properties and N<sub>2</sub>O emission.

## 3.2 Material and Methods

### 3.2.1 Experimental details

#### 3.2.1.1 Plot experiment and grazing trial

The effect of compaction caused by animal treading and wheel tracks on various soil properties was examined under field conditions. The effect of compaction caused by wheel tracks on N<sub>2</sub>O emission from various sources of N input was examined by conducting a plot experiment and the effect of compaction caused by animal treading on various soil physical properties was measured after a grazing event (designated Field experiment and Grazing trial, respectively, Table 3.1). Table 3.1 provides a list of the various measurements taken in the field experiment and the grazing trial.

**Table 3.1** Various measurements taken in the field experiment and the grazing trial (✓ monitored; – not monitored)

Measurements	Field experiment	Grazing trial
<b>Physical measurements</b>		
Bulk density	✓	✓
Oxygen Diffusion Rate	✓	✓
Penetrometer Resistance	✓	✓
Soil water potential	✓	✓
Water Filled Pore Space	✓	–
Herbage Yield	✓	–
<b>N<sub>2</sub>O emission</b>	✓	–
<b>Chemical measurements</b>	✓	–
Mineral N	✓	–
DOC	✓	–
pH	✓	–



The sites and soil type of the field experiment and the grazing trial were at different locations and the characteristics of the soil for both the experiments are shown in Table 3.2.

**Table 3.2 Chemical and physical properties of the soils from the 0-5 and 5-10cm depths in the field experiment and the grazing trial. The values in the bracket represent the standard error of mean of the four replicates**

Properties	Field experiment		Grazing trial	
	Manawatu sandy loam		Tokomaru silt loam	
	0-5cm	5-10cm	0-5cm	5-10cm
pH	6.1 (±0.06)	6.3 (±0.08)	5.9 (±0.04)	6.1 (±0.07)
Bulk Density (g cm <sup>-3</sup> )	1.18 (±0.05)	1.18 (±0.07)	1.01 (±0.04)	1.01 (±0.06)
Total N (%)	0.30 (±0.03)	0.192 (±0.05)	0.35 (±0.03)	0.22 (±0.04)
Total C (%)	3.27 (±0.43)	1.9 (±0.26)	3.64 (±0.52)	2.18 (±0.22)
C:N	10.9 (±0.52)	9.8 (±0.48)	10.4 (±0.47)	9.7 (±0.29)
CEC (cmol kg <sup>-1</sup> )	16.1 (±2.38)	—	22.3 (±1.26)	—

To examine the compaction caused by wheel tracks a plot experiment was conducted during September-December, 2002 on sheep-grazed permanent legume-based pasture at Massey University's Frewens Research Block, Turitea campus, Palmerston North (New Zealand). The soil at the site is Manawatu fine sandy loam, classified as weathered fluvial recent soil (Table 3.2). The grid reference of the location is NZMS1, N149/101305 (Hewitt, 1998) at latitude of 40°23'S and longitude of 175°37'E. The research farm is located 40 m above mean sea level. A paddock grazed by sheep rather than cattle was chosen for the plot experiment to reduce the variability in N<sub>2</sub>O emissions induced by pre-trial excretal deposition, which is higher in the rotationally grazed cattle pastures than set-stocked sheep pastures. A plot was fenced off two weeks before the commencement of the experiment to avoid further stock access during the experimental period.

The experiment comprised of two main treatments (uncompacted and compacted) to which four N sources (natural cattle urine, potassium nitrate, ammonium

sulphate and urea) all at the rate of 600 kg N ha<sup>-1</sup> and a control (water only) were applied, each replicated four times. The N sources were added in solution form for uniform distribution of the treatments. The natural cattle urine, potassium nitrate, ammonium sulphate, urea and water treatments will be hereafter referred to as urine, nitrate, ammonium, urea and water, respectively. To obtain uniformly compacted soil vehicle wheels were chosen as the compacting instrument rather than stock hooves. Compaction was obtained through driving ten adjacent parallel wheel tracks of a Toyota Hilux Utility vehicle. The total pressure of the vehicle on the ground was 632 kPa. The vehicle was driven through the experimental strip at 2.78 m sec<sup>-1</sup>, and a total of 10 passes of the vehicle were made; all passes were made in the same direction. All soil samples and measurements were taken in the middle of the wheel tracks of the vehicle.

The grazing experiment consisted of a single grazing event of moderate intensity and a control where no grazing occurred. The soil at the site is Tokomaru silt loam, classified as Argillic-fragic Perch-gley Pallic Soil (Hewitt 1998) or a Typic Fragiaqualf (Soil Survey Staff 1998). Grazing was done in a plot at a stocking rate of 4.7 cows/100m<sup>2</sup> with the average weight of each cow being 600 kg; grazing for one and half hours to achieve the moderate level of treading damage (Menneer *et al.* 2005) (plate 3.1).

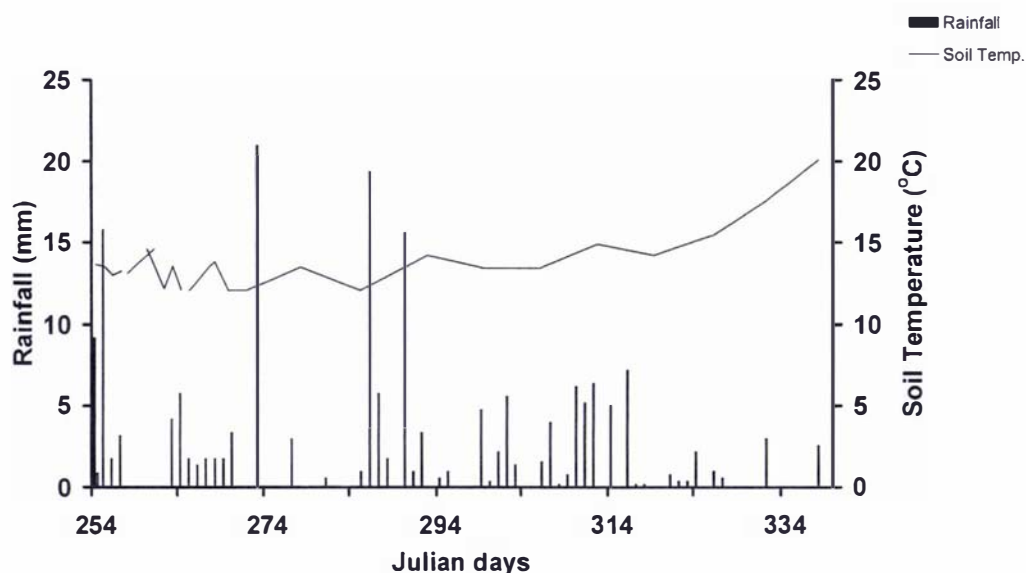


**Plate 3.1**      **Effect of intensive grazing on soil compaction due to cattle treading on Tokomaru silt loam**

A control plot was set up in the same paddock where no grazing event occurred. Four soil samples were collected for measuring the bulk density (BD) of the soil whereas penetrometer resistance (PR) and oxygen diffusion rate (ODR) were measured at ten places within the plot. The measurements for the grazing trial were made only for

a period of three weeks because the paddock was grazed every three weeks as part of the normal farm rotation.

Soil temperatures (at 5 cm depth) and precipitation for the experimental period were normal compared to the 30 year average (Figure 3.1). The 30 year mean rainfall during Sep-Dec ranged between 82-90 mm/month and is fairly evenly distributed (<http://www.niwasience.co.nz/ncc/cu/2002>). The rainfall during 2002 was 73 mm, 67.6 mm and 45.4 mm for the months of September, October and November, respectively. The rainfall was higher during the initial period of the experiment than for the rest of the measurement period which lead to water logging in some of the chambers under compacted soil. The average soil temperature was 14°C during the experimental period.



**Figure 3.1** Soil temperatures at 10cm depth and daily precipitation during the compaction experiment period (10 September, 2002 to 4 December, 2002; 254 - 337 Julian days)

### 3.2.2 Nitrous oxide measurement

The N<sub>2</sub>O fluxes were measured for the field experiment between 10<sup>th</sup> September and 4<sup>th</sup> December 2002 using the closed chamber technique (Saggar *et al.* 2002). Four chambers per N treatment were used. The chambers (Plate 3.2), 25 cm in diameter, were inserted about 10 cm into the soil and were allowed to equilibrate with the soil for 2 days. Chamber heights were measured to calculate the volume of each chamber. The water and N treatments were added within the chamber to monitor N<sub>2</sub>O emission and

outside the chamber in an area of 0.125 m<sup>2</sup> (0.5m x 0.25m) to obtain soil samples for analysis. Background N<sub>2</sub>O flux was measured for the site one day before the application of the water and N treatments. During the first week, measurements of the N<sub>2</sub>O emissions were made daily to capture major changes in N<sub>2</sub>O fluxes. This was followed by measurements on alternate days for two months and then once a week for rest of the experimental period as the fluxes decreased, approaching the background levels. Everyday after sealing the chambers with lids, three gas samples were taken from each chamber at times t<sub>0</sub>, t<sub>30</sub> and t<sub>60</sub> (Time 0 min, 30 min and 60 min after the closing of the chamber, respectively). To minimise the variation in the flux pattern, sampling was always carried out between 10am and 1pm. During the course of measurement the chambers were covered with baskets, which were insulated with aluminium foil to minimise fluctuations in temperature. The 25ml of the collected gas samples was transferred to a 12.5 ml vacuumed glass vials. These vials were placed on an automatic sampler of the Shimadzu GC-17A gas chromatograph with a <sup>63</sup>Ni-Electron capture detector and analyzed. N<sub>2</sub>O (mg m<sup>-2</sup> hr<sup>-1</sup>) flux was estimated from the measurements made at three time periods (t<sub>0</sub>, t<sub>30</sub> and t<sub>60</sub>) using the following equation:

$$F = \rho \times \frac{V}{A} \times \frac{\Delta c}{\Delta t} \times 273(T + 273) \quad (1)$$

Where;

F = flux (mg m<sup>-2</sup> hr<sup>-1</sup>)

ρ = density of gas (mg m<sup>-3</sup>)

V = Volume of chamber (m<sup>3</sup>)

A = Base area of chamber (m<sup>2</sup>)

Δc / Δt = Average rate of change of N<sub>2</sub>O concentration with time (ppmvh<sup>-1</sup>)

T = Temperature in the chamber (°C)

The N<sub>2</sub>O flux gradient measured for the three time periods was mostly linear in nature but when that was not the case non-linear flux values were used in estimating the total N<sub>2</sub>O flux. Integration of the fluxes over the measurement period was done separately for all the replicates and then averaged to get the total N<sub>2</sub>O flux from the treatment.



**Plate 3.2** Chamber used in measuring the N<sub>2</sub>O emissions from the field

### 3.2.3 Soil sampling and analysis

Soil bulk density of the compacted and uncompacted treatments for both the grazing trial and the plot experiment was determined using undisturbed soil cores (4.75 cm in diameter) taken in 2 cm depth increments to a depth of 6 cm. Four replicate cores were taken at each depth from compacted and uncompacted areas of the plots, respectively.

Four soil samples were collected randomly on all days of N<sub>2</sub>O measurement from each site from 0-5 cm and 5-10 cm depths to determine soil water content. Field moist soil samples were weighed ( $M_t$ ) and oven dried (105°C) to a constant mass ( $M_s$ ). Gravimetric soil water content (SWC) was calculated (Eq 2):

$$SWC = \frac{M_t - M_s}{M_s} \times 100 \quad (2)$$

The volumetric soil water ( $\theta_v$ ) content was then calculated by multiplying the gravimetric SWC with the soil bulk density ( $\rho_b$ ). The water filled pore space (WFPS) was calculated as follows (Eq 3):

$$WFPS = \frac{\theta_v}{\text{Total soil porosity}} \quad (3)$$

Where, total soil porosity was calculated by the formula (Eq 4)

$$\text{Total soil porosity} = 1 - \frac{\rho_b}{\rho_s} \quad (4)$$

The particle density of soil was assumed to be 2.65 g cm<sup>-3</sup>.



Soil samples to determine the pH, mineral N (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) and dissolved organic carbon (DOC) content for compacted and uncompact soil were collected from each site from 0-5 cm and 5-10 cm depths on all days of N<sub>2</sub>O measurement from outside the chamber area where treatments were applied. Field moist samples were sieved (< 2mm) soon after collection. A sub-sample (5g) was extracted with 2M KCl solution by shaking for 1 hr (1:5 soil: solution). The extracts were analysed for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> by standard colorimetric methods (Keeney & Nelson 1982) on an autoanalyser.

Another sub-sample (5g) was extracted with 0.5M K<sub>2</sub>SO<sub>4</sub> (1:4 soil: solution) for determining DOC by the dichromate oxidation method (Tate *et al.* 1988) using spectrophotometer.

Soil pH was measured at a 1:2.5 soil: water ratio using a combined electrode pH meter (Blakemore *et al.* 1987).

### 3.2.4 Soil water potential

The soil water potential of the undisturbed soil cores from the field experiment and grazing trial was measured at 0.1, 1 and 10 bar suctions using the pressure plate apparatus (Loveday 1974). The pressure plate helps to determine relationship between soil wetness and matric suction and provides information about the pore size distribution and the available water holding capacity of the soil.

### 3.2.5 Penetrometer resistance

Penetrometer resistance (PR) was measured using a hand penetrometer (Bradford 1986) on the 1<sup>st</sup>, 21<sup>st</sup> and 90<sup>th</sup> day after the compaction treatment for the plot experiment and on 1<sup>st</sup>, 7<sup>th</sup> and 21<sup>st</sup> day after the grazing event for the grazing trial. The grazing event occurred after every 3 weeks in the paddock so measurements for the soils physical parameters were measured for 3 weeks only. The penetrometer was a cylindrical probe with a flat foot (2 cm diameter) which is used to measure the resistance offered by soil to probe penetration. The resulting resistance is the unconfined compressive strength, measured in kg cm<sup>-2</sup> (1kpa = 98.1 kg cm<sup>-2</sup>).

### 3.2.6 Oxygen diffusion rate

The oxygen diffusion rate (ODR) was measured concurrently using ten replicate platinum electrodes (Glinski & Stepniewski 1985) inserted to depths of 5 and 10cm below the soil surface. The electrodes were left overnight after installation to equilibrate with the soil solution. A voltage of 0.65 V was applied for 3 min before the current between each electrode and a brass anode was read against an Ag/AgCl reference electrode with a Jensen oxygen diffusion rate meter. The ODR was calculated using the equation (Eq 5):

$$\text{ODR } (\mu\text{g O}_2 \text{ cm}^{-2} \text{ min}^{-1}) = 0.059 \times \text{MC } (\mu \text{ A}) \quad (5)$$

Where, MC is the observed microelectrode current

The ODR measurements were made on the 1<sup>st</sup>, 21<sup>st</sup> and 90<sup>th</sup> day after the compaction treatment for the plot experiment and on the 1<sup>st</sup>, 7<sup>th</sup> and 21<sup>st</sup> day after the grazing event for the grazing trial.

### 3.2.7 Dry matter (DM) yield

The herbage within the chambers and outside the chamber area was regularly cut to a 2 cm height and the total DM yield for different treatments was recorded.

### 3.2.8 Statistical methods

The split-plot design with compaction as the main treatment and N sources as sub plot treatment was applied to the field experiment. The means and standard error of means were calculated for bulk density, WFPS, water retentivity, ODR, PR, soil mineral N concentrations and soil DOC values from the plot experiment and the grazing trial. Total emission data was subjected to an analysis of variance to determine the statistical significance of compaction (n = 24) and N sources (n = 8), using SAS for the Windows software package. Calculated indices were analysed using a test of least significant difference (LSD). The 5% confidence level is regarded as statistically significant.

Regression and correlation analysis between N<sub>2</sub>O emission and various soil properties was conducted using the SAS package.

## 3.3 Results and discussion

Table 3.1 shows the various measurements made in the grazing trial and the field experiment that have been reported in this chapter.

### 3.3.1 Soil physical characteristics

Compaction at the grazing trial site and at the experimental plot site caused significant changes in soil bulk density (Table 3.3), PR (Figure 3.2), soil matric potential (Figure 3.3) and ODR (Figure 3.4) values. The effect of soil compaction on these changes in soil physical behaviour was short lived.

#### 3.3.1.1 Bulk density

Compaction caused initial increases in soil bulk density in both the experimental plots and at the grazing site, with significant differences between the compacted and uncompacted soils in the bulk density observed at all depths (Table 3.3). These differences diminished with time and no difference in the bulk density between the compacted and uncompacted soil was observed by the end of each experiment. The bulk density of compacted soil (average soil depth of 0-6 cm) was higher than the uncompacted soil by 6.7% (end of 3 weeks) and 4.9% (end of 1 week) for the field experiment and the grazing trial, respectively.

At the experimental plots, where compaction was achieved through driving close parallel tracks, the mean bulk density at 0-6cm depth in the beginning of the experiment increased significantly (11%) with compaction (Table 3.3). The effect of compaction was evident in all the three soil depths of 0-2 cm, 2-4 cm and 4-6 cm though the effect was found to decrease with depth (18.6%, 10.2% and 3.4% for 0-2 cm, 2-4 cm and 4-6 cm soil depths, respectively). Similarly in the grazing trial, the initial increase in soil bulk density induced by cow treading decreased with depth (Table 3.3). On average, at a 0-6 cm soil depth, cattle treading caused bulk density to increase from 1.02 to 1.09 g cm<sup>-3</sup> (a 6.8% increase).

The increase in bulk density caused by compaction due to farm machinery has been reported elsewhere (Torbert & Wood 1992; Ball *et al.* 2000). Many studies have investigated the changes in soil bulk density due to compaction by heavy grazing (Drewry *et al.* 2001; Menneer *et al.* 2005). Scholefield & Hall (1986) calculated that a



530 kg cow would exert 250 kPa of vertical stress while walking on level ground. Orodho *et al.* (1990) in New Mexico showed an 8% increase in soil bulk density (1.50 vs 1.38 g cm<sup>-3</sup> in sandy loam soil) due to grazing, however Menneer *et al.* (2005) reported a non-significant increase in bulk density on a Te Kowhai silt loam soil 3 days after grazing with cows had generated moderate to severe pugging. The depth of soil compaction induced by treading varied depending on the animal weight and soil moisture conditions. While Vzzoto *et al.* (2000) reported that animal treading increased soil density at the first 5 cm soil depth, Terashima *et al.* (1999) in an another study reported that treading affected bulk density to a depth of 20 cm with the greatest effect in the top 5 cm, though the effect depended on the moisture status of the soil.

**Table 3.3      Distribution of bulk density (g cm<sup>-3</sup>) with depth for the compacted and uncompacted soils at the field experiment and the grazing trial**

Soil depth	Field experiment			Grazing trial		
	Manawatu sandy loam			Tokomaru silt loam		
	Day 1	Day 21	Day 90	Day 1	Day 7	Day 21
<b>Compacted</b>						
0-2 cm	1.40	1.36	1.21	1.12	1.1	1.09
2-4 cm	1.30	1.25	1.18	1.10	1.06	1.01
4-6 cm	1.23	1.20	1.17	1.04	1.04	1.03
Mean	1.31	1.27	1.19	1.09	1.07	1.04
<b>Uncompacted</b>						
0-2 cm	1.18	1.18	1.18	1.01	1.01	1.00
2-4 cm	1.18	1.18	1.18	1.04	1.04	1.03
4-6 cm	1.19	1.20	1.19	1.00	1.01	1.02
Mean	1.18	1.19	1.18	1.02	1.02	1.02
LSD (0.05)						
Compacted vs uncompacted	0.02	0.05	0.04	0.05	0.04	0.03
LSD (0.05) Depth wise	0.07	0.06	0.05	0.03	0.04	0.06

### 3.3.1.2 Penetrometer resistance

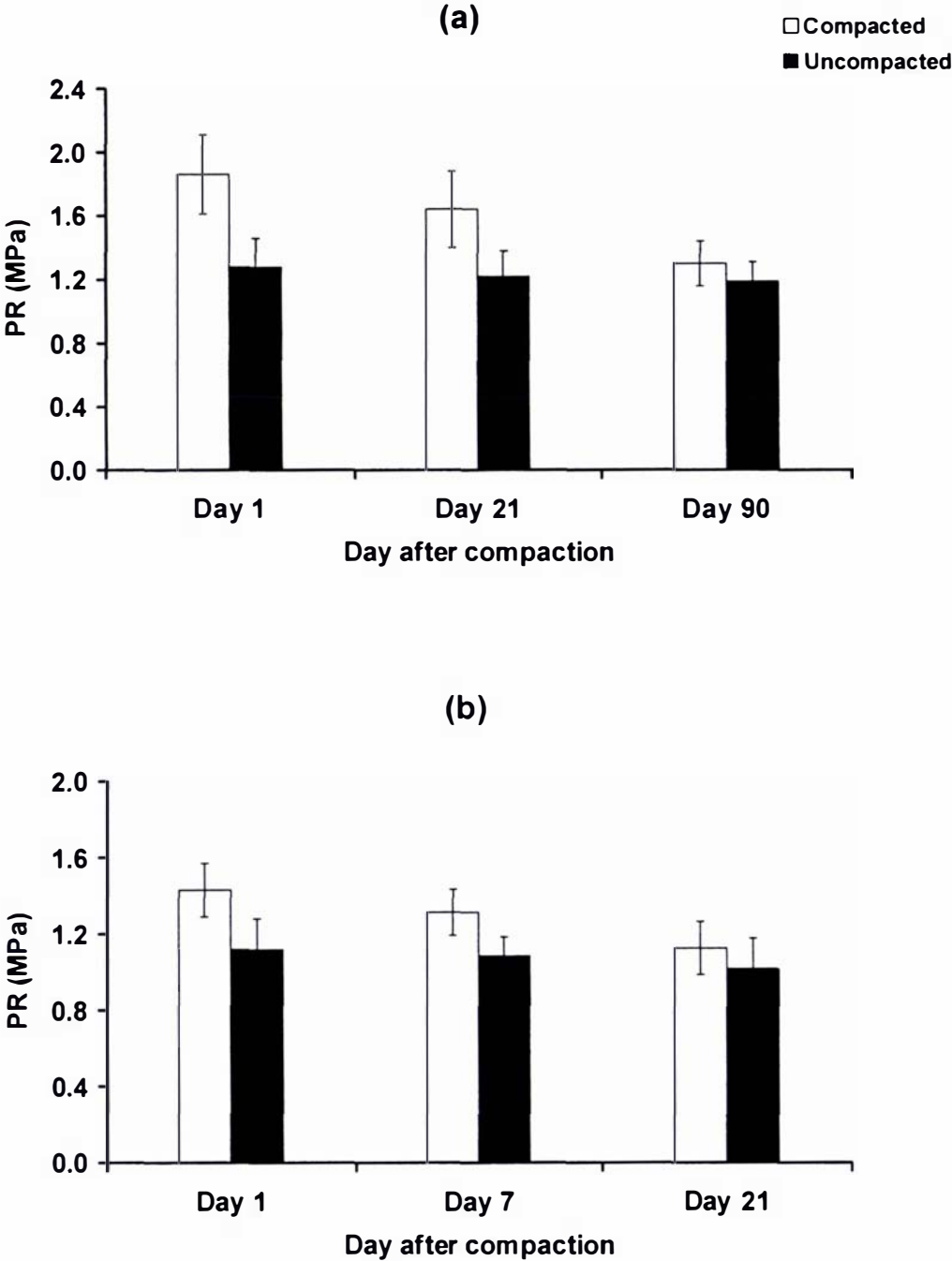
The PR values for both the compacted and the uncompacted soil of the field and the grazing experiment were found to decrease with time (Figure 3.2). Overall, compacted soil provided more resistance to the penetrometer probe than the uncompacted soil.

The mean PR values for compacted soil were significantly higher on day 1 and day 21 (1.86 and 1.64 MPa, respectively) than the uncompacted soil (1.28 and 1.22 MPa) for the experimental plots. The resistance to the penetrometer decreased with time for the compacted soil and by day 90 the difference in the PR between the compacted and uncompacted soil was not significant.

At the grazing site, initially the soil compacted by cattle hooves had significantly higher PR than the uncompacted control soil (Figure 3.2). But this difference was insignificant by day 21. These results suggest the effect of soil compaction on ODR is short lived as is its effect on soil bulk density.

Overall the soils at the field experiment maintained a higher resistance for both the compacted and the uncompacted soil over the grazed experiment site (Figure 3.2) which is attributed to the difference in soil texture and structure between the two field sites.

Significant differences in PR related to grazing have been reported by Chanasyk & Naeth (1995) and Gijsman & Thomas (1996). Although PR is more sensitive to compaction than bulk density (Rodd *et al.* 1999) and provides a valuable indication of the state of compaction, few researchers have used this parameter to quantify the effect of animal treading on soil compaction (Chanasyk & Naeth 1995; Burgess *et al.* 2000).

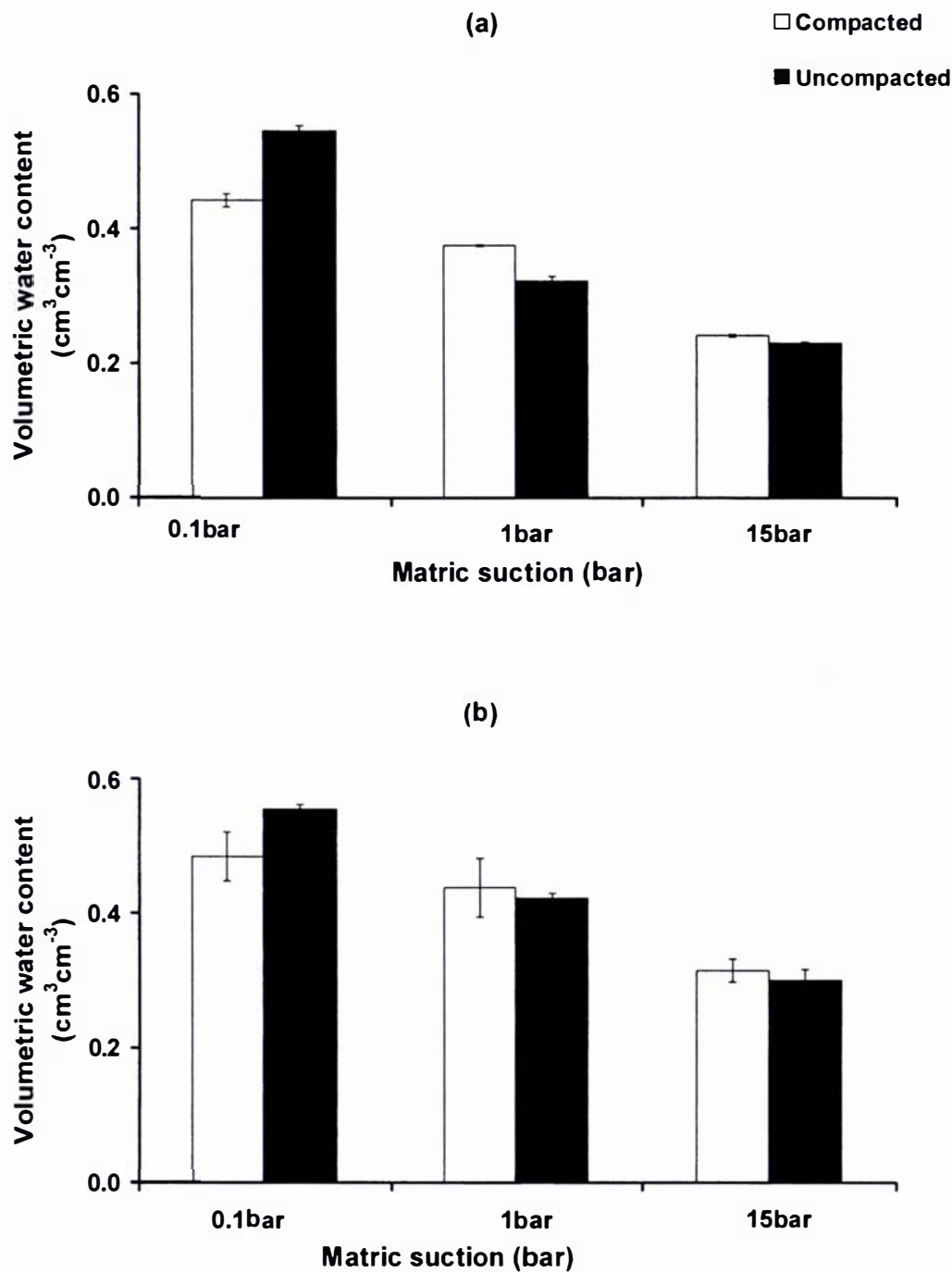


**Figure 3.2** Effect of compaction on penetrometer resistance (0-5 cm soil depth) for (a) the field experiment on Manawatu sandy loam and (b) grazing trial on Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

### 3.3.1.3 Soil water potential

Soil water content measured at the three potentials of 0.1, 1 and 15 kpa at the 0-5 cm soil depth for the field experimental site suggested that the uncompacted soil had lower water content, except at higher potential, than the compacted soil (Figure 3.3).

At the 0.1 bar suction, which represents field capacity, water content in the uncompacted soil was 22.7% higher than the compacted soil. At the 1 bar and 15 bar suctions the compacted soil had 15.6% and 4.3% higher water content values than the uncompacted soil. The results for the soil water potential under the grazing experiment were slightly different from those for the plot experiment. At the 0.1 bar suction the compacted soil had lower water content than the uncompacted soil but at higher suction values of 1 and 15 bar no significant differences was observed between the two. The results could be explained on the basis that compaction is known to decrease total porosity by decreasing the number of large interaggregate pores. It is the macropores that drain at low suction ranges hence lower water content was recorded for compacted soils at the 0.1 bar suction. On the other hand, the volume of intermediate size pores is likely to be somewhat greater in a compacted soil as some of the original large pores have been squeezed to intermediate size pores by compaction. This supports the results of water retention obtained at 1 bar.



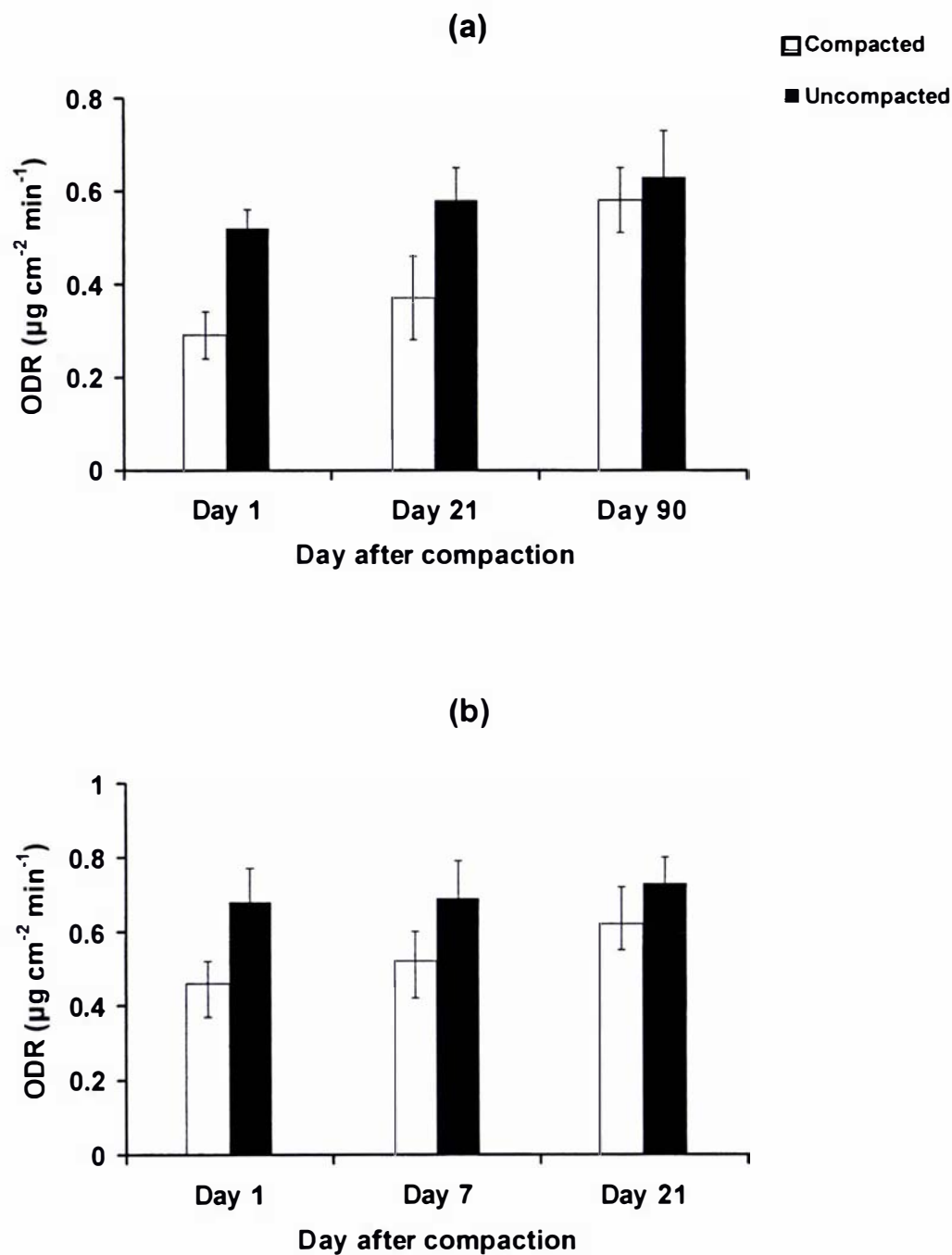
**Figure 3.3** Effect of compaction on soil water retentivity at 0-5 cm depth for (a) the field experiment on Manawatu sandy loam and (b) the grazing trial on Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

### 3.3.1.4 Oxygen diffusion rate

The mean ODR value at 5 cm soil depth showed an increasing trend over time. This was true for both the compacted and uncompacted soils and at both the experimental sites.

In the field experiment, the mean ODR value increased from  $0.29 \mu\text{g cm}^{-2} \text{min}^{-1}$  at the beginning of the experiment to  $0.58 \mu\text{g cm}^{-2} \text{min}^{-1}$  by the end of the experiment for compacted soil. The rate of increase for uncompacted soil was less compared to the compacted soil with the ODR value increasing from  $0.52 \mu\text{g cm}^{-2} \text{min}^{-1}$  on the 1<sup>st</sup> day to  $0.63 \mu\text{g cm}^{-2} \text{min}^{-1}$  on the 90<sup>th</sup> day (Figure 3.4). At this site on day 1 the ODR in the uncompacted soil was 79.3% higher than that in the compacted soil suggesting that the diffusion of oxygen was low in the latter soil. Similarly, in the case of the grazing site the ODR value was 47.8% higher for the compacted soil than in uncompacted soil on day 1 which decreased to 17.4% by the 21<sup>st</sup> day (Figure 3.4). The results show that the ODR value for the compacted soil at the grazing site was 58.6% higher than at the experimental site. This difference was comparatively less for the uncompacted site (30.8%).

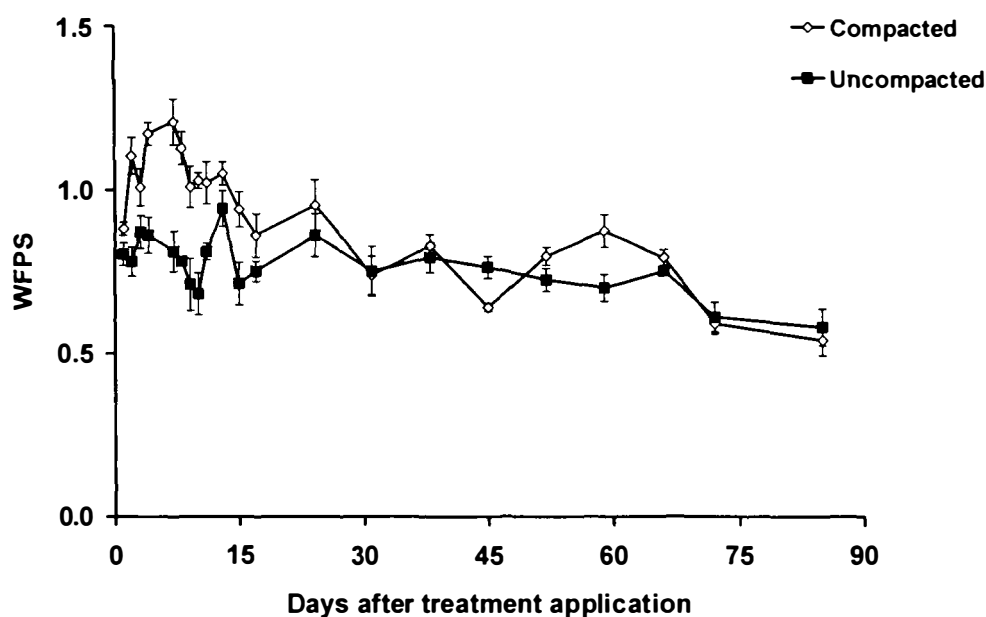
Macro-pore continuity is important to the aeration status of the soil and the lower ODR values observed in the compacted soil were probably caused by the reductions in the macro-pore continuity (Carter *et al.* 1994). Differences in ODR between the compacted and uncompacted soils could be due to the ponding of water in the compacted soil during the initial period of the experiment because of heavy rain, leading to completely saturated soil. With the passage of time as the soil recovers from compaction the ODR values for the compacted soil tend to return to values similar to the uncompacted soil.



**Figure 3.4** Effect of compaction on oxygen diffusion rate (ODR) values ( $\mu\text{g cm}^{-2} \text{min}^{-1}$ ) for (a) the field experiment on Manawatu sandy loam and (b) the grazing trial on Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

### 3.3.1.5 Water filled pore space

Water filled pore space (WFPS) was higher for the compacted soil (0.54 to 1.21) than for the uncompact soil (0.59 to 0.94). The compacted soils were completely saturated, with WFPS reaching above field capacity for most of the measurement period (Figure 3.5). During the initial stages of the experiment, water ponding was noticed in some of the chambers, which led to an increase in soil water content and hence the higher WFPS. The increase in WFPS occurred due to a decrease in air filled porosity (Hansen *et al.* 1993; Drewry *et al.* 2001; Teepe *et al.* 2004).



**Figure 3.5** Water filled pore space (WFPS) distribution for the compacted and uncompact soil over the experimental period for the field experiment on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

## 3.3.2 Nitrous oxide emission

### 3.3.2.1 Effect of compaction

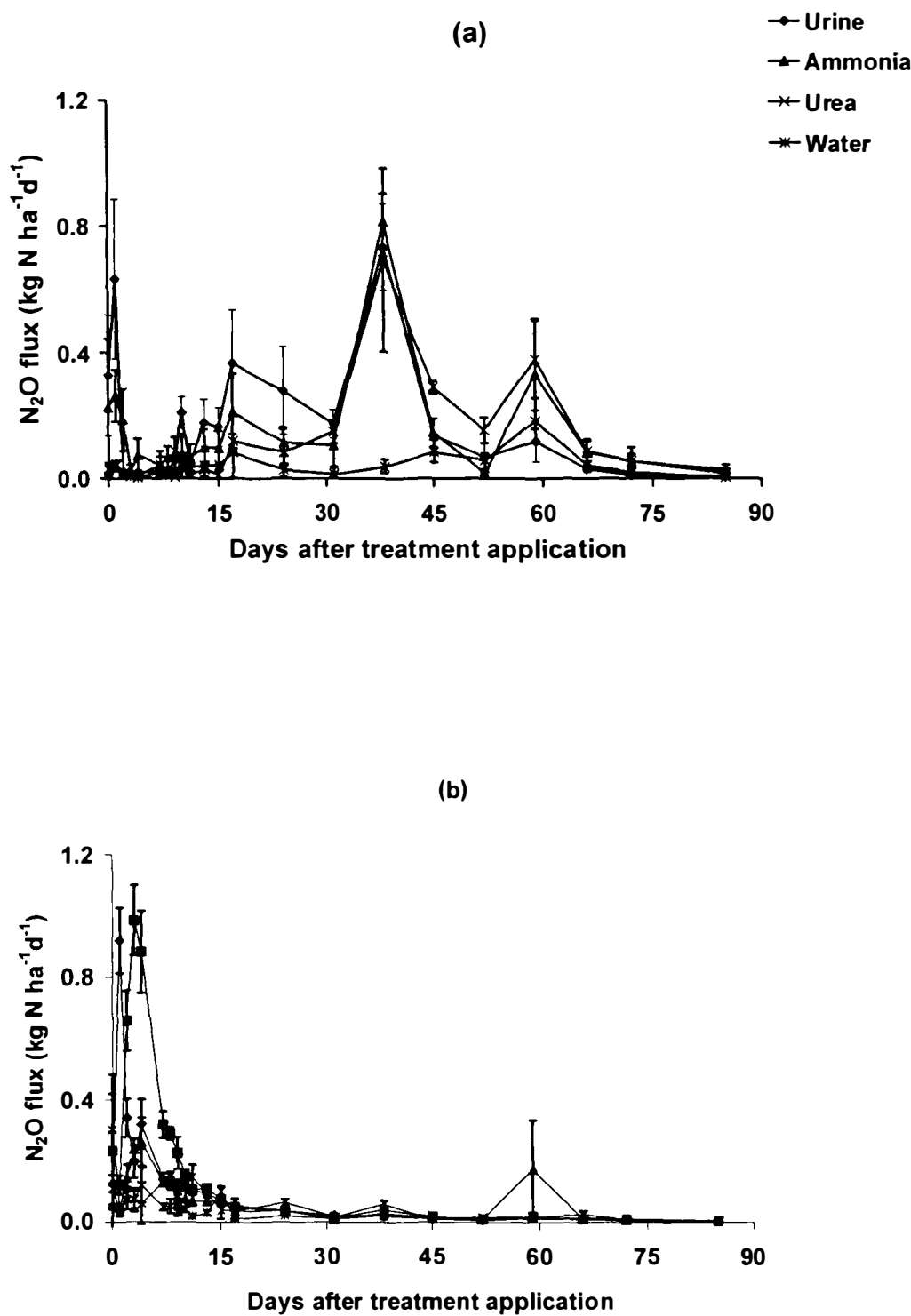
The application of different N sources to both the compacted and uncompact soil resulted in the immediate emission of N<sub>2</sub>O. The emissions followed a general



pattern of rapid emission immediately after the application of the N-source and a progressive decline over time for both the compacted and uncompacted soils and for all the sources applied (urea or ammonia sources, Figures 3.6a and b; nitrate sources, Figure 3.7).

The effect of compaction on N<sub>2</sub>O emission varied amongst the N sources, with the nitrate source behaving differently from the rest. For the nitrate treatment, a single peak was observed one week after the application was obtained (Figure 3.7) whereas for other N-sources (urine, ammonium and urea) two N<sub>2</sub>O peaks were obtained, first immediately after the application and the second a month later. Initially the emission was lower from the compacted soil than from the uncompacted soil (Figures 3.6a & b). Monaghan & Barraclough (1993) also observed an initial lag phase in N<sub>2</sub>O emissions after the application of cattle urine and then emission increased following a rapid increase in soil NO<sub>3</sub><sup>-</sup> concentration. In our experiment, the observed delay in N<sub>2</sub>O emissions in the compacted soil may be due to the fact that high soil moisture conditions at the beginning of the experiment were not conducive for N mineralization. Notably this lag period was not evident for nitrate treatment under compaction nor did it occur in the uncompacted soil, which had lower soil water content (WFPS). A two phase N<sub>2</sub>O emission pattern was observed under uncompacted soil for all the N sources (Figure 3.6 b). Phase 1, within 1-3 days of treatment application, was the time when N<sub>2</sub>O reached high concentrations. The second phase was the declining phase in N<sub>2</sub>O concentration.

The total N<sub>2</sub>O fluxes for the entire experimental period ranged from 2.62 to 61.74 kg N<sub>2</sub>O-N ha<sup>-1</sup> for the compacted soil and 1.12 to 4.37 kg N<sub>2</sub>O-N ha<sup>-1</sup> for the uncompacted soil (Table 3.4). The total N<sub>2</sub>O losses for the compacted soil were significantly higher than for the uncompacted soil (Figures 3.6a and b). Overall, compaction caused a seven-fold increase in N<sub>2</sub>O emission (Table 3.4).



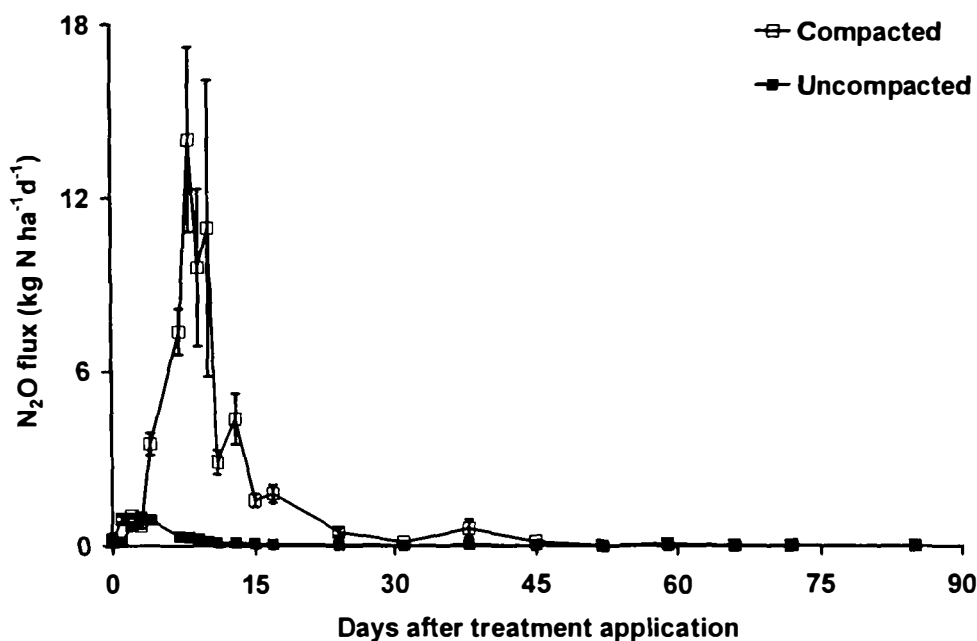
**Figure 3.6** N<sub>2</sub>O fluxes (kg N ha<sup>-1</sup> d<sup>-1</sup>) under the (a) compacted treatment and (b) uncompacted treatment at the experimental plots on Manawatu silt loam. Each value represents a mean of twenty replicates with standard deviation shown by vertical bars.

**Table 3.4** Total N<sub>2</sub>O-N emitted (kg N ha<sup>-1</sup>) over the experimental period from the N sources applied to compacted and uncompact soil at the experimental plots on Manawatu silt loam

Treatment	N <sub>2</sub> O-N emitted (kg N ha <sup>-1</sup> )		
	Compacted	Uncompact	Mean
Urine	9.17	2.94	6.05
Nitrate	61.74	4.37	33.05
Ammonium	9.17	2.64	5.90
Urea	9.11	2.13	5.62
Water	2.62	1.12	1.87
Mean	18.35	2.64	
LSD(0.05)	LSD(0.05)	LSD(0.05)	
Compacted vs. Uncompact	Compacted + uncompact mean	Treatments n = 4	
n = 24	n = 8		
3.43	3.93	5.94	

### 3.3.2.2 Effect of N sources

The N sources affected the N<sub>2</sub>O emissions, with the effect being more pronounced in the compacted soil. As mentioned earlier two emission peaks were observed for urine, ammonium and urea treatments in compacted soil (Figure 3.6a). The first peaks were found immediately after the treatment application and were 0.634, 0.264 and 0.041 kg N<sub>2</sub>O-N ha<sup>-1</sup>d<sup>-1</sup> for urine, ammonium and urea, respectively. Within a day the emission rate decreased. This declining phase was followed by a steady rise in emissions with peak emissions of 0.733, 0.816 and 0.693 kg N<sub>2</sub>O-N ha<sup>-1</sup>d<sup>-1</sup> observed a month after treatment application for urine, ammonium and urea, respectively. This was not the case for nitrate, where only a single peak of 14.02 kg N<sub>2</sub>O-N ha<sup>-1</sup>d<sup>-1</sup> was observed (Figure 3.7). On the other hand a single emission peak of 0.919, 0.984, 0.262 and 0.149 kg N<sub>2</sub>O-N ha<sup>-1</sup>d<sup>-1</sup> was found for urine, nitrate, ammonium and urea treatments, respectively under the uncompact soil (Figure 3.6b).



**Figure 3.7** N<sub>2</sub>O fluxes (kg N ha<sup>-1</sup> d<sup>-1</sup>) under the nitrate treatment for compacted & uncompacted soils at the experimental plots on Manawatu silt loam. Each value represents a mean of twenty replicates with standard deviation shown by vertical bars

Most of the N<sub>2</sub>O emissions (85-90%) from the nitrate treatment of the compacted and uncompacted soil occurred within 3 weeks of the application. The proportion of total N<sub>2</sub>O emitted during this period was low for urine, ammonium and urea, being 32.6%, 20.2% and 8.6%, respectively for the compacted soil. However, in the uncompacted soil from 54 to 81% of N<sub>2</sub>O was emitted within 3 weeks of the urine, ammonium and urea applications. This difference in N<sub>2</sub>O emission from urine, ammonium and urea treatments for the compacted and uncompacted soils were negligible after 7 weeks.

The N<sub>2</sub>O emission from the control treatment ranged from 0.001 to 0.079 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup>. Among the various N sources applied, nitrate treatment resulted in the highest N<sub>2</sub>O emission (Figure 3.7). When expressed as a percentage of the applied N the N losses as N<sub>2</sub>O from the compacted soil were 9.87%, 1.09%, 1.09% and 1.08% of the applied nitrate, urine, ammonium and urea, respectively; and were 0.54%, 0.30%, 0.25% and 0.16% for nitrate, urine, ammonium and urea, respectively from the uncompacted soil. Among the N sources, total emissions for the entire experimental period were the lowest from the urea treatment though not statistically different from

the emission from urine or ammonium (Table 3.4). This was true for both the compacted and uncompact soils.

### 3.3.3 N transformation in soil

#### *Field experiment*

Before the addition of N sources the soil mineral N ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) concentration was similar for the compacted and uncompact soils with a mean value of 13.46 and 10.24 mg kg<sup>-1</sup> soil for  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , respectively. As expected, soil  $\text{NO}_3^-$  and  $\text{NH}_4^+$  contents increased with the addition of N sources and then declined with time. The average and range of the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations for the entire experimental period are presented in Table 3.5. The mineral--N data for the compacted and the uncompact soil during the entire experimental period has been appended in graph form in appendix 1.

Within a day of nitrate application the soil  $\text{NO}_3^-$  concentration increased from an initial value of 13.46 mg kg<sup>-1</sup> soil to 228 mg kg<sup>-1</sup> soil in the compacted and 209.4 mg kg<sup>-1</sup> soil in the uncompact within a day of the addition of the treatment. The concentration of  $\text{NO}_3^-$  decreased over time and by the 10<sup>th</sup> day mineral N equivalent to 90.4% and 94.8% of the added  $\text{NO}_3^-$  had disappeared from the top 0-5cm soil layer of the compacted and uncompact treatments, respectively. However, in the case of urine, ammonium and urea treatments, a slow build-up of  $\text{NO}_3^-$  occurred. It was observed that the rate of N mineralization (measured by the maximum  $\text{NO}_3^-$  build-up) was slower for urea (19 and 37 mg kg<sup>-1</sup>soil d<sup>-1</sup> for the compacted and uncompact soils, respectively) than urine (25 and 47 mg kg<sup>-1</sup>soil d<sup>-1</sup> for the compacted and uncompact soils, respectively) or ammonium (45 and 54 mg kg<sup>-1</sup>soil d<sup>-1</sup> for the compacted and uncompact soils, respectively) treated soils.

Nitrification of ammonium-N and urea-N to  $\text{NO}_3^-$  slowed down due to compaction. The maximum concentration of 185.7, 193.2 and 168.9 mg  $\text{NO}_3^-$  kg<sup>-1</sup>soil was observed 7, 4 and 8 days after treatment application for urine, ammonium and urea, respectively. The peak concentrations under the uncompact soil were attained by day 4, reaching 163.4, 176.7 and 154 mg  $\text{NO}_3^-$  kg<sup>-1</sup>soil for urine, ammonium and urea, respectively. The overall trend of the change in the  $\text{NO}_3^-$  concentration in the soil was similar for all the N sources.

**Table 3.5** Average and range of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentration (mg kg<sup>-1</sup>soil) in compacted and uncompact soil for the 0-5 and 5-10 cm soil depths of Manawatu silt loam

Treatment	Concentration (0-5 cm)		Concentration(5-10 cm)	
	Average	Range	Average	Range
<b>NO<sub>3</sub><sup>-</sup> Concentration</b>				
<b>Compacted</b>				
Urine	77.96	17.89 - 185.68	28.69	8.40 – 58.56
Nitrate	106.12	14.87 – 228.02	47.40	10.02 – 91.30
Ammonium	83.55	14.67 – 193.21	26.97	9.33 – 48.45
Urea	79.14	12.90 – 168.95	29.59	7.34 – 50.62
Water	16.91	10.32 – 26.9	18.08	4.27-36.90
<b>Uncompacted</b>				
Urine	78.96	14.35 – 163.38	16.63	9.14 – 24.31
Nitrate	92.04	13.79 – 209.39	49.79	10.73 – 86.79
Ammonium	90.04	15.39 – 176.69	28.50	12.65 – 49.39
Urea	76.33	14.90 – 154.04	29.82	9.43 – 56.89
Water	18.61	10.32 – 28.16	11.49	5.06 – 15.59
<b>NH<sub>4</sub><sup>+</sup> Concentration</b>				
<b>Compacted</b>				
Urine	76.64	11.97 – 198.66	11.98	7.06 – 226.6
Nitrate	23.01	3.68 – 47.86	7.53	3.54 – 15.32
Ammonium	98.41	18.96 – 219.73	16.83	7.2 – 32.30
Urea	75.75	10.60 – 179.85	12.89	4.81 – 25.63
Water	14.03	4.09 – 33.99	6.54	4.02 – 7.52
<b>Uncompacted</b>				
Urine	80.45	4.25 – 187.56	8.40	3.99 – 15.24
Nitrate	18.29	4.29 – 47.41	5.98	3.98 – 8.24
Ammonium	99.21	17.40 – 208.43	9.88	3.77 – 17.05
Urea	74.59	8.17 – 168.69	8.26	3.05 – 15.92
Water	14.39	8.24 – 29.86	5.07	4.62 – 6.84

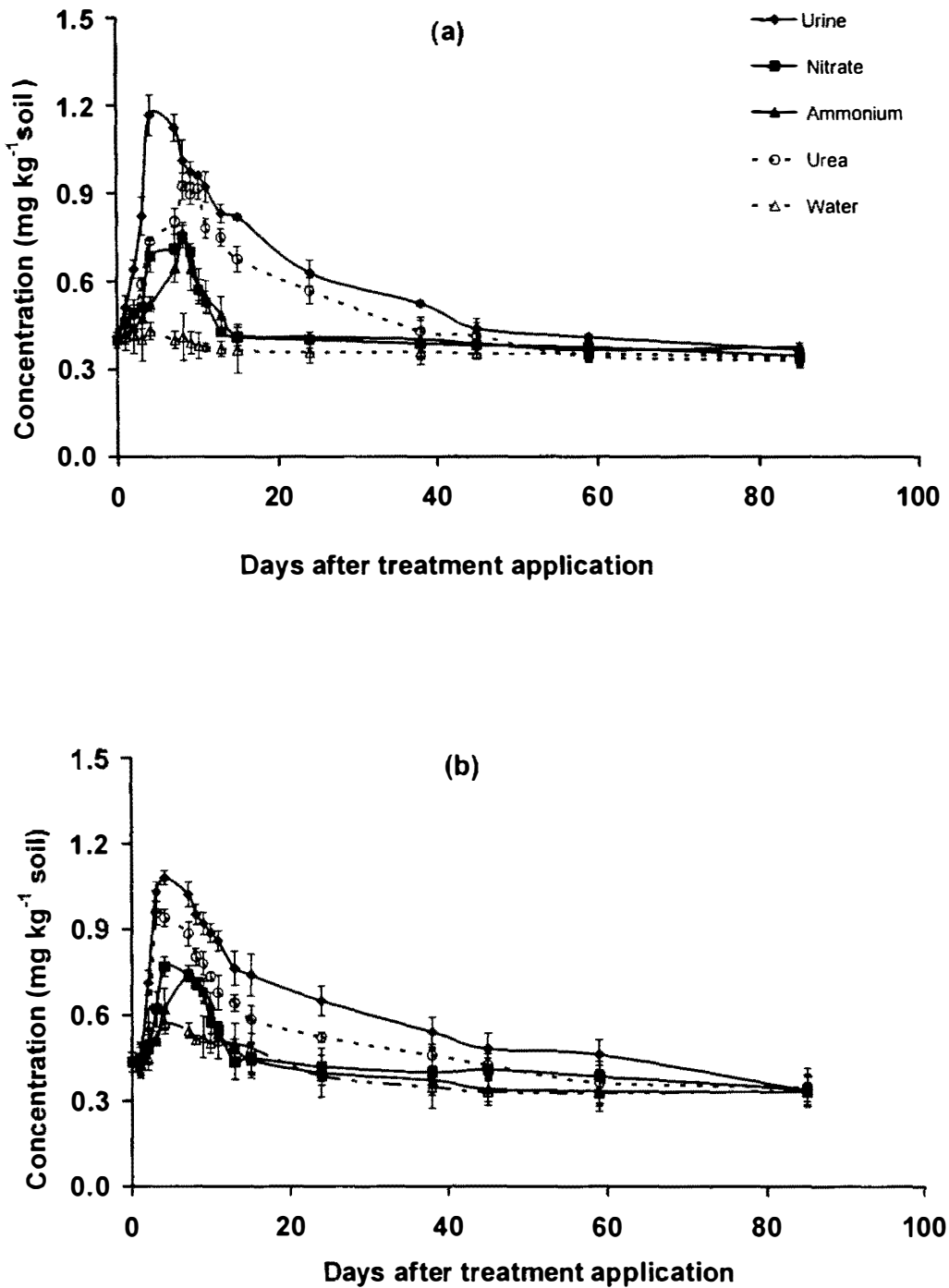
For 3 days after the application of ammonium, urine and urea the mean concentration of  $\text{NH}_4^+$  increased significantly in both the compacted and uncompacted soils, after 3 days the concentration started to decrease with time until the end of the measurement period. Highest concentrations were observed for the ammonium treatment. The  $\text{NH}_4^+$  concentrations increased at a faster rate for urine ( $63 \text{ mg NH}_4^+ \text{ kg}^{-1} \text{ soil d}^{-1}$  and  $51 \text{ mg NH}_4^+ \text{ kg}^{-1} \text{ soil d}^{-1}$  for compacted and uncompacted soil, respectively) than for urea ( $46 \text{ mg NH}_4^+ \text{ kg}^{-1} \text{ soil d}^{-1}$  and  $57 \text{ mg NH}_4^+ \text{ kg}^{-1} \text{ soil d}^{-1}$  for compacted and uncompacted soil, respectively). Over the initial 10 day period, mineral-N equivalent to 72-82% and 84-87% of the added  $\text{NH}_4^+$  for the compacted and uncompacted soils, respectively, had disappeared from the top 0-5cm soil layer of the urine, ammonium and urea treatments.

It was also observed that for the urea treatment the rate of build-up of  $\text{NO}_3^-$  was much smaller relative to the corresponding disappearance of  $\text{NH}_4^+$ . It could be due to the products of nitrification diffusing to less aerobic zones where they become the substrate of denitrifying organisms in locations adjacent to their production (Petersen *et al.* 1991). Velthof *et al.* (1996b) reported a similar pattern and suggested that denitrification rates for  $\text{NH}_4^+$  fertilized soils may have been dependent on the release of  $\text{NO}_3^-$  from the nitrification of ammonium fertilizer. Abbasi & Adams (1998), measuring the nitrification and denitrification potential of the grassland soil, indicated that the potential of the latter was 4-5 times greater than the former. Thus generally the rate of accumulation of  $\text{NO}_3^-$  is not expected to be similar to the rate of decline of  $\text{NH}_4^+$ .

### 3.3.4 Dissolved organic carbon

The concentration of DOC in the Manawatu soil prior to N treatment application was low, comprising of only 1.25% of the total soil organic carbon which were comparable with values of 3.18% reported by Bolan *et al.* (1996) in another field experiment, under grazed pastures.

The DOC levels increased markedly with the addition of N-Sources, under both compacted and uncompacted soils. In general, DOC concentration peaked within a week of the addition of the N sources and then declined gradually, levelling off by the 45<sup>th</sup> day of measurement (Figure 3.8) for all the N sources. No effect of compaction was observed on DOC concentration during the entire experimental period.



**Figure 3.8** Dissolved organic carbon (DOC) (mg kg<sup>-1</sup>) distributions in (a) compacted and (b) uncompacted soils in the field experiment on Manawatu sandy loam for water and different N sources in the field plot experiment. Each value represents a mean of four replicates with standard deviation shown by vertical bars



Within N sources, urine application created the highest DOC concentrations under both compacted and uncompacted soil (average concentrations of 0.74 and 0.73 mg kg<sup>-1</sup> for compacted and uncompacted soil, respectively). These concentrations were significantly different from all the N sources except urea treatment. Monaghan & Barraclough (1993) found a significant increase in soluble carbon levels in the soil up to 7 days after urine application, although the effect of urine on carbon buildup was observed immediately after the addition of urine (5 hrs). This was attributed to the supply of carbon in urine and the solubilisation of organic carbon from the decomposing roots of the urine affected grass. In our study it took 4-6 days for the peak concentrations to appear.

### 3.3.5 Soil pH

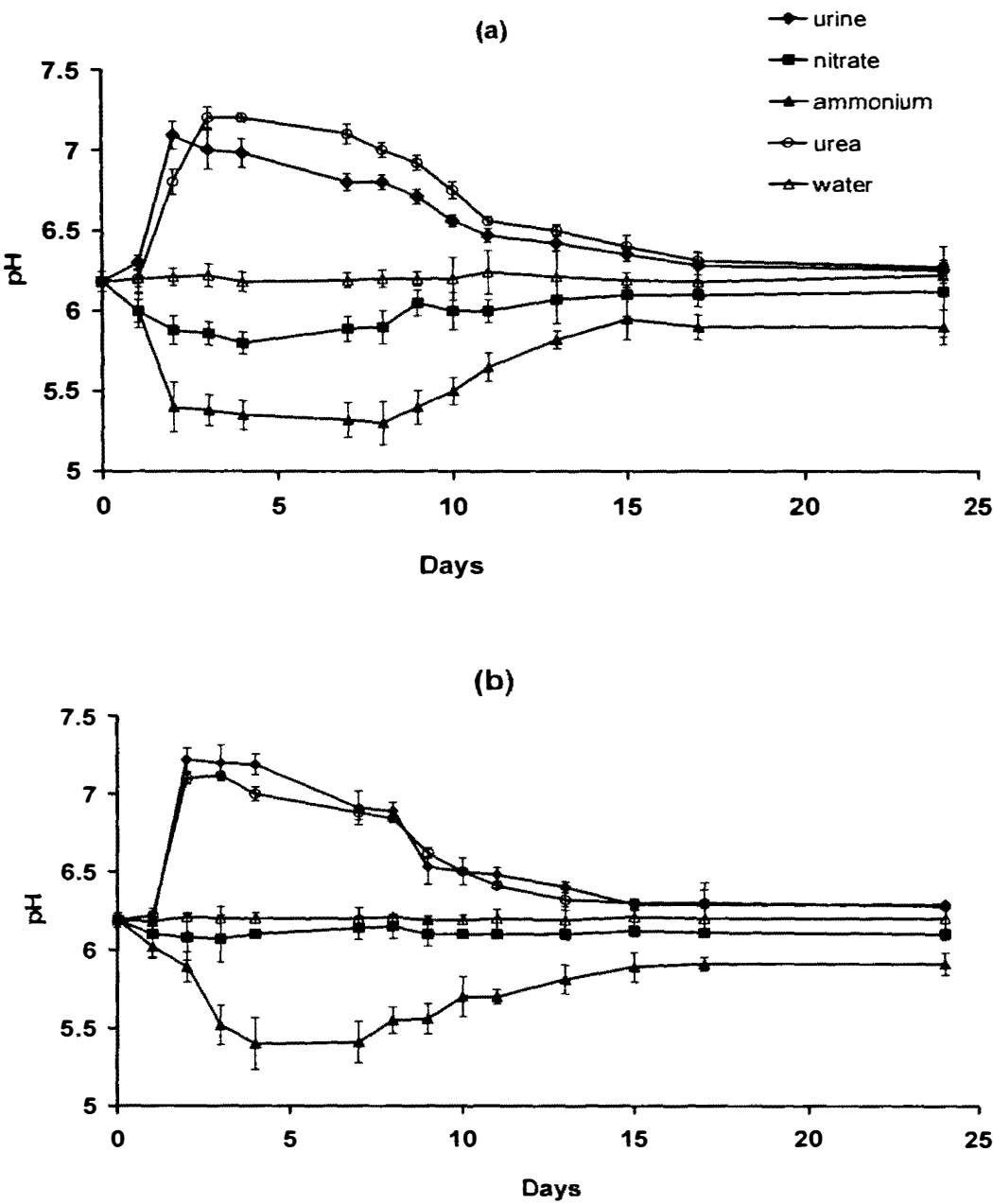
The pH of the soil where water (control treatment) was added remained almost the same for the entire period and was not affected by compaction.

The pH of the soil was found to vary with the addition of different N sources under both compacted and uncompacted soil. The change in pH for different N sources under compacted and uncompacted soils is shown in Figure 3.9. During the experimental period ammonium treatment resulted in the lowest pH (5.3 and 5.4 for compacted and uncompacted soils, respectively), where as urea and urine treatment resulted in the highest pH (7.2 in both cases) for compacted and uncompacted soil, respectively.

Under urine treatment, the increase in pH occurred within a day of the addition of urine with the pH remaining significantly higher than the rest of the N sources for 3 days. The pH then started to decrease, though the fall in pH was gradual. pH was found to stabilize by day 10 after the addition of both the treatments. The trend was similar for compacted and uncompacted soils (Figure 3.9).

For urea treatment, the pH increased from an initial 6.18 to 7.2 for compacted soils and to 7.12 for uncompacted soils. A significant difference in pH was observed between compacted and uncompacted soils where urea was applied. Except for an initial higher pH value for uncompacted soil (7.1) than compacted soil (6.8) on day 2, compacted soil maintained a significantly higher pH throughout the measurement period over the uncompacted soil. This may be attributed to a low level of nitrification

in the compacted soil as compared to the uncompactd soil, resulting in the release of less protons to the soil.



**Figure 3.9** pH distributions at 5 cm soil depth in (a) compacted and (b) uncompactd soils for water and different N sources in the field experiment on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

As expected, the mean pH in the urea and urine treated plots was higher than the water plots. In contrast, the mean soil pH of the ammonium treated plots was low. When urea-based fertilizers are applied to soils, the naturally present urease enzyme hydrolyzes the urea to  $\text{NH}_4^+$ . The hydrolysis reaction produces enough  $\text{OH}^-$  ions to temporarily raise the pH of the soil around the urea fertilizer. Rapid rise in pH is found to occur within 24 hours of the addition of the fertilizer. The hydrolysis of the urine urea is often more rapid than that of pure urea when added to soil under similar conditions (Sherlock & Goh 1983). The pH of urine is high (8.6) which favors its rapid hydrolysis when brought in contact with soil (Haynes & Williams 1992).

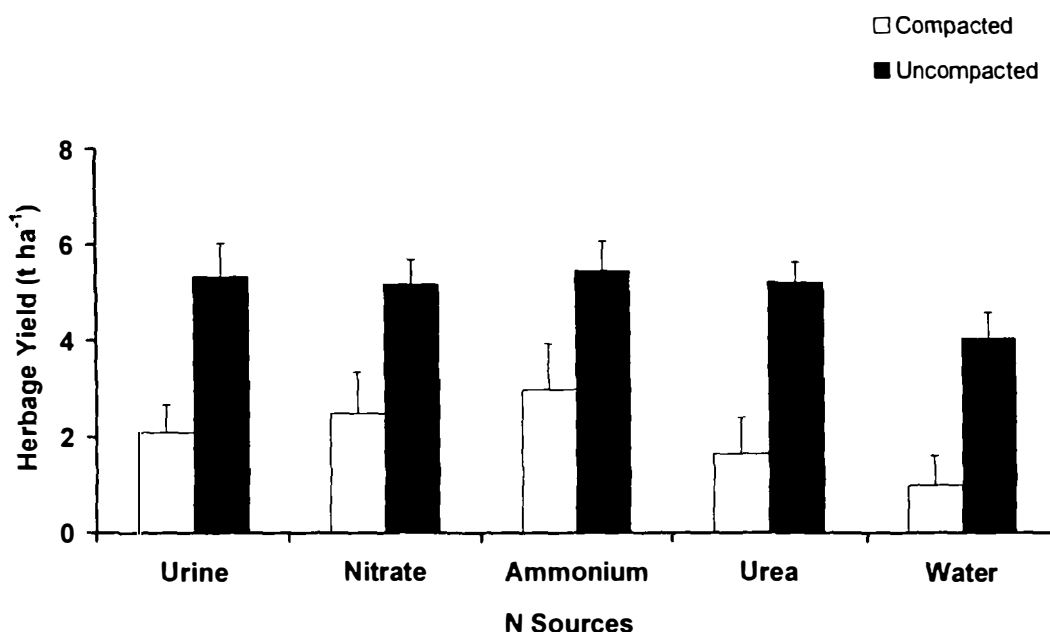
In soils where ammonium sulphate was added as the N source, pH was found to decrease for both compacted and uncompact soil. Ammonium ions in soil are subjected to ready oxidation (nitrification). Nitrification generates two protons per ion of  $\text{NH}_4^+$  nitrified, which results in an increase in soil acidity.

Nitrate treatment also showed a decline in the pH, though the decline was not as pronounced as the ammonium treatment. For uncompact soil nitrate treatment did not show any significant differences in pH from water treatment, although the values were slightly lower than that observed under water treatment. A slight decrease in soil pH with the addition of nitrate treatment is possibly due to accelerated mineralization of soil organic matter or cation exchange mechanisms with  $\text{K}^+$  ions (nitrate was added in the form of  $\text{KNO}_3$ ) displacing  $\text{H}^+$  ions from soil colloids (Clough *et al.* 2003a). This might have happened in the urine treatment as well but could have been overshadowed by the higher pH changes occurring due to urea hydrolysis.

### 3.3.6 Dry matter yield

The dry matter (DM) yield from compacted treatment was significantly lower than uncompact treatment (Figure 3.10) with the average DM production of 2.05 and 5.05 t ha<sup>-1</sup> for compacted and uncompact soils, respectively. The application of N sources caused an increase in DM. The yield response was 1.88, 2.50, 3.32 and 1.08 kg DM yield kg<sup>-1</sup> added N for urine, nitrate, ammonium and urea treatments, respectively, under compacted soil. Highest herbage accumulation was obtained under ammonium treatment though the difference in DM between ammonium and nitrate treatments was not significant.

The yield response for uncompacted soil was 7.38, 6.97, 7.43 and 7.03 kg DM yield kg<sup>-1</sup> added N for urine, nitrate, ammonium and urea, respectively. No difference in DM yield was observed among the N-sources with the yield from all sources being significantly higher than the control treatment.



**Figure 3.10** Total herbage productions in (a) compacted and (b) uncompacted soils for water and different N sources in the field experiment on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

Reduction in pasture production occurs due to the negative impact of compaction on soil physical properties (McCalla *et al.* 1984; Holt *et al.* 1996), especially reduced aeration due to increased bulk density and reduced WFPS. Menneer *et al.* (2005) reported that one cattle treading event caused moderate and severe pugging which decreased pasture yield 16% and 34%, respectively, compared with a non-pugged control treatment. Soil aeration greatly influences plant growth (Glinski & Lipiec 1990) and there are critical threshold ODR values below which root growth and nutrient uptake becomes inhibited. The low herbage yield in compacted soil is consistent with the low ODR values reported earlier (Figure 3.4).

### 3.4 General discussion

Increases in BD (Table 3.3) and PR (Figure 3.2) and decreased soil matric potential (Figure 3.3) and ODR (Figure 3.4) provided evidence that soil compaction had been created both in the field experiment, where close parallel tracks of the wheel were used to create compaction and in the grazing trial, where cattle were allowed to graze at moderate intensity.

Irrespective of the N source, enhanced N<sub>2</sub>O emissions from compacted soil were observed in our experiment. The plausible explanation for this effect is that soil compaction increased the volume of soil in an anaerobic state, resulting in reduced aerobic microbial activity and increased denitrification. Both decreased aerobic respiration and increased denitrification with increasing WFPS are caused by a reduction in oxygen diffusion through soil (Aulakh *et al.* 1991b). The compacted soils remained saturated (Figure 3.5) for a large part of the study period indicating a reduction in the proportion of larger pores and more pore space being filled with water. Also the continuity of pores was probably reduced with increasing bulk density, resulting in reduced oxygen diffusion. Torbert & Wood (1992) reported that WFPS was useful as an index of soil N loss via denitrification, and bulk density plays a major role in controlling N<sub>2</sub>O emissions. Abbasi & Adams (2000b) observed a linear relationship between WFPS in the soil and N<sub>2</sub>O production in clayey loam grassland soil compacted by repeated passes of the tractor. They suggested that in low moisture soils there is enhanced oxygen diffusion into the soil thus limiting N<sub>2</sub>O production, and favouring nitrification. Higher rates of N<sub>2</sub>O fluxes from soils which have WFPS above field capacity are in agreement with the findings of Bandibas *et al.* (1994).

In our experiment the mean WFPS for the entire experimental period for compacted soil was 0.93. As reviewed by Davidson *et al.* (1991), 30-70% is the optimal WFPS range for nitrification above which denitrification becomes an increasingly important source of N<sub>2</sub>O emission. The high N<sub>2</sub>O emission observed in the compacted soil in the presence NO<sub>3</sub><sup>-</sup> is probably due to high denitrification rates rather than that from nitrification. Nitrous oxide emission caused by incomplete nitrification might have played only a minor role in our investigation because of high moisture content in the soil. Moreover, considering the high WFPS values in our experiment, a significant fraction of the N loss through denitrification would have probably ended up as N<sub>2</sub>

(Hansen *et al.* 1993). Thus, measured N<sub>2</sub>O emissions probably constitute only a portion of the nitrogen loss caused by denitrification.

As stated earlier, for the compaction treatment, the soil within the chamber was initially waterlogged. During this time, nitrification then subsequently denitrification were delayed, which led to a decrease in N<sub>2</sub>O emission especially from the ammonical N sources. Once the conditions became suitable for nitrification, the emissions increased and hence the 2<sup>nd</sup> emission peak was observed. Similar observations were reported by van Groenigen *et al.* (2005). The first peak of N<sub>2</sub>O emission for these N sources (urine, urea and ammonium) is probably not because of the N addition but rather from mineralised soil N and readily decomposable C released, due to N source application (e.g. solubilisation of soil carbon due to an increase in pH after urine and urea application (Williams *et al.* 1999). As completely saturated conditions were not found under the uncompacted soils, the emissions were much more consistent. Saturated conditions in the compacted soils are consistent with flooded hoof marks left in pastures badly damaged by winter cattle treading.

Reduced pasture production a consequence of soil compacted could have further increased denitrification activity and hence the N<sub>2</sub>O emission (Ball *et al.* 1999). Bakken *et al.* (1987) found that the compaction of wet soil increased denitrification by 3-4 fold and decreased wheat yield by 25%. The observed restricted growth increased the likelihood of emission by reducing the uptake of available N and of the plant available water (Ball *et al.* 1999).

Among the N sources NO<sub>3</sub><sup>-</sup> provided a ready source of N for denitrification to occur, whereas for the rest of the sources, N must undergo nitrification prior to denitrification. Rates of nitrification in highly compacted grassland soils are relatively slow compared with the process of denitrification with N<sub>2</sub>O emissions from soils to which nitrate had been added were 3-8 times greater than those where ammonium was added (Abbasi & Adams 1998, 2000a). The high soil moisture conditions that prevailed under compacted soil in the beginning of the experiment further hindered the nitrification process. McTaggart *et al.* (1997) and Velthof *et al.* (1996a) drew similar conclusions from N<sub>2</sub>O measurements in grassland soils. Thus fertilisation of compacted soils with NO<sub>3</sub><sup>-</sup> readily stimulates N<sub>2</sub>O release by denitrification.

Nitrous oxide emission was higher from urine than urea. The hydrolysis of the urine urea is more rapid than that of pure urea under similar conditions. The main reason is the presence of hippuric acid, a minor nitrogenous constituent of animal urine

which is known to have a stimulatory effect on urea hydrolysis (Whitehead *et al.* 1989; Haynes & Williams 1993). Immediate release of N<sub>2</sub>O on urine application has also been reported by Sherlock & Goh (1983), Koops *et al.* (1997a), de Klein *et al.* (2003) and Clough *et al.* (2004). Sherlock & Goh (1983) proposed that the initial stimulation of N<sub>2</sub>O emission on the urine application could either be explained by chemodenitrification or by anaerobiosis in microsites as a result of CO<sub>2</sub> generated from the rapid hydrolysis of the urine urea.

Clayton *et al.* (1997) observed that the total N<sub>2</sub>O emission from urea was four times higher than (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, but we did not observe any significant difference between emissions from ammonium and urea sources. It might be possible that the increased soil pH due to the application of urea decreased the N<sub>2</sub>O emission. When denitrification is the main source of N<sub>2</sub>O, emission tends to decrease with increasing pH (Granli & Bockman 1994).

To look into the effect of WFPS, mineral-N and the DOC concentration in soil, the correlation of N<sub>2</sub>O emissions with these properties was evaluated (Table 3.6a). The correlation coefficients between N<sub>2</sub>O emission and soil properties showed that emissions were better correlated with WFPS and NO<sub>3</sub><sup>-</sup> concentration, with correlation being highly significant. Examination of the depth wise distribution of the NO<sub>3</sub><sup>-</sup> concentration in both soils (Table 3.6b), emissions were better correlated with the NO<sub>3</sub><sup>-</sup> concentration in 5-10cm ( $r = 0.39$ ) soil than 0-5cm ( $r = 0.22$ ) soil. In contrast, the N<sub>2</sub>O emissions were notably significantly correlated with WFPS in the upper layer as compared to the lower layer.

The above mentioned soil properties (WFPS, mineral-N and the DOC concentration in soil) were used as the independent variables in a step-up multiple regression analysis to select the best combination of the properties describing the N<sub>2</sub>O emissions. Multiple regressions between N<sub>2</sub>O emission and soil properties (WFPS, mineral-N and the DOC concentration in soil) explained 20% and 28% of the variation in N<sub>2</sub>O emissions for compacted and uncompacted soils, respectively (Table 3.7). WFPS and mineral N (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) concentration were significant variables ( $P < 0.05$ ) in both compacted and uncompacted soils with DOC being non significant. Combining the data for both the compacted and uncompacted soils together further reduced the regression coefficient (Table 3.7) with only 19% of the variability being accounted for.

**Table 3.6** Correlation coefficients for relationships between N<sub>2</sub>O emission and (a) mean soil properties for two depths (b) soil properties at different depths in the field experiment on Manawatu sandy loam. \*\*\*, \*\*, \* depicts level of significance at <0.001, <0.01 and <0.05, respectively. (N<sub>2</sub>O = kg N ha<sup>-1</sup>d<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and DOC = mg kg<sup>-1</sup> soil)

(a)

Soil properties	N <sub>2</sub> O	WFPS	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	DOC
N <sub>2</sub> O	1.00	0.21***	0.21***	-0.06	0.06
WFPS		1.00	0.10	0.05	0.34***
NO <sub>3</sub> <sup>-</sup>			1.00	0.57***	0.51***
NH <sub>4</sub> <sup>+</sup>				1.00	0.57***
DOC					1.00

(b)

Soil properties	WFPS 0-5cm	WFPS 5-10cm	NO <sub>3</sub> <sup>-</sup> 0-5cm	NO <sub>3</sub> <sup>-</sup> 5-10cm	NH <sub>4</sub> <sup>+</sup> 0-5cm	NH <sub>4</sub> <sup>+</sup> 5-10cm	DOC
N <sub>2</sub> O	0.30***	0.14	0.22**	0.39***	-0.11	0.02	0.58
WFPS 0-5cm	1.00	0.35***	0.38***	0.21***	0.33***	0.38***	0.22**
WFPS 5-10cm		1.00	-0.00	-0.01	-0.01	0.30***	-0.11
NO <sub>3</sub> <sup>-</sup> 0-5cm			1.00	0.44***	0.46***	0.46***	0.51***
NO <sub>3</sub> <sup>-</sup> 5-10cm				1.00	-0.14	0.19*	0.15
NH <sub>4</sub> <sup>+</sup> 0-5cm					1.00	0.40***	0.45***
NH <sub>4</sub> <sup>+</sup> 5-10cm						1.00	0.32***
DOC							1.00



Although in the present study we were able to establish significant regression relationships between N<sub>2</sub>O emission and some of the soil properties (WFPS and mineral N) it may not be possible to accurately predict N<sub>2</sub>O emission from soils using such empirical regression relationships. These estimates are based on a large sample ( $\geq 150$ ) and therefore are measurably unbiased and reliable, however the model is not of much use for future prediction purposes as this only explains 20% (for compacted soil) and 28% (for the uncompacted soil) of the overall variability of the N<sub>2</sub>O emission.

**Table 3.7 Results of the multiple linear regression analysis relating N<sub>2</sub>O emission with various soil properties in the field experiment on Manawatu sandy loam. (N<sub>2</sub>O = kg N ha<sup>-1</sup>d<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and DOC = mg kg<sup>-1</sup> soil)**

Treatment	Regression Equation	R <sup>2</sup>
Compacted	N <sub>2</sub> O = -2.27 + 3.37 WFPS + 0.01 NO <sub>3</sub> <sup>-</sup> - 0.02 NH <sub>4</sub> <sup>+</sup>	0.20
Uncompacted	N <sub>2</sub> O = -0.14 + 0.25 WFPS + 0.002 NO <sub>3</sub> <sup>-</sup> - 0.0003 NH <sub>4</sub> <sup>+</sup> - 0.102 DOC	0.28
Combined	N <sub>2</sub> O = -2.04 + 2.89 WFPS + 0.008 NO <sub>3</sub> <sup>-</sup> - 0.01 NH <sub>4</sub> <sup>+</sup>	0.19

The poor correlation between N<sub>2</sub>O emission and soil properties has been observed by other researchers (Clayton *et al.* 1997; Barton & Schipper 2001) especially under grassland systems (Yamulki *et al.* 1998; Anger *et al.* 2003). Davidson & Hackler (1994) attributed the low correlation values to the inability in measuring the soil properties at the micro site scale, whereas Clayton *et al.* (1997) related it to the existence of threshold values for soil factors affecting denitrification and nitrification. Furthermore, linear regression may be limited if the various other effects of compaction on N<sub>2</sub>O emissions occur at the same time. This could cause the relationship between N<sub>2</sub>O and soil properties to be non-linear. The non significant correlation between DOC and N<sub>2</sub>O emission observed in our study could be due to this non linear and possibly synergistic relationship between N<sub>2</sub>O emission and carbon availability (Barton & Schipper 2001).

## 3.5 Conclusions

Physical parameters were useful in characterizing the effects of compaction treatment. Although, the level of compaction created due to grazing was less than the compaction created artificially by the wheel traction of the vehicle, continuous grazing by sheep and cattle throughout the year is known to create more compaction and hence such relatively high emissions as obtained in this experiment can be expected from the compacted sites of intensively grazed pastures.

The main conclusions that can be drawn from this study are as follows:

- ❖ Soil compaction increased the bulk density, PR and WFPS and decreased the ODR in the soil.
- ❖ Soil compaction caused a seven-fold increase in the N<sub>2</sub>O flux clearly indicating that changes in soil physical properties due to soil compaction strongly affect the N<sub>2</sub>O fluxes. As the degree of compaction is highest when the soil is relatively moist, grazing events should be regulated depending on the soil water content of the soil.
- ❖ Highest emissions were measured, with nitrate application being ten times more than those from other N-sources (urine, ammonium and urea) for compacted soil, suggesting that the choice of fertilizer can go a long way in mitigating N<sub>2</sub>O emissions in compacted grasslands.
- ❖ The differences between N<sub>2</sub>O emissions from compacted and uncompacted soil are so large that the relationship between grazing period and variations in soil strength caused by soil and climatic conditions (e.g. winter grazing) will be important in determining actual N<sub>2</sub>O loss.
- ❖ Research to quantify N<sub>2</sub>O loss from New Zealand pastures should be designed to accommodate the temporal and spatial variability, including the age of the urine spot, soil compaction and soil moisture and temperature conditions.

The results in this chapter have demonstrated that the rate of emission of N<sub>2</sub>O from pasture soils is affected by both the compaction and source of N input. In New Zealand, increasingly farm effluents are being treated through land application which provides an important source of N input. Besides providing N, effluents are also known

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to be rich in carbon, an important substrate required for stimulating N<sub>2</sub>O emission. Thus the quality of effluent is likely to have an influence on the N<sub>2</sub>O emissions and it needs to be seen how different types of effluent will affect the emission, which is the focus of next chapter.

## Chapter 4

# Effect of type of farm effluent on nitrous oxide emission

### 4.1 Introduction

Increased intensification of pastoral agriculture in New Zealand over the last decade has led to increasing amounts of effluent being generated (Longhurst *et al.* 2000). In New Zealand annually, about 70 million m<sup>3</sup> of effluent are generated from dairy sheds, 4 million m<sup>3</sup> from pig farms and 50 million m<sup>3</sup> from meat processing plants (Saggar *et al.* 2004b). There has been an increasing effort made to develop an efficient effluent management system which is environmentally sustainable.

Farm effluent management, in New Zealand, is subject to Regional Council and Dairy Industry regulations. With the Regional Councils consent, the irrigation of the effluents onto land has become a preferred treatment option for their disposal. This practice avoids the point source discharge of wastes to surface waters and allows an economic return by recycling wastewater nutrients within soil-plant-root systems (Luo *et al.* 2004). But this policy has been made without due regard to its impact on the air quality.

One of the major nutrients of concern in most of the effluents is N. The conditions suitable for denitrification exist at many effluent irrigation sites (Russell *et al.* 1993). Though denitrification is considered beneficial in reducing the NO<sub>3</sub><sup>-</sup> leaching to ground water, the N<sub>2</sub>O gas, a minor product of denitrification is an important greenhouse gas and it interferes with the formation of the stratospheric ozone and also

accelerates its destruction (Crutzen 1981). Increased N<sub>2</sub>O emissions have been reported from the land application of dairy farm, piggery and meat effluents (Russell *et al.* 1993; Whalen 2000). Per unit of N applied per hectare, farm effluents increase N<sub>2</sub>O emission through denitrification more than inorganic N fertilisers. This is because they add readily available carbon, ammonium-N and water to soils, which increases the soils biological oxygen demand (BOD) whilst reducing oxygen diffusion rates through water filled pores, respectively (Barton & Schipper 2001).

Optimum use of these effluents requires knowledge of their composition, not only to maximise their benefits, but also to minimise environmental damage. The chemical composition of an effluent depends upon its origin and treatment process (Roberts *et al.* 1992; Luo *et al.* 2004). Thus, effluents generated from different farming systems may lead to different levels of gaseous emissions, after land application primarily due to their differences in chemical composition. However, there has been no New Zealand study in which N<sub>2</sub>O emission from various effluent sources have been compared.

The present study was, therefore, undertaken to determine the effect land application of different farm effluents (Treated farm dairy effluent, untreated farm dairy effluent, treated piggery farm effluent and treated meat effluent) have on N<sub>2</sub>O emissions from soil. It was also undertaken to establish whether any differences in N<sub>2</sub>O emission amongst land applied effluents could be attributed to the differences in their composition and/or to the soil conditions prevalent at that time.

The specific objectives of this study are:

- To examine the effect of different effluents on N<sub>2</sub>O emission.
- Effect of treatment of dairy shed effluent on N<sub>2</sub>O emission.
- To examine the differences in N<sub>2</sub>O emission from different effluents applied in autumn and winter seasons.
- To examine the effect different effluents have on changes in mineral N and soluble C.
- To establish regression relationship between effluent properties and N<sub>2</sub>O emission, and between soil properties and N<sub>2</sub>O emission as affected by effluent irrigation.

## 4.2 Material and Methods

### 4.2.1 Experimental site and soil characteristics

A field-plot study was undertaken to study the effect of treated farm dairy effluent (TFDE), untreated farm dairy effluent (UFDE), treated piggery farm effluent (TPFE) and treated meat effluent (TME) on the N<sub>2</sub>O emissions following autumn application (27<sup>th</sup> February - 9<sup>th</sup> June, 2003) and winter application (9<sup>th</sup> July - 2<sup>nd</sup> September, 2003) to sheep-grazed permanent legume-based pasture at Massey University's Frewens Research Block. These periods are hereafter called autumn and winter applications. The soil characteristics have been explained in detail in Chapter 3 (Table 4.1).

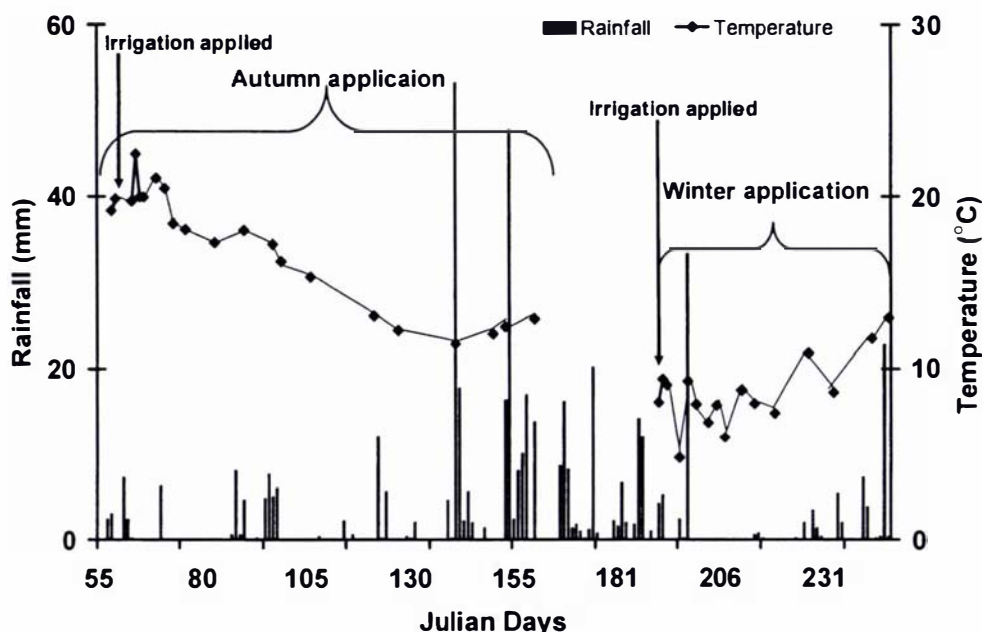
**Table 4.1 Chemical and physical properties of the Manawatu sandy loam soil**

Properties	Soil Depth	
	0-5cm	5-10cm
pH	6.1	6.3
Bulk Density (Mg m <sup>-3</sup> )	1.18	1.18
Total N (%)	0.30	0.19
Total C (%)	3.27	1.9
C:N	10.9	9.8
CEC (cmol kg <sup>-1</sup> )	16.1	—

The rainfall distribution and air temperature for the autumn and winter applications are shown in Figure 4.1. Total rainfall received during the 102 days of the measurement period for the autumn application was 279.4 mm and that for the 56 days measurement period during the winter application was 96.6 mm. The rainfall was not very evenly distributed with dry spells experienced during the first two months of the autumn application. 115 mm of rainfall was received during the last week of the measurement period. Rainfall during the experimental period (March – May and July – August) was below normal compared to the 30 year average (1971-2000). The 30 year mean rainfall during the months of March, April, May, July and August were 74, 76, 94, 94 and 82 mm, respectively. The rainfall obtained during

these months in the year of the experiment was 29.8, 26.8, 107.4, 95.4 and 28 mm for the months of March, April, May, July and August, respectively.

The mean average air temperatures for the autumn application ranged between 11.1 and 18.5°C against a 30 year average range of 11.2 to 16.5°C. The air temperatures for the winter application were almost within range of the 30 years average temperatures observed for that time period. The soil temperatures were in the range of 11.4 to 22.5°C (average of 17.2°C) and 6.0 to 13.0°C (average of 8.6°C) for the autumn and winter application, respectively.



**Figure 4.1** Soil temperatures at 5 cm depth and daily rainfall during the experiment period for autumn (27th February, 2003 to 9th June, 2003; 58 to 160 Julian days) and winter (9th July, 2003 to 2nd September, 2003; 191 to 246 Julian days) applications

## 4.2.2 Experimental design

The experimental site was fenced off six months prior to the commencement of the experiment to avoid further stock access during the experimental period and to eliminate the effect of grazing on gaseous emission. The experiment comprised of six treatments: four effluents namely treated farm dairy effluent (TFDE), untreated farm dairy effluent (UFDE), treated piggery farm effluent (TPFE) and treated meat effluent (TME), water and control. The water and control treatments were included to separate

the effects of soil moisture and N and C inputs through effluent application on N<sub>2</sub>O emission. Each of these treatments was applied to a 2m<sup>2</sup> (2m x 1 m) area plot with a 0.5 m wide buffer strip around each plot. The plots were lined with a 7.5cm deep polythene sheet to restrict the surface flow of the applied treatment. Each treatment was replicated four times in a randomised block design.

Treated farm dairy effluent was collected from the outlet of the aerobic pond whereas the UFDE was collected from the inlet of the anaerobic pond. The piggery effluent was also treated in a two pond system and was collected from the aerobic pond. All the three effluents were collected from the private dairy farms located near Massey University. The meat effluent, collected from the Oringi meat-processing plant located 10km south of Dannevirke New Zealand, had also been treated in the settlement pond. The effluents were collected and stored at 4°C prior to application the next day. A sample from each effluent was kept aside for analysis. The characteristics of the effluents are presented in Table 4.2.

All the effluents were applied at a hydraulic loading rate of 25mm with the total volume of effluent applied for each plot being 50 litres. The results in chapter 3 indicated that soil moisture level as measured by WFPS had a significant impact on N<sub>2</sub>O emission. Hence it was decided to apply the effluents at a constant hydraulic loading (not at a constant N loading). The herbage in all the plots was mowed to 2 cm height before applying the treatments. Treatments were applied evenly to each plot as a 50 L volume using a watering can with a rosette attachment.

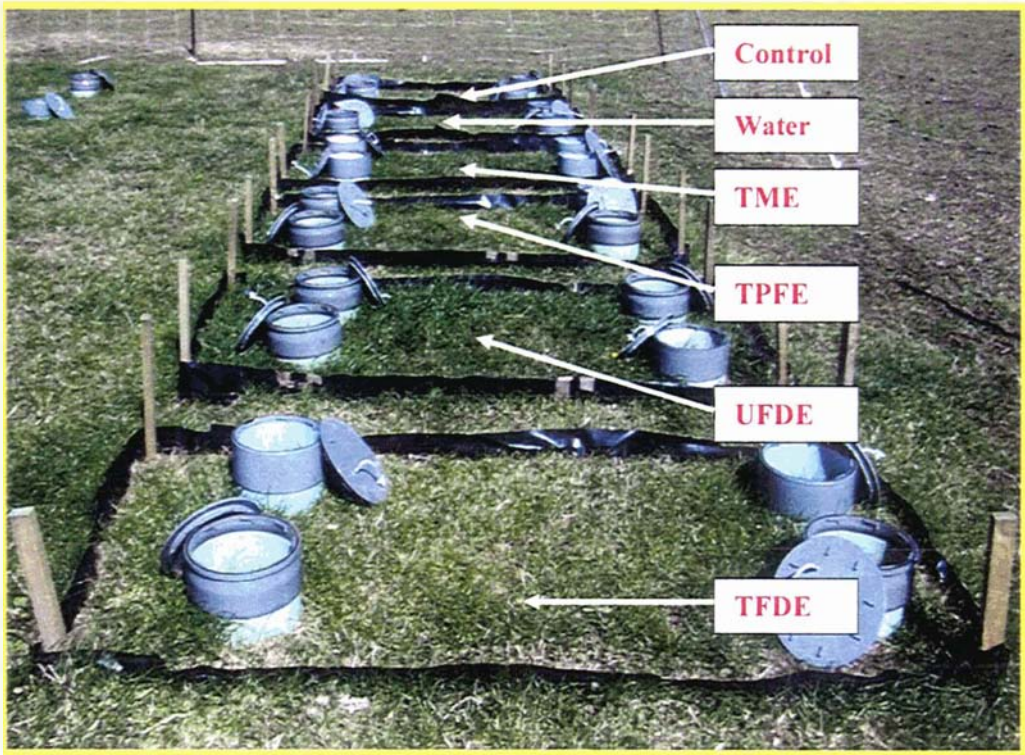


**Table 4.2** Characteristics of the different effluents applied in autumn (27th February, 2003) and winter (9th July, 2003)

Properties	Autumn application				Winter application			
	TFDE	UFDE	TPFE	TME	TFDE	UFDE	TPFE	TME
Total suspended solids (mg l <sup>-1</sup> )	221.3	770.3	393.7	96.0	253.4	630.1	321.8	114.5
pH	7.6	7.9	7.8	7.3	7.8	7.8	7.7	7.1
Total N (mg l <sup>-1</sup> )	75.15	251.9	56.9	164.7	52.1	197.3	92.4	135
NH <sub>4</sub> <sup>+</sup> -N (mg l <sup>-1</sup> )	51.9	176.3	42.7	115.3	36.5	118.4	69.3	108
NO <sub>3</sub> <sup>-</sup> -N (mg l <sup>-1</sup> )	0.06	0.04	0.11	0.06	0.07	0.08	0.07	0.10
Total Carbon (mg l <sup>-1</sup> )	729	3173	592	1828	490	2388	906	1445
Dissolved organic carbon (mg l <sup>-1</sup> )	14.9	59.3	17.8	31.6	10.8	40.8	23.6	32.1
C:N ratio	9.7	12.6	10.4	11.1	9.4	12.1	9.8	10.7
Chemical oxygen demand (mg l <sup>-1</sup> )	91.0	337.0	265.0	281.0	95.0	286.0	274.0	236.0
Biochemical oxygen demand (mg l <sup>-1</sup> )	97.0	224.0	196.0	185.0	82.0	221.0	194.0	166.0
Total P (mg l <sup>-1</sup> )	24.0	28.0	21.0	15.0	19.0	18.0	33.0	15.0
Total K (mg l <sup>-1</sup> )	161	178	154.7	52.6	153	167	112.2	61.7

**4.2.3 Nitrous oxide measurement**

The N<sub>2</sub>O fluxes were measured periodically for autumn application and winter application using a closed chamber technique as described in Saggar *et al.* (2002; 2004b). Four chambers per treatment were used. The chambers, 25 cm in diameter, were inserted about 10 cm into the soil immediately after the effluent application. Background N<sub>2</sub>O flux was measured for the site one day before the application of the treatments. During the first week, N<sub>2</sub>O emission measurements were made daily to capture major changes in N<sub>2</sub>O fluxes. This was followed by measurements on alternate days for two months and then once a week for rest of the experimental period as the fluxes decreased, approaching the background levels. The calculation of N<sub>2</sub>O flux from these gaseous measurements has been described in detail in Chapter 3 of the thesis. The lay-out of the field plot experiment is shown in Plate 4.1.



**Plate 4.1** Layout of the effluent irrigation experiment showing the plot arrangement and the various treatments added.

## 4.2.4 Analysis

### 4.2.4.1 Effluent analysis

Samples of effluent were analysed for suspended solids, pH, total N, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, total carbon, dissolved organic carbon, chemical oxygen demand (COD), biological oxygen demand (BOD), total phosphorous, total potassium and electrical conductivity by the procedures published in standard methods (APHA 1998).

### 4.2.4.2 Soil analysis

To determine the WFPS, mineral N (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) and dissolved organic carbon (DOC) content for all the treatments four soil samples were collected on the days of N<sub>2</sub>O measurement from the 0-5cm depth from plots outside the chamber area where treatments were applied. Field moist samples were sieved (< 2mm) soon after collection. A sub-sample (5g) was extracted with a 0.5M K<sub>2</sub>SO<sub>4</sub> solution by shaking for 1 hr (1g soil: 4 ml extractant). The extracts were analysed for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> by standard colorimetric methods (Keeney & Nelson 1982) on an auto analyser and for DOC by the dichromate oxidation (Tate *et al.* 1988) method using a spectrophotometer. Sub-samples of soil were kept for determining the WFPS. The field moist soil samples were weighed (M<sub>i</sub>) and oven dried (105°C) to a constant mass (M<sub>s</sub>). Gravimetric soil water content (SWC) was calculated as described in Eq. 2 of Chapter 3 of this thesis. This was then used to calculate the WFPS (Eq. 3; Chapter 3) of the soil for the effluent irrigated and control soils.

### 4.2.4.3 Herbage analysis

To determine the effect of different effluents on pasture productivity, herbage was cut to 2cm height at the beginning of the application. After the autumn application three harvests were taken from the sward and one harvest after the winter application. The cumulative dry matter (DM) yield was recorded from each plot. The dry matter response was also calculated by the formula:

$$DM \text{ response} = \frac{DM \text{ from effluent irrigated plot} - DM \text{ from control plot}}{N \text{ added through effluent}}$$

The total N contents of the plant samples were determined by the Kjeldahl digestion method (Mckenzie & Wallace 1954).

The added N that was recovered in the dry matter yield was calculated by dividing the difference of the total N that was recovered in the effluent treated plots and that recovered in the control plot with the N added through the effluent.

#### **4.2.5 Oxygen diffusion rate**

Oxygen diffusion rate (ODR) measurements were made on day 1, 7 and 14 to look into the difference in the diffusion rate between the treatments for both the autumn and the winter applications by the method described in Chapter 3.

#### **4.2.6 Statistical methods**

An analysis of the variance was carried out using a SAS for Windows v8 software package. The least significant differences (LSD) were calculated to estimate the differences between the treatments. The 5% confidence level is regarded as statistically significant.

The regression and correlation analysis between various soil properties and N<sub>2</sub>O emission and various effluent and soil properties was conducted using the SAS package.

### **4.3 Results and Discussion**

#### **4.3.1 Properties of the effluents**

The effluents used in this study were collected from the same locations for both the autumn application and the winter application. The effluent characteristics varied somewhat between the autumn and the winter application due to seasonal variations in processing (Table 4.2). However these variations were within the range of the characteristics typical for these effluents found in literature (Heatley 1996). Typically, C: N ratios of all the effluents were less during the winter application as compared to the autumn application. On average, all the effluents were high in total nitrogen content with most of the mineral N being present in the form of NH<sub>4</sub><sup>+</sup> with almost negligible concentrations of NO<sub>3</sub><sup>-</sup>. Dairy untreated effluent and ME were found to have a high C:

N ratio (Table 4.2) but were within the range reported in other studies (Cameron *et al.* 1995; Di *et al.* 1998; Hawke & Summers 2003; Luo *et al.* 2004; Wang *et al.* 2004).

The data on TSS, COD, BOD and nutrients in the effluent samples collected from the anaerobic inlet pipe (i.e., untreated effluent) and the oxidation pond outlet pipe (i.e., treated effluent) indicate that the pond system achieved considerable reduction in the concentration of TSS, COD and BOD whereas there was no significant difference in the concentration of nutrients between the two effluents. It has been reported elsewhere that the two pond system was effective in removing the suspended solids, COD and BOD but not the nutrients (Hickey *et al.* 1989; Mason 1997). While the suspended solid is removed by gravity sedimentation and the breakdown of carbon constituents by microbial degradation, the removal of soluble organic carbon (i.e., BOD) is achieved through its complete oxidation by the micro-organisms (Bolan *et al.* 2004c). Poor nitrification of NH<sub>4</sub><sup>+</sup> in the oxidation pond as a result of sludge build-up in the pond bottom, is the main reason for little change in the N content between the treated and the untreated effluent (Mason 1997).

### 4.3.2 Nitrous oxide emission

All the effluent sources were found to affect the N<sub>2</sub>O emissions in both seasons (Figure 4.2 a, b). Emissions were found to increase immediately after the application of the effluent. It was true for all the effluents and for both the irrigation events. After an initial increase in emissions, N<sub>2</sub>O loss was found to decrease progressively with the passage of time. The emission pattern was slightly different for the two applications, with a two peak emission observed during the autumn application (Figure 4.2 a) and only one peak observed during the winter application (Figure 4.2 b).

#### 4.3.2.1 Autumn application

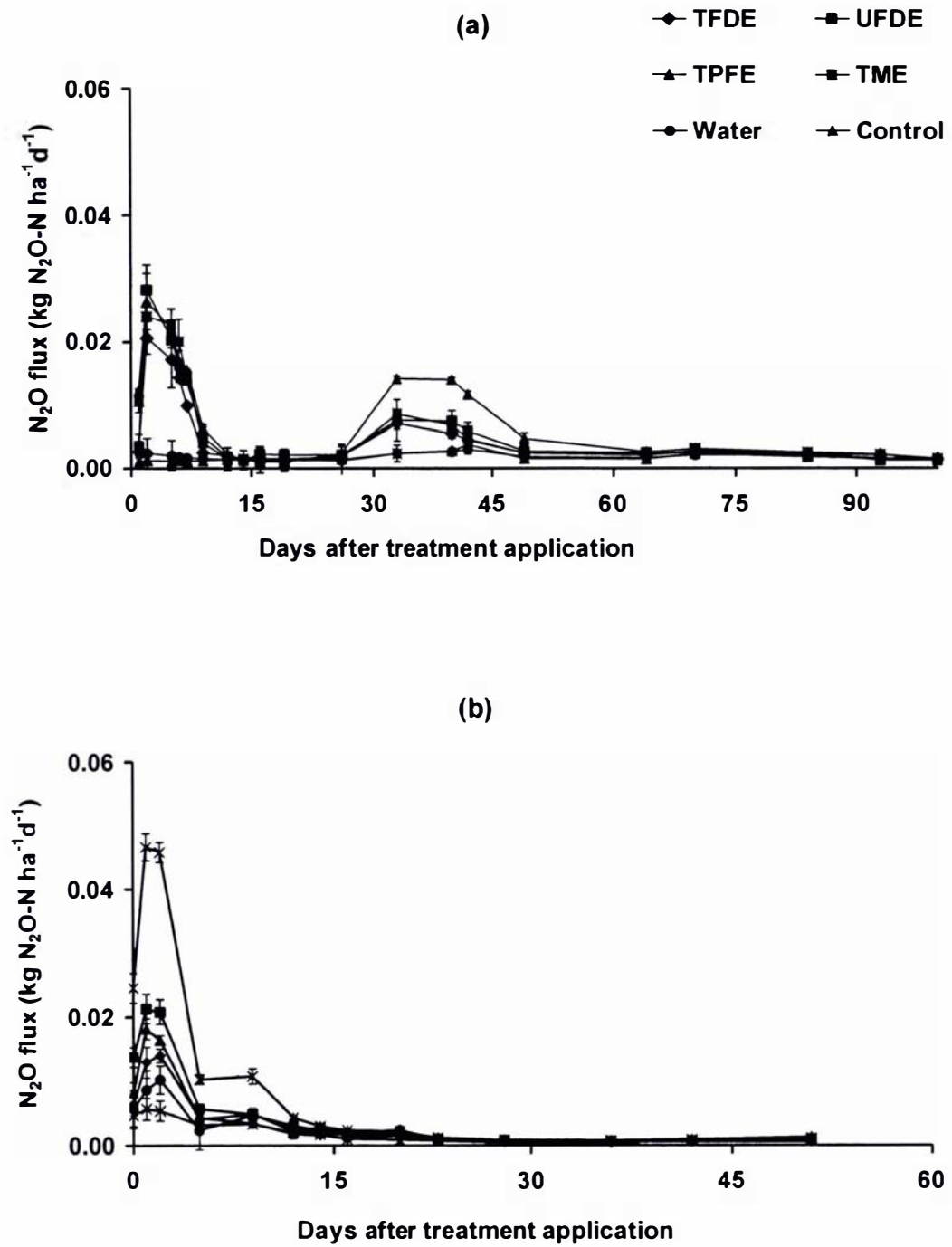
Peak emissions of 0.21, 0.028, 0.026 and 0.024 kg N ha<sup>-1</sup> d<sup>-1</sup> were obtained for TFDE, UFDE, TPFDE and TME treatments, respectively within 24-36 hrs after the effluent application (Figure 4.2 a) which represented 17 to 24 fold increases over pre-application emission rates. A two fold increase in the emission rate was also observed due to the application of water, though the effect was short lived with water having significantly higher emissions for only the first five days after application. A comparison of emission data for various effluents over the measurement period showed

that the effect of the effluent diminished after two weeks. Within these initial two weeks, N<sub>2</sub>O emissions from TPFE treatment remained higher than the rest of the treatments. The difference between the UFDE and TME treatments diminished after 2 days of the treatment application. A second peak in emission was observed for all the treatments (including water and control) a month after the treatment application, which corresponded with a major rainfall event (Figure 4.2a). The second peak emission was highest from TPFE (0.014 kg N ha<sup>-1</sup> d<sup>-1</sup>) followed by TME (0.009 kg N ha<sup>-1</sup> d<sup>-1</sup>), UFDE (0.008 kg N ha<sup>-1</sup> d<sup>-1</sup>), TFDE (0.007 kg N ha<sup>-1</sup> d<sup>-1</sup>), control (0.004 kg N ha<sup>-1</sup> d<sup>-1</sup>) and water (0.003 kg N ha<sup>-1</sup> d<sup>-1</sup>).

The results show significantly higher emissions from all effluent irrigation treatments compared with the control and water treatments. The overall emissions from the effluent treatments were 85-183% higher than those from the water treatment. This increase was much higher when compared with the control treatment (98-203%).

During the autumn application, TPFE emitted the highest N<sub>2</sub>O-N among the effluents used, with emission reaching 0.585 kg N ha<sup>-1</sup> or 2.17% of the total added effluent-N, over the experimental period (Table 4.3). It was significantly higher than the rest of the treatments. Emissions from untreated dairy effluent (0.447 kg N ha<sup>-1</sup>) and TME (0.456 kg N ha<sup>-1</sup>) were not significantly different. Untreated dairy effluent resulted in higher emissions (0.447 kg N ha<sup>-1</sup>) compared with the treated dairy effluent (0.382 kg N ha<sup>-1</sup>), which gave the least emission among the effluents. However, the proportion of effluent-N emitted was higher for the TFDE (0.87%) than for the UFDE (0.42%).





**Figure 4.2** N<sub>2</sub>O fluxes (kg N ha<sup>-1</sup> d<sup>-1</sup>) following the (a) autumn application and (b) winter application of water and a range of effluent types to sheep-grazed pasture on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars.

**Table 4.3** N<sub>2</sub>O fluxes following the autumn and winter application of water and a range of effluent types to sheep-grazed pasture on Manawatu sandy loam

Type of Effluent	N added through effluent (kg N ha <sup>-1</sup> )		N emitted (kg N ha <sup>-1</sup> )		Emission factor %	
	Autumn	Winter	Autumn	Winter	Autumn	Winter
TFDE	21.8	13.0	0.382	0.102	0.87	0.23
UFDE	61.0	49.3	0.447	0.153	0.42	0.16
TPFE	27.5	23.1	0.585	0.130	1.43	0.25
TME	39.5	33.8	0.456	0.286	0.67	0.63
Water	0.0	0.0	0.207	0.101	—	—
Control	—	—	0.193	0.072	—	—
LSD (0.05%) Treatments n = 4			0.023	0.036		
LSD (0.01%) Treatments n = 4			0.032	0.050		

#### 4.3.2.2 Winter application

During the winter application the trend in emission was slightly different from that of the autumn application. Only one peak in emission was observed immediately after the application of the effluent (Figure 4.2 b). The peak emission was highest for the TME effluent (0.047 kg N ha<sup>-1</sup> d<sup>-1</sup>) followed by the UFDE (0.021 kg N ha<sup>-1</sup> d<sup>-1</sup>), TPFE (0.018 kg N ha<sup>-1</sup> d<sup>-1</sup>) and TFDE (0.014 kg N ha<sup>-1</sup> d<sup>-1</sup>). Meat effluent maintained statistically higher emission than the rest of the treatments for the first 14 days after effluent application. By day 28, the effect of effluent application had diminished to the extent that all treatments showed statistically similar N<sub>2</sub>O fluxes. The daily N<sub>2</sub>O fluxes from the treatments where effluents were applied were 1-183% higher than that from the water treatment and 42-297% higher than the control treatment.

During winter application, TME resulted in the highest N<sub>2</sub>O emission reaching 0.286 kg N ha<sup>-1</sup> (0.84%) of the total effluent-N added. There was no significant difference in N<sub>2</sub>O emissions from TPFE and UFDE and emissions from TFDE, TPFE and water. The percentage values of added N lost as N<sub>2</sub>O are 0.23, 0.16, 0.25 and 0.63% for TFDE, UFDE, TPFE and ME treatments, respectively.



Comparing the N<sub>2</sub>O emissions from all the treatments for the autumn and winter applications it was observed that the maximum mean fluxes for all the effluents except the TME were higher for the autumn application than for the winter application. Meat effluent along with the water and control treatments had higher emissions during the winter application than the autumn application. Comparing the peak emissions of the control treatment indicated 4 times higher emission during the winter application than the autumn application. The percentage of the added N emitted as N<sub>2</sub>O was lower for the winter application than the autumn application (Table 4.3). Although it was difficult to compare N<sub>2</sub>O emission between the autumn and winter applications because of the difference in the monitoring period between these two seasons (96 days for autumn and 54 days for winter), by the time monitoring was stopped the N<sub>2</sub>O emission had reached the background level for both the seasons.

Other studies have shown highly variable courses for peak N<sub>2</sub>O emission response following animal waste application. Sharpe & Harper (1997) and Whalen *et al.* (2000) reported maximum responses within several hours of swine-effluent applications. Nitrous oxide emission was found to decrease progressively from the time of the application of various effluent sources. Russell & Cooper (1987) also observed that following an effluent irrigation event, the N<sub>2</sub>O production rate increased rapidly and reached a peak, which fell again to background levels as aerobic conditions re-established. Khan (1999) in his field study also reported higher emissions from piggery effluent than from treated dairy factory effluent being 1.9% and 0.1–0.3% of the applied N as N<sub>2</sub>O emissions from piggery effluent and treated dairy effluent, respectively.

Higher N<sub>2</sub>O emissions from effluent treatments in comparison to the control are because of the enhanced denitrification activity resulting from increased C availability and/or from decreased soil aeration. Petersen, (1999) observed that lowering the C content of animal slurry had decreased N<sub>2</sub>O emissions. Effluents have been shown to promote conditions conducive to denitrification by creating an anaerobic environment abundant in inorganic N and readily oxidisable C (Comfort *et al.* 1988).

The reasons for the effect of effluent irrigation on N<sub>2</sub>O emission and the difference in N<sub>2</sub>O emission among various effluents are explained in the discussion section.

4.3.3 Oxygen diffusion rate

It was observed that the ODR values decreased immediately after the application of the treatments (water and effluents) (Table 4.4). Oxygen diffusion rate values for the water treatment fell by 12.5 and 9.7% as compared to the control treatment whereas this reduction ranged from 17.2 to 36% and 9.7 to 30.7% for the effluent treatments in the autumn and winter application, respectively. By the end of the 3<sup>rd</sup> week the difference in the ODR values had diminished with only UFDE treatment being statistically different from the control.

**Table 4.4** ODK reading ( $\mu\text{g cm}^{-2} \text{ min}^{-1}$ ) from the 10cm soil depth following the autumn and winter application of water and a range of effluent types to sheep-grazed pasture on Manawatu sandy loam

Treatments	Autumn application			Winter application		
	Day 1	Day 7	Day 14	Day 1	Day 7	Day 14
TFDE	0.53	0.56	0.58	0.50	0.56	0.60
UFDE	0.41	0.45	0.52	0.43	0.49	0.54
TPFE	0.51	0.54	0.59	0.49	0.52	0.59
TME	0.46	0.50	0.58	0.48	0.50	0.58
Water	0.56	0.59	0.65	0.56	0.58	0.62
Control	0.64	0.65	0.65	0.62	0.63	0.65
LSD	0.04	0.06	0.08	0.05	0.05	0.07

Oxygen diffusion rate values were affected by the type of the effluent. Among the effluents, UFDE registered the lowest ODR values for both the irrigations and for all the three measuring dates. This was followed by the TME treatment though during both the irrigation events, no significant difference was observed among the UFDE and TME after a week (Table 4.4). A decrease in ODR resulting from effluent irrigation can be attributed to both the decrease in soil aeration, as measured by WFPS and the increased consumption of O<sub>2</sub> by the easily oxidisable carbon in the effluent. Bolan, (2002) observed a decrease in ODR when poultry manure was applied to soil and they attributed it to the increased consumption of O<sub>2</sub> by the easily oxidisable carbon in the manure and its release as CO<sub>2</sub> after the effluent application. A decrease in soil aeration

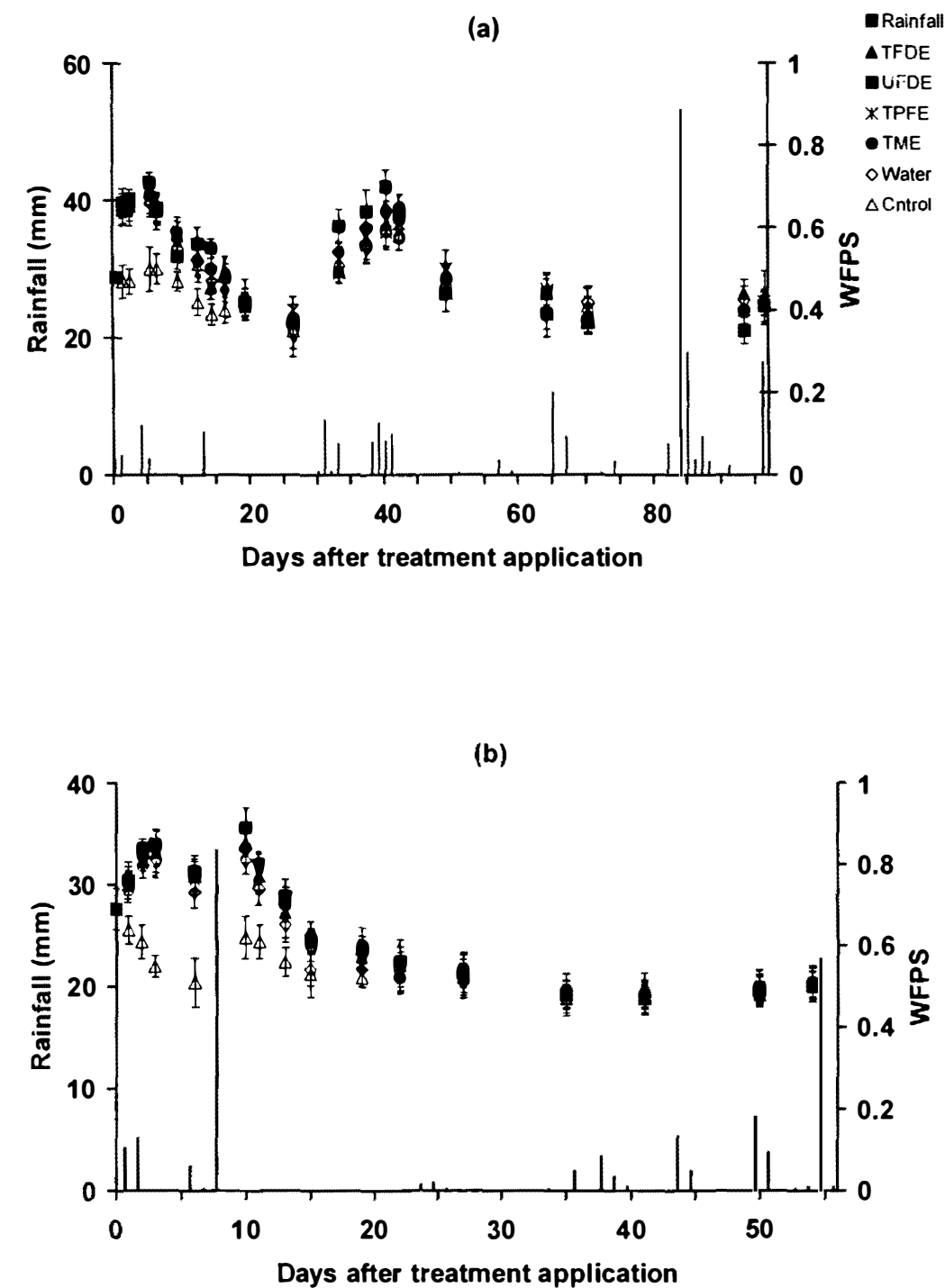
as a result of the effluent application has been reported elsewhere as well (Barton & Schipper 2002; Sharpe & Harper 2002).

#### 4.3.4 Water filled pore space

The autumn of 2002-03 was the driest in a decade with the average rainfall being 50% below normal and a significant soil moisture deficit occurring throughout the autumn season (<http://www.niwascience.co.nz/ncc/cu/2003>). Predominantly dry conditions prevailed in March, April and the first half of May of the year 2003. This was also reflected in the WFPS distribution during the experiment. Figure 4.3 shows the WFPS distribution during the course of the experiment for different treatments. During the 1<sup>st</sup> effluent irrigation the conditions were very dry and the soil in the control plot remained below the field capacity for the whole of the experimental period. The WFPS, under control treatment, ranged from 0.35 to 0.58 throughout the measurement period. The WFPS did show an increasing trend in the middle of the experiment which coincided with the rainfall event, but it soon stabilised. The WFPS of all the effluent irrigated plots were significantly higher than the control treatment only for two weeks after the application of the treatments. No significant difference was observed in the WFPS between the effluent and water treatment and also within the effluents themselves.

A total of 96.6 mm of precipitation was received during the winter application event with 47% of it within a week of the effluent application. Therefore, the WFPS were higher than the field capacity for all the treatments in the beginning of the experimental period. The WFPS increased further with the addition of the effluent and water treatments reaching a maximum of 0.86. The differences in the WFPS between the irrigated and the control became non-significant after 15 days from the treatment application (Figure 4.3).

WFPS has been considered an important component regulating N<sub>2</sub>O emission from the soil. The application of effluent has often been shown to increase the WFPS of the soil (Sharpe & Harper 1997; Whalen 2000) although the extent of increase depends on the moisture status of the soil at the time of the irrigation and the amount of irrigation applied.



**Figure 4.3** Rainfall and WFPS distribution for all the treatments for (a) autumn application and (b) winter application of water and a range of effluent types to sheep grazed pasture on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

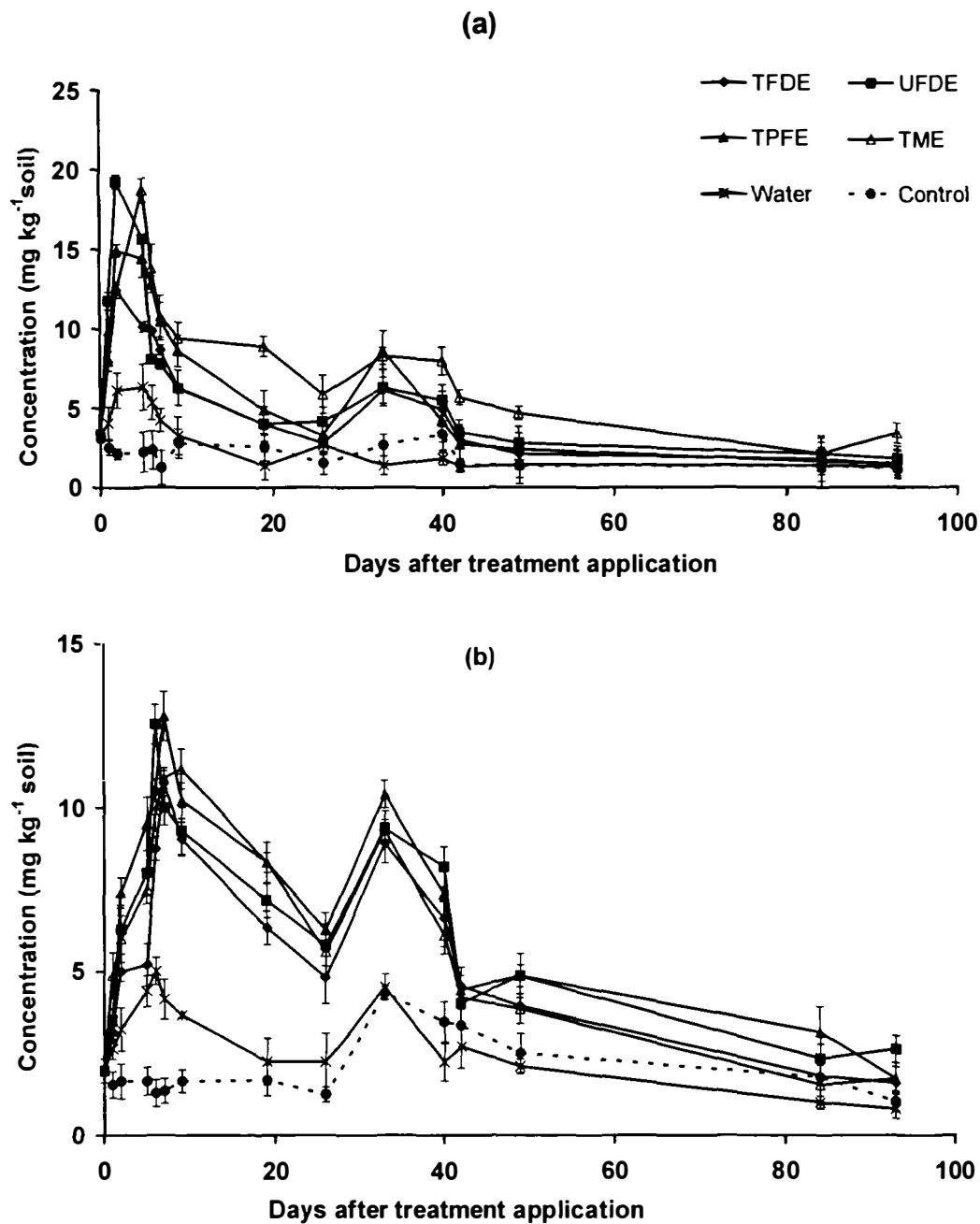
### 4.3.5 N transformation in soil

#### 4.3.5.1 Autumn application

Nitrate and ammonium concentrations in the soil prior to the application of water and effluent treatments were 1.97 and 3.25 mg kg<sup>-1</sup> soil. The mineral N concentrations in the control treatment remained more or less the same during the entire measurement period (Figure 4.4a and b).

The addition of treatments (effluent and water) increased the mineral concentration of the soil significantly over the control treatment. The concentrations reached peak values within a week and then decreased with time, reaching the background level by the end of the experiment. A second peak of the mineral N concentration was observed during the 5<sup>th</sup> week of the measurement which coincided with a major rainfall event. The control treatment also showed a slight increase in the mineral N concentration during this time.

Treatments that included the addition of water and effluents showed an immediate increase in soil NH<sub>4</sub><sup>+</sup> levels with the levels rising from 3.25 mg kg<sup>-1</sup> soil to as high as 19.26 mg kg<sup>-1</sup> soil (UFDE), registering a 6 fold increase in concentrations (Figure 4.4a). Water maintained a higher NH<sub>4</sub><sup>+</sup> concentration than control during the initial 7 days after water addition (Figure 4.4a) with no significant difference after that. In the case of the effluents the increases in NH<sub>4</sub><sup>+</sup> concentrations observed above the control; soil accounted for 74.3, 85.4, 89 and 79.4% of the total added NH<sub>4</sub><sup>+</sup> from the TFDE, UFDE, TPFE and TME effluents, respectively. In all effluent treatments highest levels of NH<sub>4</sub><sup>+</sup> were attained within 2 days of the addition of the effluent. Thereafter, NH<sub>4</sub><sup>+</sup> concentrations showed a rapid decline with no difference observed among the treatments after 42 days of treatment addition.



**Figure 4.4** Distribution of soil (a)  $\text{NH}_4^+$  concentration (b)  $\text{NO}_3^-$  concentration at 5cm depth following the autumn application of water and a range of effluent types to sheep grazed pasture on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

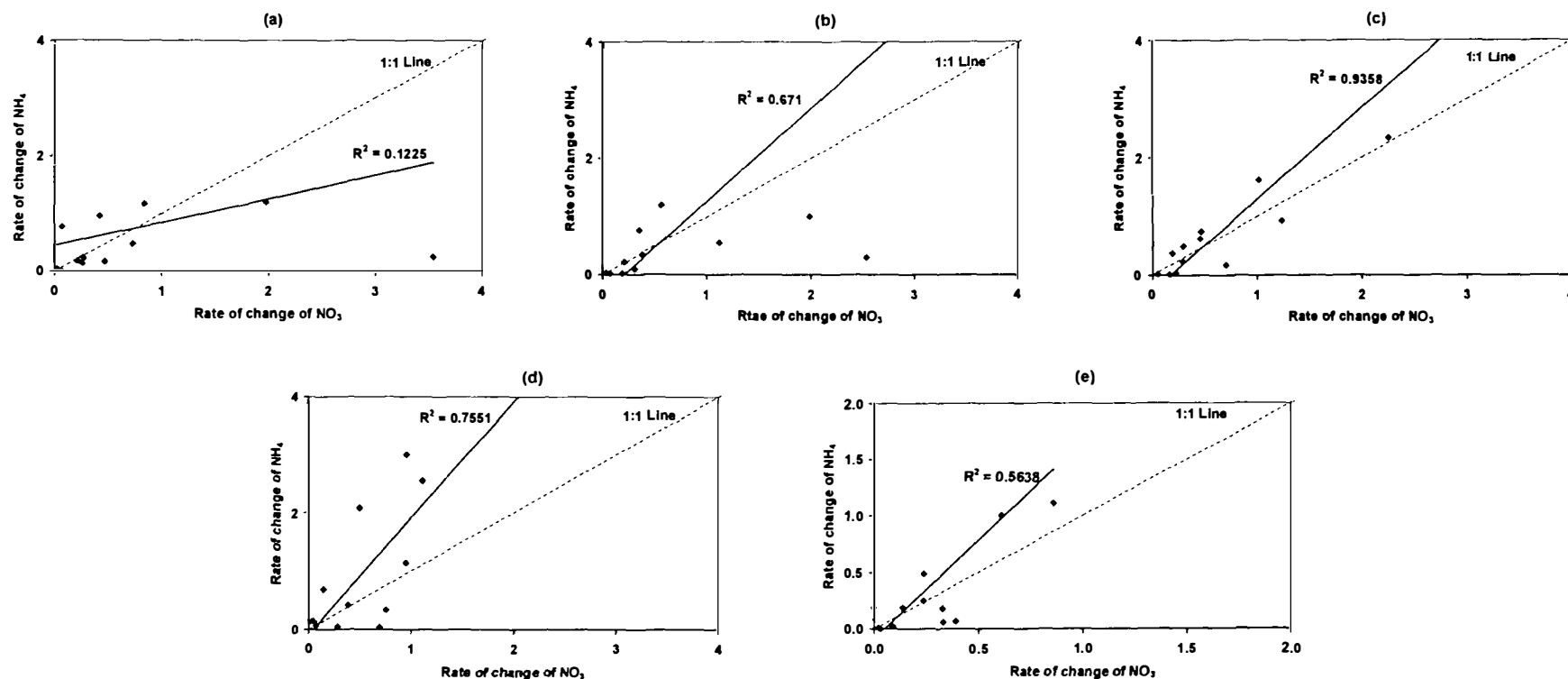
Among the effluents, the highest  $\text{NH}_4^+$  concentration was found under UFDE treatment ( $19.26 \text{ mg kg}^{-1}\text{soil}$ ), which was not significantly different from the TME ( $18.71 \text{ mg kg}^{-1} \text{ soil}$ ) with TPFE and TFDE having lower peak concentrations of  $14.93$  and  $12.45 \text{ mg kg}^{-1} \text{ soil}$ , respectively.

Gradually increasing NO<sub>3</sub><sup>-</sup> concentrations accompanied the decreasing NH<sub>4</sub><sup>+</sup> concentrations for effluent treatments with concentrations reaching 10.7, 12.5, 12.8 and 11.2 mg kg<sup>-1</sup> soil for TFDE, UFDE, TPFE and TME, respectively. Increases in nitrate concentration were not observed until a week after the addition of the effluents. There was no difference in the NO<sub>3</sub><sup>-</sup> concentration in soil amongst the effluent treatments 6 weeks after the application of effluents (Figure 4.4b).

The change in NH<sub>4</sub><sup>+</sup> concentration with time was rapid in the soil with about 85% of the NH<sub>4</sub><sup>+</sup> being lost by the 26<sup>th</sup> day of the addition of the effluent. An increase in the NH<sub>4</sub><sup>+</sup> level was also observed during the 5<sup>th</sup> week after the addition of the treatments. The concentration of NO<sub>3</sub><sup>-</sup> was more elevated during this period than the NH<sub>4</sub><sup>+</sup> concentration.

The net rate of change in NH<sub>4</sub><sup>+</sup> concentration with time, calculated from the day peak concentration of NH<sub>4</sub><sup>+</sup> was obtained in the soil, was higher for the effluent treatments than the water and control. The rate of change in the soil of NH<sub>4</sub><sup>+</sup> concentrations became negative after the 6<sup>th</sup> day for all the treatments, indicating the commencement of nitrification. The net rate of change of NH<sub>4</sub><sup>+</sup> was highest for TPFE (5.33 mg N kg<sup>-1</sup> soil d<sup>-1</sup>). The net rate of nitrification (build up of NO<sub>3</sub><sup>-</sup> in the soil) was also significantly higher for the effluent treatments than the water and control treatments with the highest being observed under the TPFE (6.91 mg N kg<sup>-1</sup> soil d<sup>-1</sup>) though it was not statistically different from TME (6.42 mg N kg<sup>-1</sup> soil d<sup>-1</sup>) and TFDE (6.78 mg N kg<sup>-1</sup> soil d<sup>-1</sup>).

Figure 4.5 compares the rate of change of NH<sub>4</sub><sup>+</sup> with that of NO<sub>3</sub><sup>-</sup> (absolute values) for the four effluents added during the autumn application. The rate of change was calculated by expressing the difference in the concentration of NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup> on two consecutive measurement days on per day basis. As is evident from the graphs, the rate of change of NH<sub>4</sub><sup>+</sup> was higher than that of NO<sub>3</sub><sup>-</sup> for all the effluents except TFDE (Figure 4.5a) where the opposite trend was evident. The r<sup>2</sup> values for the UFDE, TPFE and TME were 0.67, 0.94 and 0.76, respectively whereas the r<sup>2</sup> value of TFDE (0.12) was very low. The differences in the rates of change of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> could be attributed to ammonia volatilisation, the immobilisation and plant uptake of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, the denitrification and/or leaching of NO<sub>3</sub><sup>-</sup>. The differences in the rate of change of mineral N could also be related to the rate of changes in ODR values (Table 4.4) and DOC values (Figure 4.8) resulting from effluent irrigation.



**Figure 4.5** Relationship between rates of change in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentration (absolute values) with time ( $\text{mg N kg}^{-1} \text{ soil d}^{-1}$ ) calculated over the entire measurement period after autumn application for (a) TFDE (b) UFDE (c) TPFDE (d) TME and (e) Water treatments (For the purpose of clarity all the data points are not shown in some of the figures)



#### 4.3.5.2 Winter application

The trends in soil inorganic N concentrations for all the treatments (Figure 4.6) were similar to the patterns observed in the autumn application (1<sup>st</sup> irrigation) except that no second peak in concentration was observed during the winter application.

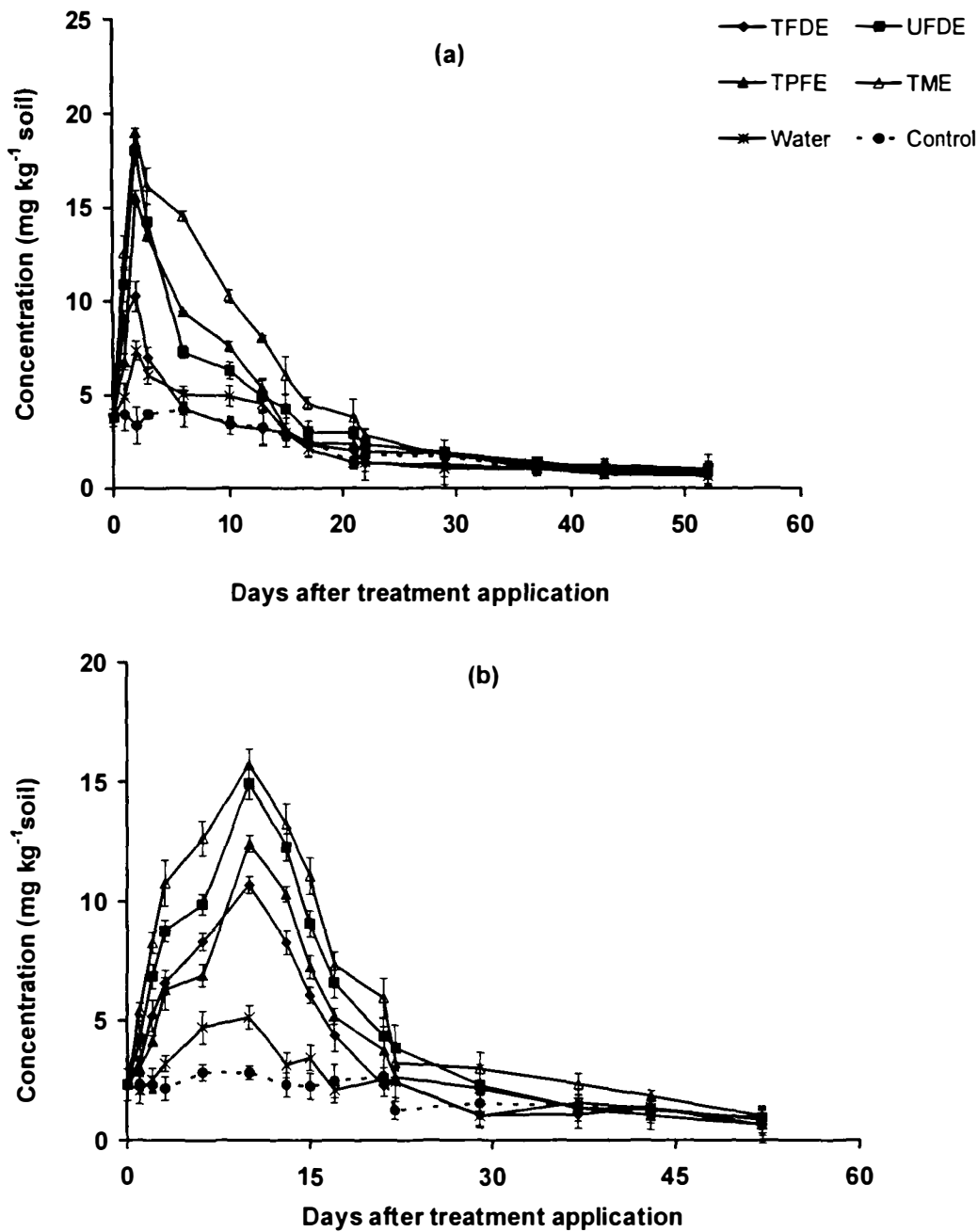
Ammonium and NO<sub>3</sub><sup>-</sup> concentrations for the control treatment deviated little from the pre application levels of about 3.78 and 2.32 mg kg<sup>-1</sup> soil throughout the 52 days observational period (Figure 4.6).

Water maintained a higher NH<sub>4</sub><sup>+</sup> concentration than control during the initial 13 days after water addition (Figure 4.6a) with no significant difference after that. Upon the application of water and effluents treatments, NH<sub>4</sub><sup>+</sup> concentration immediately (2<sup>nd</sup> day) increased to 10.2, 18, 15.5, 19 and 7.35 mg kg<sup>-1</sup> soil for the TFDE, UFDE, TPFE, TME and water treatments, respectively. These concentrations represented 68.1, 85.2, 75.5 and 77.5% of the added NH<sub>4</sub><sup>+</sup> for the TFDE, UFDE, TPFE, TME and water treatments, respectively. Thereafter the NH<sub>4</sub><sup>+</sup> decreased rapidly and reached the background reading by the 17<sup>th</sup> day.

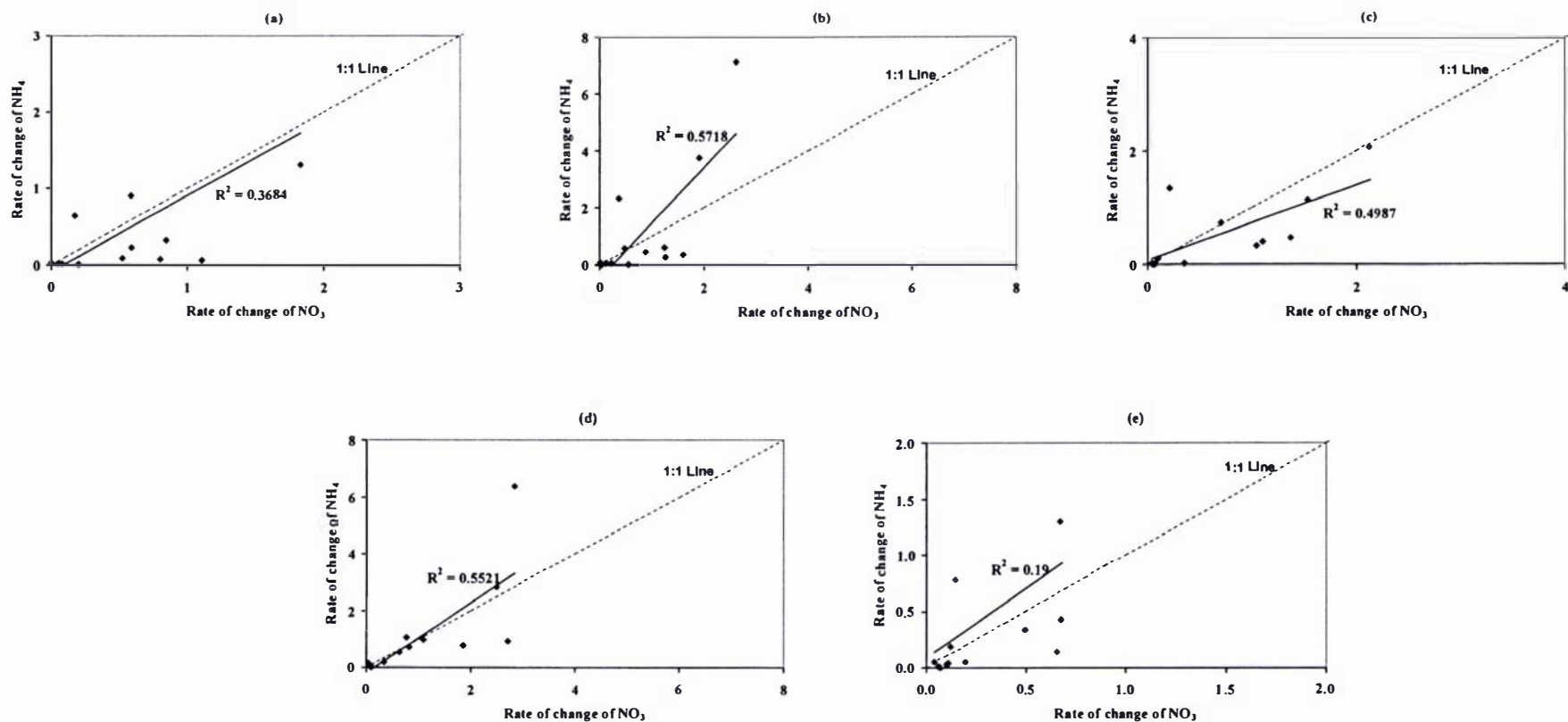
There was no increase in NO<sub>3</sub><sup>-</sup> concentration in the water treatment over the control treatment. Nitrate concentrations increased steadily from 2.3 mg N kg<sup>-1</sup> soil to 10.7, 14.9, 12.4, 15.7 and 5.1 mg N kg<sup>-1</sup> soil for TFDE, UFDE, TPFE, TME and water treatments, respectively by the 10<sup>th</sup> day. Increases in NO<sub>3</sub><sup>-</sup> concentration from the application of effluents ceased to occur after 4 weeks of the treatment application (Figure 4.6 b).

The change in NH<sub>4</sub><sup>+</sup> concentration with time was rapid in the soil, with about 85% (average of the effluents) of the NH<sub>4</sub><sup>+</sup> being lost within 3 weeks of the addition of the effluent. The loss was rapid for TFDE and slowest for TME. During the first week after the application about 85% of the applied NH<sub>4</sub><sup>+</sup> had disappeared from the TFDE plot whereas only 27% was lost from the TME treatment.

As seen in the autumn application, the net rate of change of NH<sub>4</sub><sup>+</sup> calculated for the entire measurement period was significantly higher ( $p < 0.001$ ) for the effluent treatments than the water and control. The rates of change of NH<sub>4</sub><sup>+</sup> concentrations in the soil became negative after the 3<sup>rd</sup> day for all the treatments. The net rate of change of NH<sub>4</sub><sup>+</sup> was highest for TME (8.78 mg kg<sup>-1</sup> soil d<sup>-1</sup>), which was observed immediately after the effluent application.



**Figure 4.6** Distribution of soil (a)  $\text{NH}_4^+$  concentration (b)  $\text{NO}_3^-$  concentration at 5cm depth following the winter application of water and a range of effluent types to sheep grazed pasture on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars



**Figure 4.7** Relationship between rates of change in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentration (absolute values) with time ( $\text{mg N kg}^{-1} \text{ soil d}^{-1}$ ) after winter application for (a) TFDE (b) UFDE (c) TPFE (d) TME and (e) Water treatments (For the purpose of clarity all the data points are not shown in some of the figures)

The rate of change of  $\text{NH}_4^+$  concentration was very fast at the beginning of the experiment, but the rate dropped gradually after that.

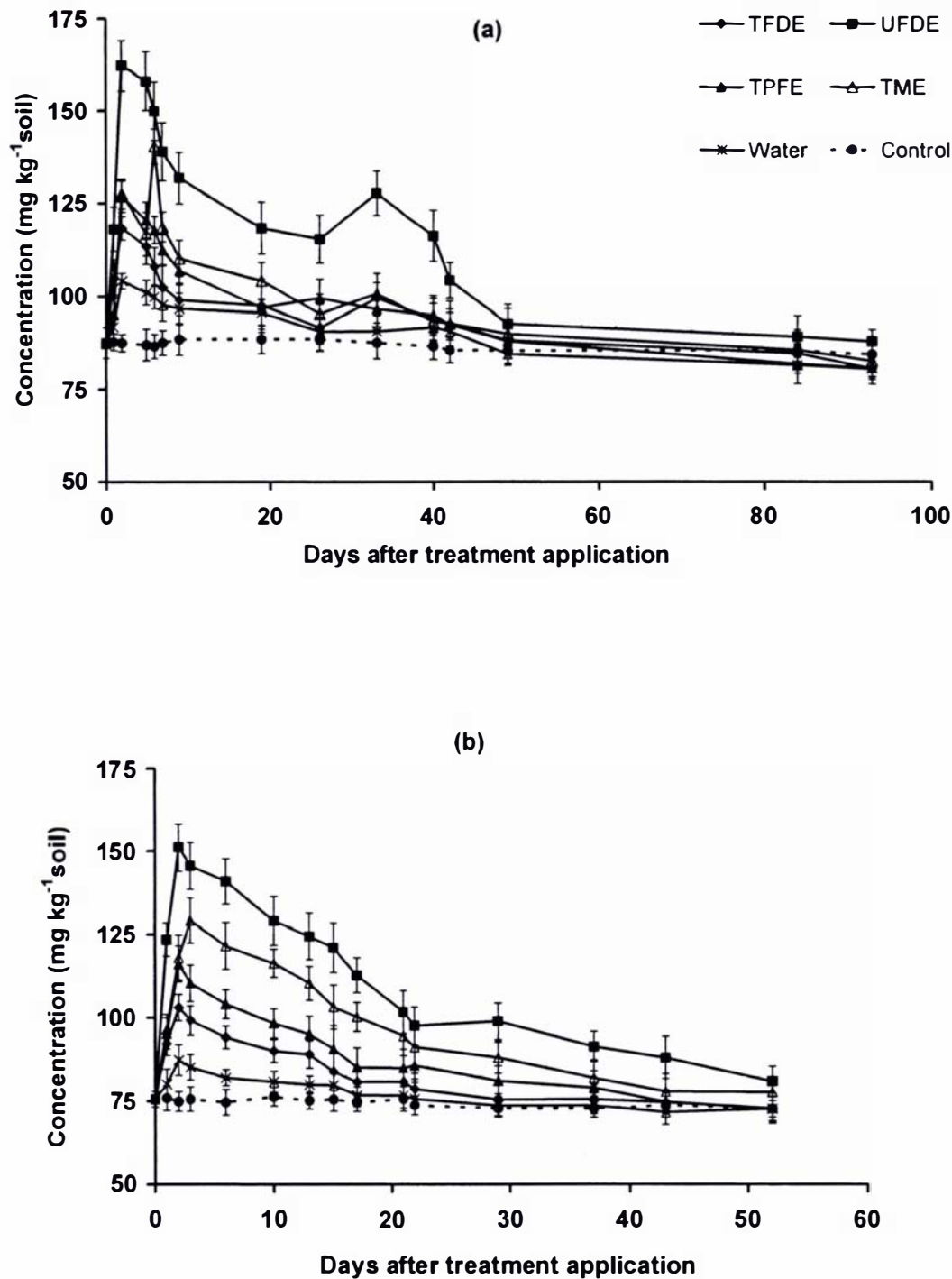
The rate of change of  $\text{NO}_3^-$  in the TFDE and TPFE irrigated soils was higher than the rate of change of  $\text{NH}_4^+$  whereas an opposite trend was observed under the TME application (Figure 4.7). The highest rate of change of  $\text{NO}_3^-$  was observed under the TME treatment ( $2.84 \text{ mg kg}^{-1} \text{ soil d}^{-1}$ ), though it was not statistically different from UFDE ( $2.62 \text{ mg kg}^{-1} \text{ soil d}^{-1}$ ). The lowest rate of change of  $\text{NO}_3^-$  was found under the TPFE treatment ( $1.13 \text{ mg kg}^{-1} \text{ soil d}^{-1}$ ), with the rate for the TFDE treatment ( $1.83 \text{ mg kg}^{-1} \text{ soil d}^{-1}$ ) being significantly higher than the TPFE treatment.

Comparing the rate of change of the mineral N concentration between the two seasons, it was observed that the net nitrification was faster during the autumn application than the winter application. On average, both the rate of change of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in soil was higher during the autumn season for all the effluents except TME where the rate of  $\text{NO}_3^-$  loss was higher during the winter application as compared to the autumn application. Higher temperatures during autumn, along with increased WFPS immediately after the application of the effluent, could have caused an increase in the N conversion during the autumn season.

An increased mineral N concentration due to the application of farm effluents has been reported by (Russell *et al.* 1991; Watanabe *et al.* 1997; Hawke & Summers 2003; Luo *et al.* 2004).

#### 4.3.6 Dissolved organic carbon

The addition of farm effluents significantly increased the amount of DOC over the control and water treatments during both the autumn and winter applications. Following an increase, the DOC concentration for all the treatments decreased steadily reaching the background level within 49 and 43 days for the autumn and winter applications, respectively. The changes in the DOC concentration are consistent with the changes in the ODR values obtained after effluent application indicating that the addition of carbon through effluent irrigation enhanced the microbial respiration.



**Figure 4.8** Soil DOC concentration at 5 cm depth following the (a) autumn application and (b) winter application of water and a range of effluent types to sheep grazed pasture on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

#### 4.3.6.1 Autumn application

During the autumn application, the concentrations of DOC were higher for all the effluents than for the water and control (Figure 4.8a). This was mainly due to the high amount of DOC supplied with the effluent. DOC values for the TFDE, UFDE, TPFE and TME were in the range of 78 to 162 mg kg<sup>-1</sup> soil with peak concentrations of 118.25, 162.14, 126.69 and 127.40 mg kg<sup>-1</sup> soil for TFDE, UFDE, TPFE and TME, respectively. A slight increase in the soil DOC concentration was also observed where water was added as a treatment with the concentration rising from 78 mg kg<sup>-1</sup> soil to 94 mg kg<sup>-1</sup> soil. The increase in DOC was significantly higher than the control treatment though no significant difference was observed 9 days after the treatment application (Figure 4.8a).

Among the effluent treatments, highest DOC concentration was observed under the UFDE treatment, which maintained a significantly higher concentration than the next highest treatment of TME for 42 days after the treatment application. The treatment effect among the TFDE, TPFE and TME treatments was not observed by the end of two weeks, when no significant difference was present in the DOC concentrations of the three treatments (Figure 4.8a).

The DOC concentration in the soil was higher than the amount added through the effluent, suggesting priming effect occurring in the soil. The increase in DOC concentration due to the effluent application was 1.94, 1.82, 3.80 and 2.21% of the total C added by the effluent.

#### 4.3.6.2 Winter application

For the winter application the trend in soil DOC levels were almost the same as the autumn application (Figure 4.8 b). The peak DOC values were 103.05, 151.18, 116.20 and 118.06 mg kg<sup>-1</sup> soil for TFDE, UFDE, TPFE and TME, respectively. The values were 1.2, 1.7, 4.0 and 2.7 times higher than the peak concentration observed for the water treatment. However, these values expressed as percentage of the total organic carbon added in the soil through effluent, were very low (3.21, 2.67, 3.19 and 3.05% for the TFDE, UFDE, TPFE and TME, respectively). The DOC concentration for the water treatment increased from the pre application concentration by 15.61% after the water addition. The DOC concentration in the soil was higher for the autumn application of

the effluents than for the winter application for all the treatments, which may be partly attributed to the residual undecomposed plant litter's contribution to DOC limited by summer dry conditions and partly to faster decomposition of the organic compounds during the autumn season than winter season. As was observed in the autumn application, a priming effect was observed in the soil during the winter application as well.

An increase in the carbon levels due to the addition of the organic sources such as effluent and manures have been reported by other researchers as well (Lowrance *et al.* 1998). Vinten *et al.* (2002) observed an increase in the DOC level for 5 days after the application of poultry manure to the soil.

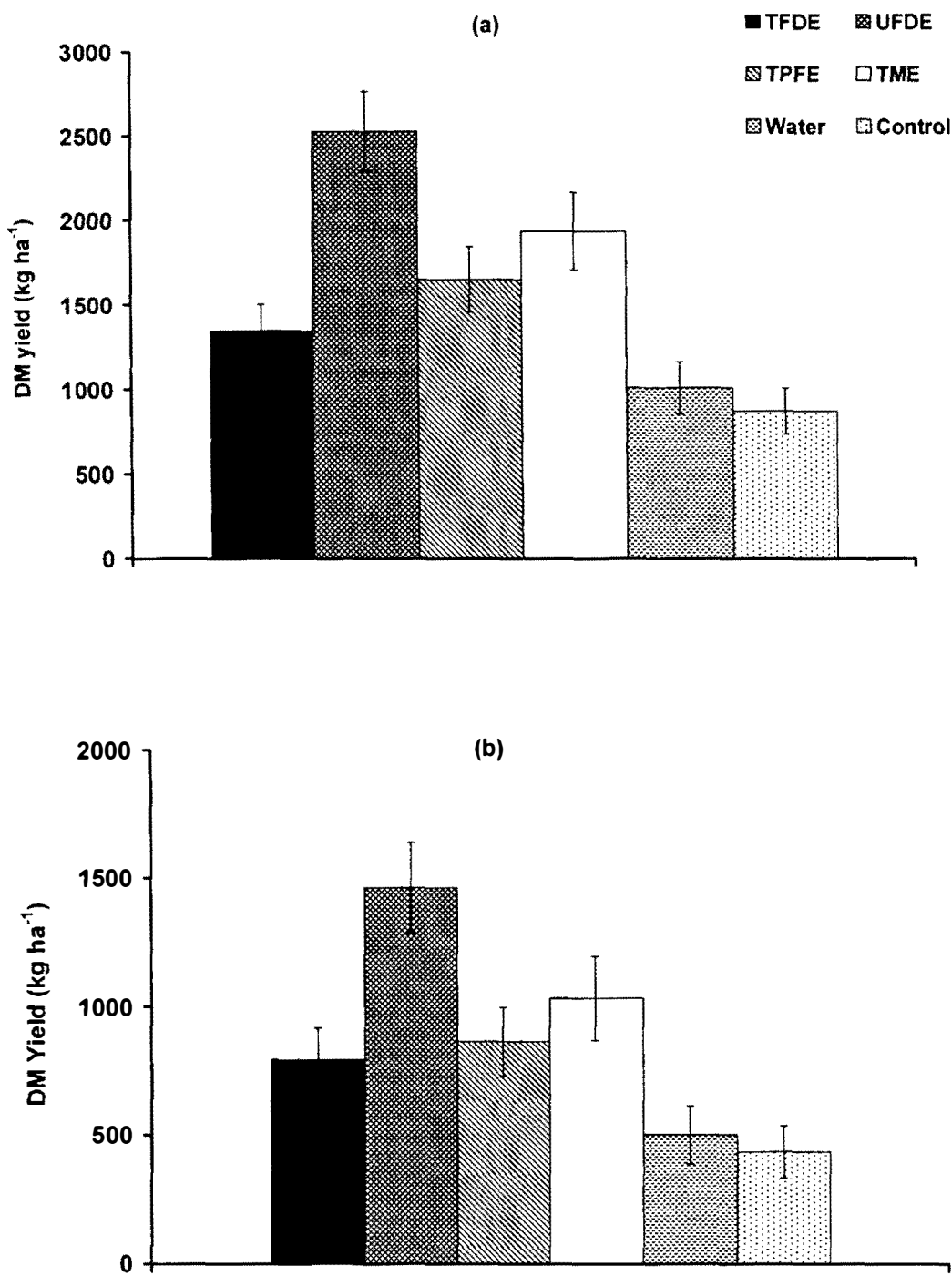
### 4.3.7 Dry matter yield and N uptake

The main herbage response was evident in the first 2 cuts for the autumn trial and for the first cut in the winter trial (Figure 4.9 a, b). The DM yield was affected by the application of the effluent, with the yields significantly higher than the water and control treatments, though the effect was found to decrease with the passage of time.

#### 4.3.7.1 Autumn application

During the autumn application, the effect of the effluent type was evident on both the total DM (TDM) as well as the DM response to the N added (DMR). Untreated farm dairy effluent achieved both the highest TDM and the DMR, being significantly higher than the rest of the effluent treatments (Table 4.5).

The TDM yield was observed to be at its highest for UFDE treatment (2531 kg ha<sup>-1</sup>) rather than for the other three effluents, namely TME (1936 kg ha<sup>-1</sup>), TPFE (1652 kg ha<sup>-1</sup>) and TFDE (1350 kg ha<sup>-1</sup>) which were at par among themselves (Figure 4.9a). The type of effluent has a significant effect on the N uptake, with UFDE plots achieving the highest recovery (73.9% of the applied N), followed by TME (68.2%), TFDE (43%) and TPFE (37.9%).



**Figure 4.9** Dry matter (DM) yield during the experiment period for (a) autumn application and (b) winter application. Each value represents a mean of four replicates with standard deviation shown by vertical bars



**Table 4.5** Total dry matter (DM) yield, percent of added N in DM and DM response to the added N in autumn and winter application

Treatments	Total DM (kg ha <sup>-1</sup> )	N added (kg ha <sup>-1</sup> )	N in DM (%)	DM response (kg DM kg <sup>-1</sup> N)
<b>Autumn application</b>				
TFDE	1350	21.87	2.71	15.5
UFDE	2531	61	3.88	24.9
TPFE	1652	27.50	2.70	23.3
TME	1936	39.50	3.44	23.4
Water	1011	-	1.91	-
Control	873	-	1.66	-
<b>Winter application</b>				
TFDE	792	13.02	2.41	22.4
UFDE	1461	49.33	3.68	19.5
TPFE	864	23.11	2.91	15.7
TME	1031	33.75	2.82	15.7
Water	501	-	1.56	-
Control	434	-	1.12	-

#### 4.3.7.2 Winter application

The effect of the effluent application on DM during the winter application was similar to that of the summer application (Figure 4.9 b). The effluent effect was evident in the TDM yield, with UFDE treatment still having the highest TDM among the effluents, though the trend of DMR values among the treatments for the winter application was slightly different from the autumn application. TFDE treatment had the highest DMR (22.4%). The DMR for TFDE and TME were similar and 3.75% less than the DMR of the UFDE (Table 4.5).

An increase in DM yield, due to the addition of effluent, has been reported in many studies (Misselbrook *et al.* 1998; Macoon *et al.* 2002; Luo *et al.* 2004). The yield response was higher than the 4.7 to 7.2 kg Dm kg<sup>-1</sup> N obtained by Bolan *et al.* (2004a) but more in range with the yield response obtained by other researchers (Crush *et al.* 1982; Ledgard *et al.* 1996).

## 4.4 General Discussion

The increase in N<sub>2</sub>O emission following effluent application observed in our study is consistent with other studies, examining the effect of land application of animal wastes on N<sub>2</sub>O emissions (Russell 1996; Lowrance *et al.* 1998; Barton & Schipper 2001). The increase in N<sub>2</sub>O emissions following effluent application varied, depending on the effluent type, as well as the season. In this section, the reasons for both the increase in N<sub>2</sub>O emission due to effluent irrigation and for the difference in N<sub>2</sub>O emission among the effluent types will be discussed. The increase in N<sub>2</sub>O emissions from the plots where only water was added shows that the emission was limited by the WFPS of the soil especially in the autumn season (Irrigation 1). The increase in N<sub>2</sub>O emission due to effluent irrigation could be attributed to several factors such as increase in WFPS, increased supply of C and N, and increase in microbial activity. The added effluents rapidly infiltrate the soil surface and become accessible for microbial community, reducing O<sub>2</sub> diffusion and providing a ready source of N and C for denitrification and/or coupled denitrification and nitrification to occur in the soil. The WFPS was very low in the beginning and increased with the addition of water and effluent leading to an increase in N<sub>2</sub>O emission. The increase in WFPS from 0.48 to about 0.69 for the autumn application and 0.69 to 0.83 for the winter application a few days following irrigation (Figure 4.3a and b), is within the range of values previously reported to favour N<sub>2</sub>O production by both nitrifiers and denitrifiers (Linn & Doran 1984).

During effluent irrigation the effluent displaces soil air and generates anoxic conditions (Russell 1996). The metabolism of effluent organic carbon by soil micro organisms will also reduce soil oxygen levels (Christensen 1985; Petersen 1999) and hence the oxygen diffusion rates (Table 4.4). The redox level in the soil provides optimum conditions required for the enhanced production of N<sub>2</sub>O. This was also true for the water treatment where ODR values were affected by the displacement of the soil air with water.

The carbon input by the effluent is another important factor in promoting N<sub>2</sub>O emissions from effluent irrigation. The DOC values for the effluents ranged from 15 to 59 mg l<sup>-1</sup> for autumn application and from 11 to 41 mg l<sup>-1</sup> for winter application. Sommer *et al.* (1996) suggest that the dissolved C compounds in liquid manure or slurries may be consumed within a few days after application.

The return to pre-application N<sub>2</sub>O emission rates within 2 weeks (Figure 4.2 a, b), of effluent application for autumn application and 3 weeks of effluent application of winter application, indicates that the immediate effect of effluent application on flux is short lived. Such short duration effects have been reported by Russell *et al.* (1991), Whalen (2000) and Barton & Schipper (2001). Although the addition of the N and C initially stimulated emission, moisture assumed a greater importance as the experiment progressed. The importance of moisture was clearly demonstrated during the autumn application when the baseline fluxes were increased by 3.4 to 6 fold after the rainfall events. A slight increase in emissions from the control plots clearly indicate that overall N<sub>2</sub>O production in this experiment was controlled by both N availability and soil moisture. An increase in the soil moisture level through effluent irrigation and rainfall achieved the dual task of bringing applied substrate into contact with the soil microbial biomass and reducing soil WFPS and consuming resident O<sub>2</sub>. Some of the N and C added by the effluent application might undergo immobilisation immediately after the addition and later slowly get converted into an available form (Whalen 2000).

Most of the N in the effluents was in ammonical form with an almost negligible amount of NO<sub>3</sub><sup>-</sup> (Table 4.2). Looking at the mineral data, it is evident that the NO<sub>3</sub><sup>-</sup> build-up starts a few days after the application of the effluent to the soil. Other studies have reported a lag period of a few days before NO<sub>3</sub><sup>-</sup> build-up starts in the effluent amended soils (Petersen 1992; Nielsen & Revsbech 1998). A 5 to 6 fold increase in soil NO<sub>3</sub><sup>-</sup> levels within a week of the addition of the treatments in this study, shows that the soil had a good population of the nitrifiers which converted the NH<sub>4</sub><sup>+</sup> to a NO<sub>3</sub><sup>-</sup> source quickly.

The rapid return of NH<sub>4</sub><sup>+</sup> to the background level and the steady decrease in NO<sub>3</sub><sup>-</sup> concentrations within a couple of weeks from plots amended with effluents, indicate that gaseous emission, immobilisation, plant uptake and nitrification had consumed most of the added N. A decrease in mineral N concentration by 45 to 71% of the added effluent N within 7 days of addition was observed during the autumn application and 54 to 81% of the added N within 10 days for winter application. The loss of N in our study is slow compared to the results reported by Sharpe & Harper (1997), who reported a 69% loss of N via NH<sub>3</sub> volatilisation alone within 24 hrs of the application of liquid swine waste application.

The N<sub>2</sub>O emission in our study was affected by the type of effluent as well. It was found that the highest emission was from TPFEE during the autumn application and

from ME during the winter application, though during both the applications, UFDE added more N and C to the soil. This could be because of the rapid mineralization of the NH<sub>4</sub><sup>+</sup> present in the TPFE and TME during the autumn and the winter applications respectively, as compared to UFDE. Piggery effluent has low mineralization potential because most of the total N is NH<sub>4</sub><sup>+</sup>, a form that is rapidly mineralised (Whalen 2000). Similarly, the anaerobic treatment of meat effluent destroys 70-90% of the organic matter (Russell & Cooper 1983) and hence most of the N is present in available form. On the other hand, UFDE has a larger proportion of organic than inorganic N, which undergoes gradual decomposition (Ellis *et al.* 1998b) and gets converted into inorganic N. This could also explain the higher percentage of added N emitted as N<sub>2</sub>O for TFDE as compared to UFDE, even though the amount of N added by the latter was 3.4 times higher than the former source. UFDE is high in organic carbon and the two pond treatment system achieves a high removal of carbon. For example, Bolan *et al.* (2004c) have noticed that by the time the effluent leaves the aerobic pond, 52% of the COD and 57% of the BOD is removed from the effluent. In FDE nitrogen is derived from both urine and dung with the majority of the nitrogen present in the dung is in a relatively immobile organic form (Di *et al.* 1998; Silva *et al.* 1999; Barkle *et al.* 2000; Longhurst *et al.* 2000). Therefore, with effluent application, while the readily mobile forms of nitrogen (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) may be rapidly leached, nitrified and or denitrified and taken up by the plants, the organic form (from the dung component of the effluent) starts to accumulate.

Also the differences in N<sub>2</sub>O emission among the effluents could be due to complete denitrification, resulting in N<sub>2</sub> emissions. Weier *et al.* (1993) showed that the addition of available C increased denitrification and also increased the ratio of the N<sub>2</sub>:N<sub>2</sub>O produced. The higher C concentration in UFDE therefore may have favoured the production of N<sub>2</sub> rather than N<sub>2</sub>O as the product of denitrification. It can be seen from the results that as the DOC concentration of the effluent increases, the percentage of the added N emitted as N<sub>2</sub>O decreases. This supports the hypothesis that the higher availability of DOC under UFDE treatment increased the microbial respiration, thereby, reducing the oxygen content of the soil atmosphere, and favouring the production of N<sub>2</sub> rather than N<sub>2</sub>O (Comfort *et al.* 1990).

The utilisation of the effluent N on grasslands, can vary depending upon the soil and climatic conditions and effluent type (Misselbrook *et al.* 1998). The added N recovered in DM was very high in UFDE treatment as compared to the rest of the

effluent treatments for both the autumn and the winter application. The higher DM response to UFDE treatment further suggests that there was a slow release of the organic N in the soil, thus enabling more of the N to be available to the plants for their uptake. Under the TPFE and TFDE treatment, as the N was present in a form readily available for denitrification, volatilisation or leaching, the recovery of N by plant uptake was low. Luo *et al.* (2004) also observed differences in plant uptake of the N between the primary and secondary treated meat processing effluents and attributed this to the difference in the form of N in these two effluents.

Correlation studies indicated that N<sub>2</sub>O emission was affected by a number of soil properties including mineral N, WFPS and DOC concentration (Table 4.6a, b). A highly significant positive correlation was found between N<sub>2</sub>O emission and the soil NH<sub>4</sub><sup>+</sup> concentration during the measurement period for both of the irrigations. A highly significant correlation was observed between WFPS and N<sub>2</sub>O flux during the autumn application event, while the relation was less significant during the winter application.

The possible reason could be that during the autumn application, the WFPS of the soil was low before the start of the experiment and was limiting microbial activity as well as denitrification. The addition of the liquid effluents led to optimum WFPS values for N<sub>2</sub>O production by both nitrification and denitrification. During the time of the winter application, the soil was considerably wet at the beginning of the experiment, so the high WFPS (0.80), along with an ample supply of N and C might have led to conditions conducive for complete denitrification to occur, leading to N<sub>2</sub> emission. Whalen (2000) found that WFPS was the best predictor of an N<sub>2</sub>O flux from soil irrigated with liquid swine effluent and the correlation of N<sub>2</sub>O with nutrient elements in the soil was low. He attributed this to the localised microbial activity present in the soil (Barton & Schipper 2001).

**Table 4.6**      **Correlation coefficients for relationships between N<sub>2</sub>O emission and soil properties for (a) autumn application (b) winter application. \*\*\*, \*\*, \* depicts level of significance at <0.001, <0.01 and <0.05, respectively. (N<sub>2</sub>O = kg N ha<sup>-1</sup>d<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and DOC = mg kg<sup>-1</sup> soil)**

<b>(a)</b>					
<b>Soil properties</b>	<b>N<sub>2</sub>O</b>	<b>WFPS</b>	<b>NO<sub>3</sub><sup>-</sup></b>	<b>NH<sub>4</sub><sup>+</sup></b>	<b>DOC</b>
N <sub>2</sub> O	1.00	0.71***	0.43***	0.84***	0.66***
WFPS		1.00	0.50	0.57***	0.46***
NO <sub>3</sub> <sup>-</sup>			1.00	0.51***	0.47***
NH <sub>4</sub> <sup>+</sup>				1.00	0.73***
DOC					1.00

<b>(b)</b>					
<b>Soil properties</b>	<b>N<sub>2</sub>O</b>	<b>WFPS</b>	<b>NO<sub>3</sub><sup>-</sup></b>	<b>NH<sub>4</sub><sup>+</sup></b>	<b>DOC</b>
N <sub>2</sub> O	1.00	0.42*	0.04	0.66***	0.37**
WFPS		1.00	0.75***	0.76***	0.60***
NO <sub>3</sub> <sup>-</sup>			1.00	0.50***	0.58***
NH <sub>4</sub> <sup>+</sup>				1.00	0.75***
DOC					1.00

The forward stepwise regression equation (Table 4.7) shows that though the mentioned soil properties were significant variables in explaining the N<sub>2</sub>O emission during the autumn application, only soil mineral-N concentration and WFPS were significant variables for the winter application with 78% and 56% of the variability being explained for the respective applications.

**Table 4.7**     **Results of the multiple linear regression analysis relating N<sub>2</sub>O emission and various soil properties (N<sub>2</sub>O = kg N ha<sup>-1</sup>d<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and DOC = mg kg<sup>-1</sup> soil)**

Treatment	Regression Equation	R <sup>2</sup>
1 <sup>st</sup> application	N <sub>2</sub> O = -0.011 + 0.001 NH <sub>4</sub> <sup>+</sup> + 0.024 WFPS - 0.0002 NO <sub>3</sub> <sup>-</sup> + 0.0002 DOC	0.78
2 <sup>nd</sup> application	N <sub>2</sub> O = -0.007 + 0.001 NH <sub>4</sub> <sup>+</sup> - 0.001 NO <sub>3</sub> <sup>-</sup> + 0.019 WFPS	0.56

## 4.5     Conclusions

- ❖ Application of all the effluents greatly enhanced N<sub>2</sub>O emissions more than the water and control treatments.
- ❖ N<sub>2</sub>O emission was affected by the type of the effluent with treated piggery farm effluent emitting the highest during autumn application and treated meat effluent emitting the highest during winter application. The difference in the N<sub>2</sub>O emission among the effluents may be attributed to the difference in their C: N ratio.
- ❖ A strong and positive correlation was observed between the N<sub>2</sub>O emission and the soil properties after the effluent irrigation.
- ❖ Regression equations were able to explain 78% and 56% of the variability in the N<sub>2</sub>O emission from the autumn and the winter applications, respectively.
- ❖ The untreated dairy effluent had the highest amount of N and C as compared to the rest of the effluents and this might have led to the production of more N<sub>2</sub> than N<sub>2</sub>O.

## Chapter 5

# Effect of rate of farm dairy effluent irrigation on nitrous oxide emission

### 5.1 Introduction

In New Zealand, the land treatment system is the preferred method for treating effluent effectively. The land treatment system is culturally acceptable, enables recycling of nutrients and water resources for sustained production, and meets the regional councils' objectives in minimising point sources of ground water and surface water pollution (Selvarajah 1996). The objective of land-based effluent application is to utilise the chemical, physical and biological properties of the soil/plant system to assimilate the waste components without adversely affecting soil quality or releasing potential contaminants to water bodies or the environment (Hawke & Summers 2003).

In recent years, the management of N to prevent ground and surface water contamination has been a key issue and a lot of research has been focussed at preventing N ending up in the water bodies through leaching (Di *et al.* 1999; Cameron & Di 2004; Di & Cameron 2004; Williams *et al.* 2005). Although intensive research has been done on the soil and the fertiliser N interaction, less information is available on environmentally sustainable N loading rates for effluent application onto land (Selvarajah 1996). Few research studies have examined in detail the complex and dynamic nature of transformations and the fate of effluent N in New Zealand pasture soils. Loading rates can be expected to vary with the type of effluent, soil type and the climatic conditions prevalent at the place of application. Regional councils across New Zealand have appeared to set maximum loading rates for effluent application based on parameters derived from studying urea application to dairy pastures (Ledgard *et al.* 1998) and they fail to take into account the heterogeneous nature of the soil in different regions (Silva *et al.* 1999).



Recommendations for effluent application are based on minimising contamination of ground water with nitrate they are not based on the level of N<sub>2</sub>O emission from the soil. The loading rates recommended might in fact cause increased N<sub>2</sub>O emission from the soil.

It is clear from Chapter 4 of the thesis that land application of farm effluents led to N<sub>2</sub>O emission. N<sub>2</sub>O emission was affected by the quality of the effluent (C: N ratio of the effluent, amount of inorganic N and total solids in the effluent). Of the different effluents produced on farms in New Zealand, treated farm dairy effluent (TFDE) is the most abundantly produced effluent.

The present study was therefore undertaken to study the loss of N from the soil by N<sub>2</sub>O emission, as affected by different N loading rates through TFDE application. The change in the soil properties (WFPS, ODR, mineral N and DOC concentration) as affected by the different rates, as well as the effect on the DM yield of the pasture in relation to the N<sub>2</sub>O emission, were also studied. The specific objectives of the study were:

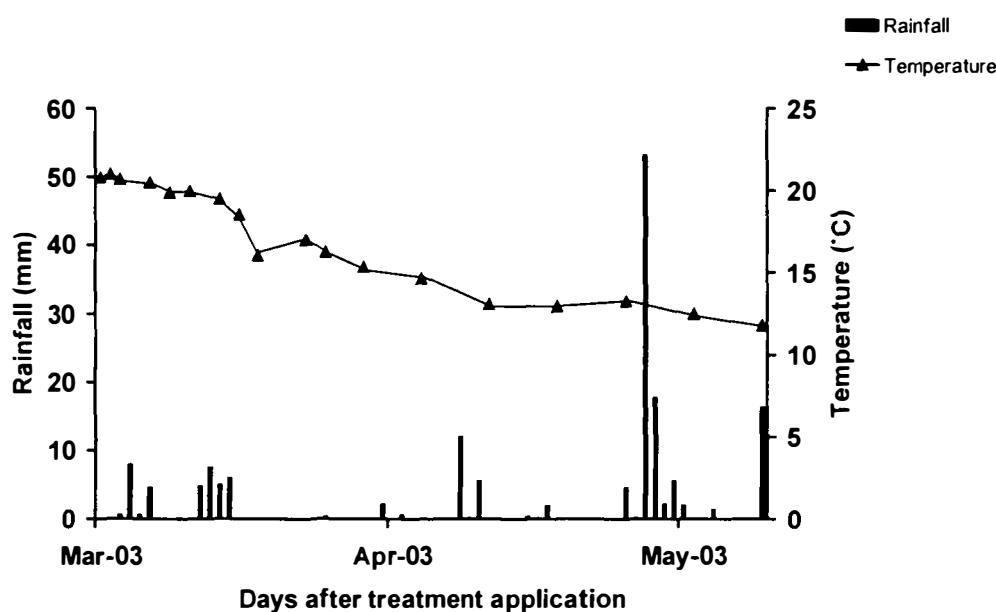
- To study the effect of different effluent loading rates on the N<sub>2</sub>O emission.
- To examine the effect of different effluent loading rates as measured by various soil physical properties on N<sub>2</sub>O emission.
- To examine the changes in soil mineral N under different TFDE loading rates and to further study the effect of the transformation on N<sub>2</sub>O emission.
- To examine the effect of different TFDE loadings on soil chemical properties and to establish predictive regression relationships between soil properties as affected by effluent loading and N<sub>2</sub>O emission.

## 5.2 Material and Methods

The effect of different loading rates of TFDE on the N<sub>2</sub>O emissions during autumn season was examined under field conditions. The field-plot experiment was conducted during 26<sup>th</sup> March – 2<sup>nd</sup> June, 2003 (10 weeks) on sheep-grazed permanent legume-based pasture at Massey University's Frewens Research Block. The soil characteristics have been explained in detail in Chapter 3 (Table 3.1).

A total rainfall of 164.4 mm was recorded during the 10 week measurement period. The rainfall was not evenly distributed with 75% of the total rainfall being received during the second half of the measurement period. Overall, the rainfall during the experimental period was below normal compared to the 30 years average. The 30 year (1971-2000) mean rainfall during the months of April and May was 76 and 94 mm, respectively. The rainfall obtained during these months in the year of the experiment was 26.8 and 107.4 mm for the months of April and May respectively.

The mean average air temperatures were found to decrease as the measurement period progressed and ranged between 11.1 and 18.5°C against a 30 year average range of 11.2 to 16.5°C. The soil temperatures were in the range of 11.4 to 22.5°C (average of 17.2°C) during the experiment. The rainfall and temperature distribution for the experiment period are shown in Figure 5.1.



**Figure 5.1** Average rainfall and soil temperature (0-5 cm) distribution during the entire experimental period at the experimental plots on Manawatu sandy loam soil

### 5.2.1 Experimental design

An experiment was conducted at the site used in the Chapter 4 experiments and followed the same procedures for establishing the plots as outlined in section 4.2.1 of Chapter 4. The experiment comprised of a total of six treatments. This included four

different effluent loading rates, a water treatment applied at the rate of the highest effluent loading rate and a control treatment where no water was added. The different hydraulic loading rates used were 25mm, 50mm, 75mm and 100mm. These effluent loadings led to N loadings of 20, 40, 61 and 81 kg N ha<sup>-1</sup>, respectively (Table 5.1). Water was applied at the rate of 100mm. These treatments will from now on be referred to as T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub> and T<sub>4</sub> (for the four effluent loadings), water treatment as T<sub>5</sub> and control as T<sub>6</sub>. Each of these treatments was applied to a 2m<sup>2</sup> (2m x 1m) area plot with a 0.5 m wide buffer strip around each plot. The plots were lined with a 7.5cm deep polythene sheet to restrict the surface flow of the applied treatment. Each treatment was replicated four times in a randomised block design.

**Table 5.1      Irrigation depth applied and the hydraulic, N and C loading rates for the various treatments**

Treatment	Irrigation depth (mm)	Volume (m <sup>3</sup> ha <sup>-1</sup> )	N Loading (kg N ha <sup>-1</sup> )	C Loading (kg C ha <sup>-1</sup> )
T1	25	250	20.14	122
T2	50	500	40.27	245
T3	75	750	60.54	367
T4	100	1000	80.56	490
T5 (Water)	100	1000	-	-
T6 (Control)	-	-	-	-

The grass in all the plots was mowed to a height of 1cm just before applying the treatments. The TFDE was collected from the Dairy No. 4 effluent pond of Massey University and stored at 4°C prior to application the next day. The characteristics of the effluent are presented in Table 5.2. Treatments were applied evenly to each plot using a watering can with a rosette attachment. At the higher loading rates the TFDE was applied over a period of 4 hours to allow effective infiltration of the effluent and avoid any runoff.

5.2.2 Nitrous oxide measurement

The N<sub>2</sub>O fluxes were measured for the experiment during the period of the 26<sup>th</sup> March – 2<sup>nd</sup> June, 2003 using the closed chamber technique (Saggar *et al.* 2002). The method has been described in detail in Chapter 3 of the thesis. During the first week, N<sub>2</sub>O emission measurements were made daily, followed by measurements on alternate days for 3 weeks and then once a week for rest of the experimental period as the fluxes decreased, approaching the background levels.

Table 5.2 Characteristics of the farm dairy effluent (TFDE) applied

Properties	Values
Total suspended solids (mg l <sup>-1</sup> )	253.4
pH	7.8
Total N (mg l <sup>-1</sup> )	80.6
NH <sub>4</sub> <sup>+</sup> -N (mg l <sup>-1</sup> )	41.6
NO <sub>3</sub> <sup>-</sup> -N (mg l <sup>-1</sup> )	0.07
Total Carbon (mg l <sup>-1</sup> )	757
Dissolved organic carbon (DOC) (mg l <sup>-1</sup> )	12.5
C:N ratio	9.4
Chemical oxygen demand (mg l <sup>-1</sup> )	95
Biochemical oxygen demand (mg l <sup>-1</sup> )	82
Total P (mg l <sup>-1</sup> )	19
Total K (mg l <sup>-1</sup> )	153

5.2.3 Analysis

5.2.3.1 Effluent analysis

Samples of effluent were analysed for suspended solids, pH, total N, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, total carbon, dissolved organic carbon, chemical oxygen demand, biological oxygen demand and total phosphorus and potassium by the procedures published in the standard methods (APHA 1998).

### 5.2.3.2 Soil analysis

Four soil samples were collected randomly on all days of the N<sub>2</sub>O measurement from each site from 0-5 cm to determine soil water content by the method described in detail in Chapter 3.

Soil samples to determine the mineral N (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) and dissolved organic carbon (DOC) content for all the treatments were collected on all the days of N<sub>2</sub>O measurement from a 0-5 cm depth from the plot outside the chamber area where treatments were applied. The methods used for analysis have been described in Chapter 3.

### 5.2.3.3 Herbage analysis

The effect of different effluent loading rates on herbage accumulation was recorded. The wet weight of herbage was recorded and determined for dry matter (DM) yield. The total N of the plant samples, dry matter response and the added N recovered for the increasing effluent application rate was determined by the formula described in Chapter 4

## 5.2.4 Oxygen diffusion rate

Oxygen diffusion rate measurements were made on the 1<sup>st</sup>, 14<sup>th</sup>, 28<sup>th</sup> and 69<sup>th</sup> day to look into the difference in the diffusion rate between the irrigated and control treatments by the method described in Chapter 3.

## 5.2.5 Statistical methods

An analysis of variance was carried out using the SAS for Windows v8 software package. Least significant differences (LSD) were calculated to estimate the differences between the treatments. The 5% confidence level is regarded as statistically significant.

Regression and correlation analysis between various soil properties and N<sub>2</sub>O emission was conducted using the SAS package.

## 5.3 Results and Discussion

### 5.3.1 Properties of the effluent

The characteristics of the effluent applied during the irrigation are summarised in Table 5.2. The effluent pH was 7.8, which is similar to the values reported in the literature (Cameron *et al.* 1995; Di *et al.* 1998; Hawke & Summers 2003; Luo *et al.* 2004; Wang *et al.* 2004). 52% of the N in the effluent was in NH<sub>4</sub><sup>+</sup> form with the concentration of NO<sub>3</sub><sup>-</sup> being almost negligible. The effluent was high in C concentration.. The effluent characteristics were within the ranges of that reported in the section 4.3.1 of Chapter 4 of the thesis.

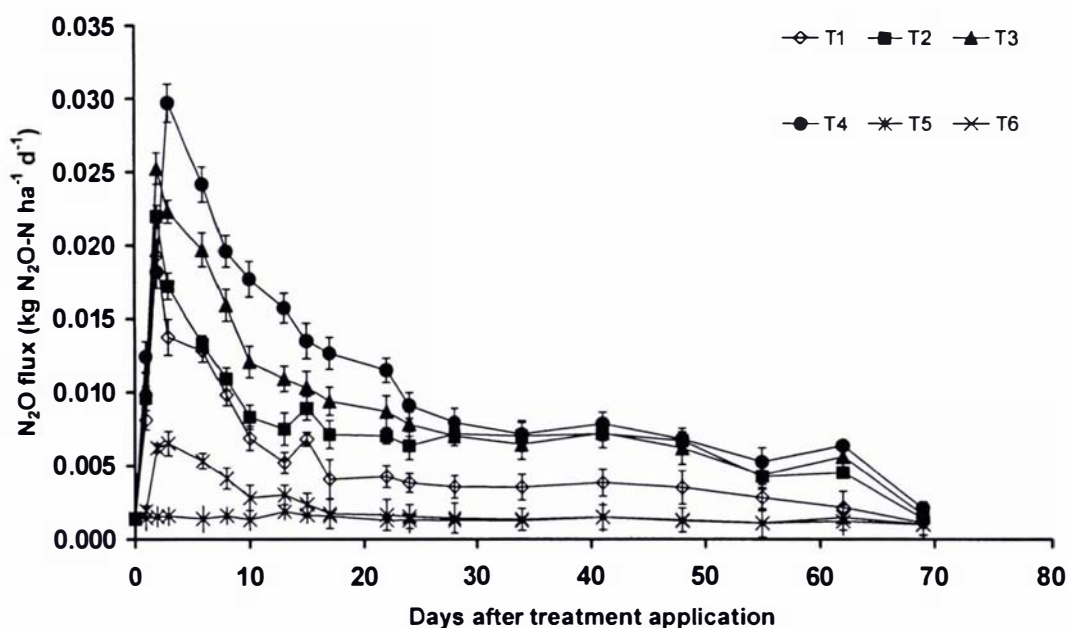
### 5.3.2 Nitrous oxide emission

The nitrous oxide emission varied with the rate of TFDE application (Figure 5.2). The addition of both water and effluent caused an increase in emissions over the control treatment. The general pattern in the emission was the same as that observed in Chapter 4 i.e. there was an immediate increase following TFDE and water application and then a progressive decrease.

Peak emissions observed within 24 to 48 hours of the application of both the effluent and water were 0.019, 0.022, 0.025, 0.030 and 0.0065 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> from T1, T2, T3, T4 and T5, respectively. The emission subsequently started to decrease for all the treatments. No change was observed in the emission from the control treatment and the emission from this plot showed little fluctuation with time. In the case of the control treatment, the emission ranged from 0.0010 to 0.0019 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> during the entire period.

The emission increased with the increasing TFDE application rate. The highest peak emission was obtained from the plots getting the highest effluent application (T4), which was 17.9% higher than the next highest treatment (T3). The daily N<sub>2</sub>O flux from the T4 treatment was significantly higher than the rest of the treatments for 22 days following treatment application, after which the flux from the T3 treatment was not significantly different from that of the T4. The daily emission from the T1 treatment was significantly different from the other effluent treatments for most of the

measurement period. The water treatment maintained a higher emission than the control treatment until day 10, after which the emissions were similar from the two treatments.



**Figure 5.2** N<sub>2</sub>O fluxes (kg N<sub>2</sub>O-N ha<sup>-1</sup>d<sup>-1</sup>) for all the effluent loading rates (T1-T4), water (T5) and control (T6) treatments at the experimental plots on Manawatu sandy loam soil. Each value represents a mean of four replicates with standard deviation shown by vertical bars. Day 0 represents a day before the application of the water and effluent

Cumulative emissions from the TFDE application were 2.4, 3.7, 4.3 and 5.1 times higher than that from the water irrigated plot and 3.6, 5.4, 6.3 and 7.6 times higher than the control plot. However, the proportion of the added N emitted decreased with the increasing rate of application, with 1.2, 1, 0.8 and 0.8% of the total N added through effluent being emitted as N<sub>2</sub>O for T1, T2, T3 and T4 treatments, respectively (Table 5.3). Almost 25% of the total emission had been recorded within a week after effluent and water application. In the case of the control treatment only 11.4% of the total had been emitted during that period.

A slight increase in the emission from all the treatments was observed in the 41<sup>st</sup> and 62<sup>nd</sup> days after the irrigation application, which coincided with the rainfall events (Figure 5.2). The total N<sub>2</sub>O emission measured from T1 was similar to the autumn application of TFDE discussed in Chapter 4. The total N<sub>2</sub>O emission from the T1

treatment (0.338 kg N<sub>2</sub>O-N ha<sup>-1</sup>) of this experiment was 11.5% lower than that observed in the TFDE treatment (0.382 kg N<sub>2</sub>O-N ha<sup>-1</sup>).

**Table 5.3**      **Total N<sub>2</sub>O emitted (kg N ha<sup>-1</sup>) over the measurement period from different effluent loading rates (T1-T4), water (T5) and control (T6) treatments at the experimental plots on Manawatu sandy loam**

Treatments	N added through effluent (kg N ha <sup>-1</sup> )	N emitted (kg N <sub>2</sub> O-N ha <sup>-1</sup> )	Emission factor (%)
T1	20.14	0.338	1.2
T2	40.27	0.476	0.96
T3	60.54	0.574	0.80
T4	80.56	0.691	0.75
T5 (Water)	-	0.135	-
T6 (Control)	-	0.091	-
LSD (0.05) n=24		0.033	

**5.3.3      Oxygen diffusion rate**

ODR values were affected by the hydraulic loading rate of TFDE. The ODR values reduced immediately after the TFDE and water application (Table 5.4). The reduction in ODR values was 14, 25, 39, 54.7 and 53.1% for the T1, T2, T3, T4 and T5, respectively. By day 28 differences in the ODR values among various treatments was reduced with only T3 and T4 treatments having statistically lower ODR than the control treatment. The water application (T5) treatment showed a faster recovery in the ODR value than the similar hydraulic loading with TFDE (T4). These differences in the rate of recovery of ODR between water and TFDE (at the same level of hydraulic loading) may be attributed to the creation of anaerobic conditions because of increased microbial activity, due to the effluent addition and subsequent lowering of the redox potential of the soil (Monaghan & Barraclough 1993).The soils had completely recovered by the end of the experiment with no difference in ODR observed among the treatments.

Among the different TFDE loading rates T4 registered the lowest ODR value, followed by the T3, T2 and T1. Immediately following application oxygen diffusion



rates were similar in the T4 and T5 treatments, (equal volumes of effluent and water) but temporary significant difference occurred at day 14 and 28 (Table 5.4).

The results fall in line with those observed in Chapter 4, where decreased diffusion rates were observed after the application of the effluents.

**Table 5.4     Soil ODR values ( $\mu\text{g cm}^{-2} \text{ min}^{-1}$ ) for all the effluent loading rates (T1-T4), water (T5) and control (T6) treatments at 4 measuring dates at the experimental plots on Manawatu sandy loam**

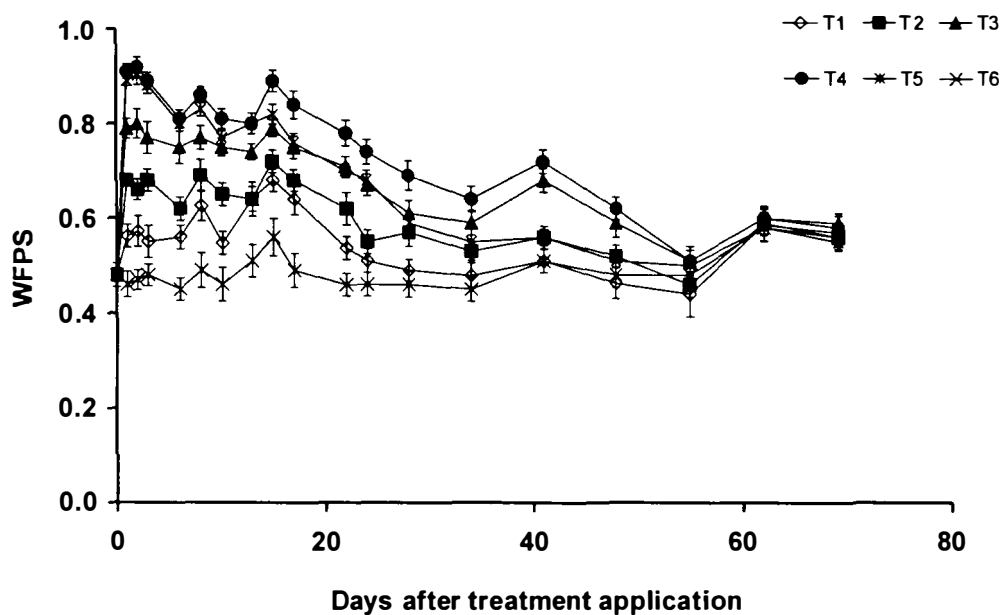
Treatments	ODR ( $\mu\text{g cm}^{-2} \text{ min}^{-1}$ )			
	Day 1	Day 14	Day 28	Day 69
T1	0.55	0.61	0.64	0.64
T2	0.48	0.59	0.62	0.64
T3	0.39	0.48	0.53	0.63
T4	0.29	0.37	0.48	0.63
T5 (Water)	0.30	0.49	0.62	0.64
T6 (Control)	0.64	0.67	0.67	0.64
LCD (0.01%)	0.04	0.05	0.04	0.06

**5.3.4        Water filled pore space**

Dry conditions prevailed at the beginning of the experiment with WFPS being 20% lower than the field capacity value (0.60). The conditions continued to be the same for a month after the application of the treatments with only 40.06 mm of rainfall being received during this period. The WFPS of the control treatment remained below the FC during this time of measurement.

Because of the dry conditions, an immediate response in the WFPS was observed with the addition of the water and effluent (Figure 5.3). Among the treatments the WFPS varied with the hydraulic loading rates; increasing with the increasing rate of effluent application. The percent increase in WFPS over the control treatment was 14.6, 29.4, 39.2 and 47.3% for T1, T2, T3 and T4, respectively and 46.1% for the T5 treatment. No significant difference was observed between the T4 and T5 treatments as the hydraulic loading was same for both the treatments.

The WFPS decreased with time for all the treatments with slight fluctuations observed coinciding with the rainfall events. The rate of decrease was more for the water treatment than the effluent treatments. It was observed that the WFPS had reduced by 33.7 and 24.2% for T5 and T4 treatments respectively, four weeks after the addition of the treatments. No difference in the treatments was observed by the end of the 8<sup>th</sup> week. Lowrance & Hubbard (2001) found consistently high WFPS compared to the control with the application of the swine effluent at the two effluent loading rates, though they did not observe any significant difference in the WFPS between the two rates, even though the second treatment had double the amount of the effluent applied as compared to the first treatment.



**Figure 5.3** WFPS distributions (0-5 cm) for all the effluent loading rates (T1-T4), water (T5) and control (T6) treatments at the experimental plots on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars. Day 0 represents a day before the TFDE was applied

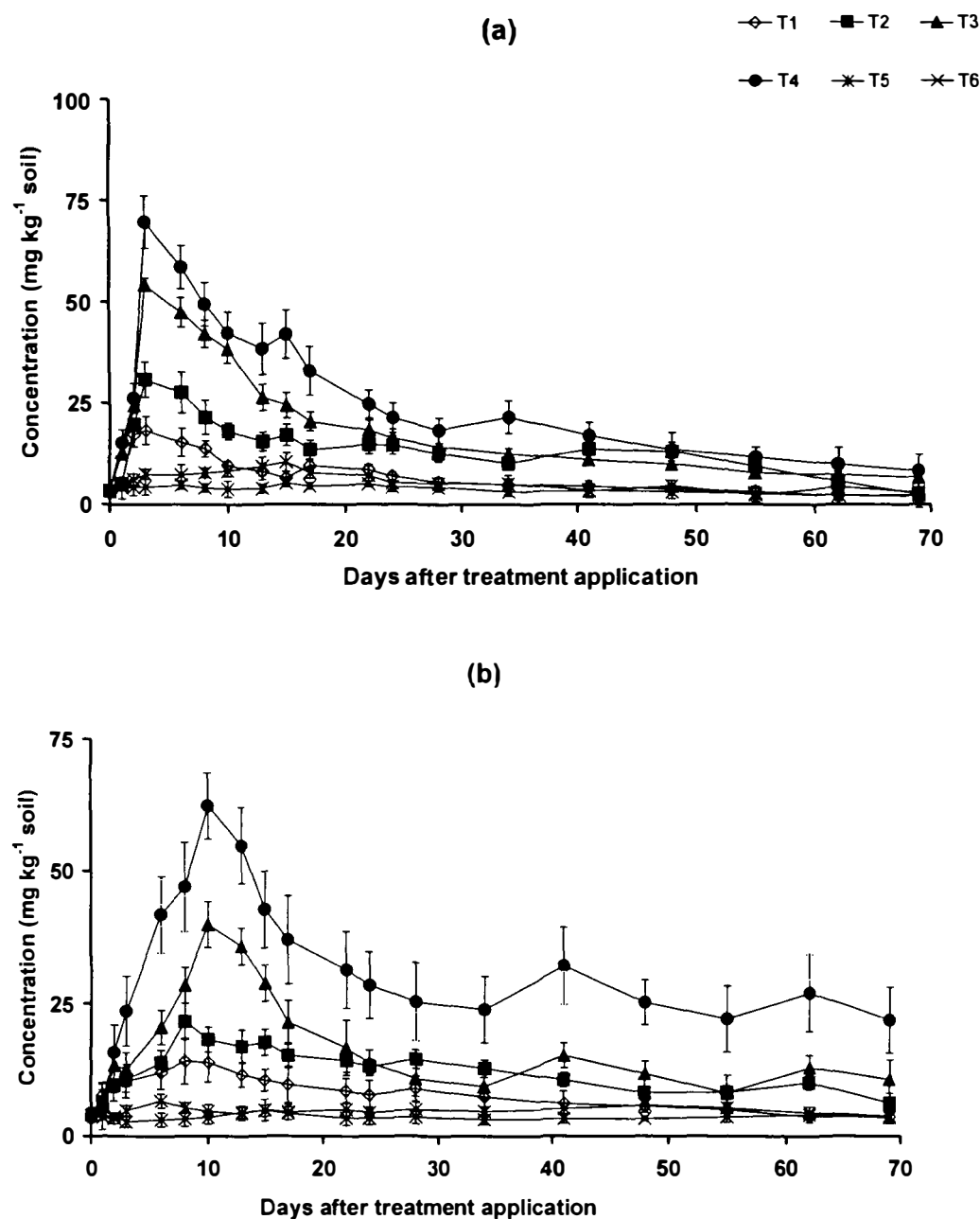
### 5.3.5 N transformation in soil

An increase in soil mineral N ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) concentrations was observed immediately after the application of the TFDE and water, whereas no change was observed in the control treatment. The general pattern of increase in the concentration

was found to differ between the NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions in the soil. The trends in the changes in the NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentrations in the soil with the addition of the TFDE are shown in Figure 5.4a and b. The general trend appears to be the same for all the four TFDE rates. Ammonium ion concentration was found to increase rapidly after the application of the effluent and then decreased progressively with time. Nitrate concentration on the other hand showed an initial lag period before peaking.

The highest NH<sub>4</sub><sup>+</sup> concentrations of 18.3, 30.9, 54.3 and 69.8 mg kg<sup>-1</sup> soil were reached within 3 days of the TFDE application for T1, T2, T3 and T4, respectively. The concentration then decreased to a minimum of 2, 2.6, 6.6 and 8.2 mg kg<sup>-1</sup> soil, which was obtained on the last day of the measurement period. An increase in NH<sub>4</sub><sup>+</sup> concentration was also observed after the application of water but there was a lag period of 15 days before the peak concentration of 10.4 mg kg<sup>-1</sup> soil was obtained. The concentration then decreased with time. Slight increases in NH<sub>4</sub><sup>+</sup> concentrations were observed for all the treatments on day 15 where water and effluent was added and on day 41 for T2, T3 and T4 which coincided with the rainfall events.

The NO<sub>3</sub><sup>-</sup> concentrations peaked on the 8<sup>th</sup> day after the TFDE application with concentrations reaching 14.1, 21.6, 39.9 and 62.3 mg kg<sup>-1</sup> soil for T1, T2, T3 and T4 treatments, respectively. The NO<sub>3</sub><sup>-</sup> concentrations in the water treatment were found to range between 3.8 to 6.7 mg kg<sup>-1</sup> soil with the peak concentrations measured 6 days after the treatment application. The range of NO<sub>3</sub><sup>-</sup> concentration for the control treatment was 3.5 to 4.8 mg kg<sup>-1</sup> soil and was not significantly different from the water treatment. The application of TFDE at different rates in T1, T2, T3 and T4 caused the NO<sub>3</sub><sup>-</sup> concentration in the soil to increase by 4.6, 7, 12.9 and 20 times compared to the control. This increase was 2 times in case of water treatment. A lag period of 8-10 days was observed for all the TFDE treatments between the application and the occurrence of peak concentrations in the soil. Among the effluent rates, the highest NO<sub>3</sub><sup>-</sup> concentration was observed in the T4 treatment reaching 5.5, 3.1 and 2.4 times that of the T1, T2 and T3 treatments, respectively. The nitrate concentrations in the soil for the four effluent treatments were 70-90% of the NH<sub>4</sub><sup>+</sup> concentration measured in those respective treatments.



**Figure 5.4** Distribution of (a) NH<sub>4</sub><sup>+</sup> (b) NO<sub>3</sub><sup>-</sup> concentration (mg kg<sup>-1</sup> soil) for all the effluent loading rates (T1-T4), water (T5) and control (T6) treatments at the experimental plots on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars. Day 0 represents a day before the application of TFDE

Studying the net rate of change of the ammonium and the nitrate concentrations in the soil after the application of the TFDE, it was observed that the rate of change of NO<sub>3</sub><sup>-</sup> was faster as compared to that of the NH<sub>4</sub><sup>+</sup> in all but T1 treatment. The rate of

change of both NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> was found to increase with the increasing rate of effluent application, with the highest rates of 7.7 and 4.6 mg kg<sup>-1</sup> soil d<sup>-1</sup> for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentration being observed for the highest level of TFDE application (T4).

### 5.3.6 Dissolved organic carbon

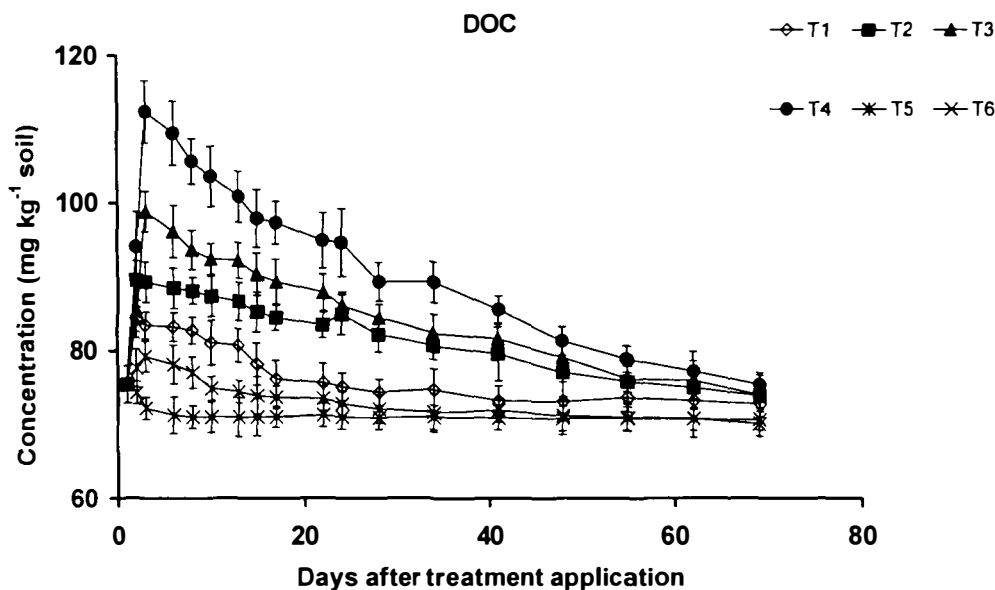
An increase on the DOC concentration of the soil occurred in all the treatments except the control treatment, after the addition of the treatment. This was anticipated as the addition of TFDE is known to add carbon to the soil. The amount of increase in the concentrations was different for different treatments. The concentration under the control treatment was stable with the concentrations ranging from 70.65 to 75.43 mg kg<sup>-1</sup> soil.

The pattern of increase in the DOC levels immediately after the treatment application is shown in Figure 5.5. The increase in the DOC concentration was observed with the increasing rate of the FDE application. The addition of FDE to the soil caused an initial rise in the levels of soil DOC within a day of the application and then this gradually decreased with time. Though the general trend was the same for all the four FDE rates, differences in the concentration levels could be observed among the treatments.

After the application of the effluent, DOC levels were found to peak within a day to the concentrations of 83.41, 89.54, 98.81 and 112.37 mg kg<sup>-1</sup> soil in the T1, T2, T3 and T4, respectively which were 10.6, 18.7, 31.0 and 49% higher than the concentration observed in the control treatment. A slight increase in the DOC concentration was also observed in the water treatment where the DOC increased from 75.43 to 79.21 mg kg<sup>-1</sup> soil a day after the addition of water. The effect of water treatment was found only for the first 10 days with no significant difference in the DOC concentrations between the water and the control treatment observed after that.

Immediately after the effluent applications, DOC concentration was higher for the highest rate of FDE application (Figure 5.5). The DOC concentration in the T4 treated soil was 34.7, 25.5 and 13.7% higher than the concentrations found under T1, T2 and T3 treatments, respectively. Concentrations in the T4 treated soil remained significantly different from the rest of the effluent treatments until day 41, after which no treatment effect was observed. T3 maintained the second highest DOC concentration in the soil followed by T2 and then T1. T1 treatment, which had the lowest hydraulic

loading rates, maintained a higher DOC concentration from water for only 13 days after the treatment application.



**Figure 5.5** Distribution of DOC concentration (mg kg<sup>-1</sup> soil d<sup>-1</sup>) for all the effluent loading rates (T1-T4), water (T5) and control (T6) treatments at the experimental plots on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars. Day 0 represents a day before the TFDE was applied.

### 5.3.7 Dry matter yield and N uptake

The effect of effluent loading on the DM yield was evident with the yields for the effluent treatments significantly higher than the water and the control (Table 5.5). The pasture DM yield increased with the increasing rate of effluent application.

The effluent loading rate affected both the total DM and the dry matter response (DMR, kg DM kg<sup>-1</sup>N) with T4 treatment having significantly higher total DM yield than the rest of the treatments (Table 5.5). No definite pattern of increase in DMR was observed with the effluent application rate. The DMR was found to decrease for T2 treatment and then increase again for the T3 and T4 treatments. The T4 plots a

significantly higher response to the added N than the rest of the treatments. The DMR ranged from 11 to 13 for all the effluent treatments (Table 5.5).

The effluent rate had a significant effect on the percent of N added recovered, it increasing with the increasing rate of effluent application. The T4 plots had a higher recovery of N in the DM than the T1, T2 and T3 treatment by 16.6, 18.5 and 8.5%, respectively. Overall the percent N recovered varied from 27 to 50% among the four rates of added effluent.

**Table 5.5** Total DM yield, percent of added N in DM and DM response of the added N at the experimental plots on Manawatu sandy loam. The values in the bracket represent the standard error of mean of the four replicates

Treatment	N added (kg ha <sup>-1</sup> )	Total DM (kg ha <sup>-1</sup> )	N in DM (%)	Added N recovered (%)	DM response (kg DM kg <sup>-1</sup> N)
T1	20.14	610 (±74)	1.51	29.5	12.56
T2	40.27	822 (±102)	1.75	27.6	11.55
T3	60.54	1084 (±120)	2.40	37.6	12.01
T4	80.56	1421 (±183)	2.84	46.1	13.21
T5 (Water)	-	506 (±137)	1.01	-	-
T6 (Control)	-	357 (±66)	0.92	-	-

The increase in the DM yield with the increasing rate of the effluent application could be attributed to the addition of both water and the nutrients through effluent irrigation. However, at a similar hydraulic loading, the DM yield was higher in the effluent treatment (T4) than the water treatment (T5). Bolan *et al.* (2004a) observed an increases in pasture DM yield with the increasing rate of dairy farm effluent, when the effluent was added at 0, 150 and 200 kg N ha<sup>-1</sup>. They found the dry matter yield response to applied N ranged from 4.1 to 7.2 kg DM Kg<sup>-1</sup> N applied, increasing with the increasing level of effluent irrigation, The degree of response is expected to be largely influenced by factors such as the application time (season), soil fertility, and climatic conditions (Ball & Field 1982; Lowe 1993).

## 5.4 General Discussion

Treated farm dairy effluent application at four hydraulic loading rates (25mm, 50mm, 75mm and 100mm) which led to (20.1, 40.3, 60.5 and 80.6 kg N ha<sup>-1</sup>) different N addition to the pasture soil caused short term changes in the soil's physical and chemical properties and N<sub>2</sub>O emission.

As is evident from the results, ODR and the WFPS were both significantly affected by the increasing TFDE application rates. The soil was low in water content with an average WFPS of 0.48 before the TFDE application. The WFPS was significantly different among the four effluent application rates. The water treatment showed a similar rise in the WFPS to the T4 treatment as both had an equal volume of water applied to the plots. But, T4 treatment maintained a higher WFPS as compared to the water treatment for a longer period after effluent application. As organic matter increases the water holding capacity of the soil (Papendick & Campbell 1981), thus the application of animal slurry to soil may create zones with high water content and consequently high O<sub>2</sub> demand (Comfort *et al.* 1988; Petersen 1992).

As the diffusion rate of gases is affected by the WFPS of the soil, the effect of different application rates on the ODR values in the soil were evident in this study. The lowest ODR rates were found in the T4 and T5 treatments, because the high amount of effluent/water added to the soil led to the displacement of the O<sub>2</sub> from the soil pores thereby causing increased anaerobic conditions. With the passage of time, the recovery in the ODR was faster in the water irrigated plots than in the TFDE irrigated plots. It is likely that some suspended organic matter in the TFDe was responsible for micropore blockage (Hawke & Summers 2003). In addition, during effluent irrigation, the effluent displaces soil air and generates anoxic conditions (Russell 1996), leading to decreased ODR values, and finally decomposition of effluent-borne organic matter reduces the O<sub>2</sub> concentration throughout the soil profile. The results as explained in section 4.3.2 of Chapter 4 are an increase anaerobic soil microsites and greater denitrification and N<sub>2</sub>O emissions. Higher emissions from T4 treatment than from T1 treatment result from a greater degree of anaerobic conditions under the former treatment than the latter.

Effluent application to land is known to add large quantities of plant nutrients, especially N (Cameron *et al.* 1997). In the present study, the build up in mineral N immediately after the TFDE application, is seen for all rates of effluent application. The majority of N in the effluent is NH<sub>4</sub><sup>+</sup> with very little N present as NO<sub>3</sub><sup>-</sup> (Table 5.2).



Hence, there is an increase in the  $\text{NH}_4^+$  in the soil immediately after the addition of the TFDE, but this only accounted for 12 - 26% of the effluent  $\text{NH}_4^+$  applied as TFDE. The unrecovered inorganic N may have been lost very shortly after application via  $\text{NH}_3$  volatilisation and denitrification, or may have been rapidly immobilised (Paul & Zebarth 1997).

A slight lag period was observed in the build up of the  $\text{NO}_3^-$  concentration. However, with time, the concentration of  $\text{NO}_3^-$  in the soil increased. Effluent application probably resulted in denitrification of the soil  $\text{NO}_3^-$  already present in the soil. Paul and Beauchamp (1989) showed that the denitrification of the soil  $\text{NO}_3^-$  occurred within hours of manure application, due to the oxidation of short-chain fatty acids present in manure which provided the electron donors for the denitrifying bacteria and also increased oxygen demand in the soil. The rate of N mineralization was found to increase with increasing rates of the TFDE application (Zaman *et al.* 1999), which was probably because of the presence of readily mineralisable organic substances contained in the TFDE (Hawke & Summers 2003). With the passage of time, as the concentration of the mineralisable substrate decreases in the soil, the rate of release of N also slows down.

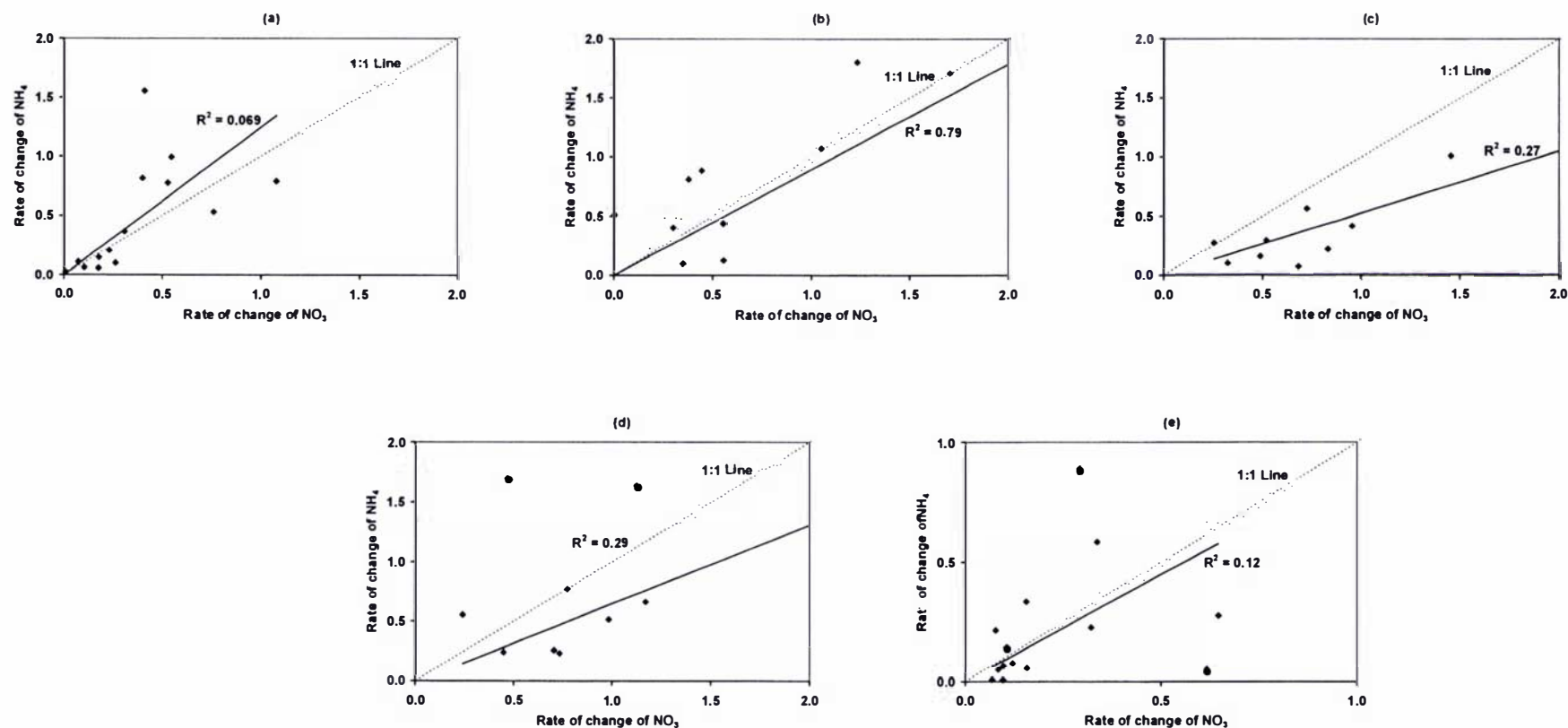
The rate of change of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the soil is shown in Figure 5.6. The procedure to calculate rate of change of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  has been explained in chapter 4 of this thesis. Although the relationship between the rate of change of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  was not significant for most of the treatments, in general for all the TFDE irrigated plots except the T1, the rate of change of  $\text{NO}_3^-$  was more than that of  $\text{NH}_4^+$ , indicating that all the  $\text{NO}_3^-$  present in the soil cannot be accounted for by the corresponding change in the  $\text{NH}_4^+$  concentration. From our experiment, the actual source of  $\text{NO}_3^-$  which was additionally released cannot be derived, but it might be because of the release of native soil N due to the addition of effluent. Nendel *et al.* (2005) concluded from their experiments that a mineralization flush occurs shortly after the addition of the organic source (compost amendment) to the soil and attributed it to a priming effect on mineralization of soil N. In this study, the nitrification of effluent applied  $\text{NH}_4^+$  was essentially complete, meaning little of the effluent added inorganic N remained as  $\text{NH}_4^+$  by the end of the experiment. The added  $\text{NH}_4^+$  must have been converted to  $\text{NO}_3^-$ , taken up by plants, or lost in the atmosphere through ammonia volatilisation.

The C input from TFDE is another important factor in promoting denitrification. The addition of TFDE significantly increased the soil DOC concentration compared to the control. This increase was probably due to the DOC applied through the effluent

(Paul & Beauchamp 1995; Zaman *et al.* 1999). The different C loading rates, which result from the varying hydraulic loading rates of effluent application, led to varying DOC concentrations in the soil. The higher DOC concentrations corresponded to the higher rates of N<sub>2</sub>O emission in the beginning. The denitrification rate is influenced by the amount of DOC entering the soil through TFDE (Lowrance *et al.* 1998). As discussed earlier higher concentrations of easily decomposable C applied with increasing rates of effluent and increased WFPS are the likely cause of conditions that favour increased N<sub>2</sub>O emission. The decline in the N<sub>2</sub>O emissions with increasing time after effluent application probably corresponded with the exhaustion of the available C substrates even though WFPS and NO<sub>3</sub><sup>-</sup> concentration were optimum for N<sub>2</sub>O emission in T3 and T4 treatments.

The changes in the WFPS, ODR and mineral N and DOC concentrations due to the varying rates of the TFDE application affected N<sub>2</sub>O emission from these treatments. The N<sub>2</sub>O emission rates increased significantly in all the treatments except the control, when pre and post-application emission rates were compared (Figure 5.2).

On average, the emissions were found to increase 3.7 to 7.6 fold with the application of the effluent and 1.5 fold from the plot where only water was added. As discussed in Chapter 4 of the thesis, TFDE application provides both N and C to the denitrifying micro organisms in the soil and thus further enhances the emission from the TFDE treated soil (Barton & Schipper 2001). Increases in the N<sub>2</sub>O emissions with the application of organic manures has been observed by other researchers (Lowrance *et al.* 1998; Arcara *et al.* 1999; Chadwick *et al.* 2000; Barton & Schipper 2001). WFPS in all the treatments except control was above the field capacity soil moisture content immediately after the application of the treatments thus suggesting that denitrification simulated by effluent application was the main source of N<sub>2</sub>O emission (Linn & Doran 1984).



**Figure 5.6** Relationship between rates of change in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentration (absolute values) with time ( $\text{mg kg}^{-1} \text{ soil d}^{-1}$ ) after treatment application for (a) T1 (b) T2 (c) T3 (d) T4 and (e) T5 (water) treatments at the experimental plots on Manawatu sandy loam (For the purpose of clarity all the data points are not shown in some of the figures)

Overall, the N<sub>2</sub>O emission increased 2 fold, with an increase in loading rate from 25mm to 100mm (i.e. from 20.14 to 80.56 kg N ha<sup>-1</sup>). Monnett *et al.* (1995) reported an eight fold increase in N<sub>2</sub>O emission when the rate of effluent (domestic wastewater) application increased from 12.5mm to 25mm. High irrigation rates increase the anaerobic soil volume over a longer period of time and thus result in greater N losses from soil due to denitrification (Sexstone *et al.* 1985).

The percentage of the added N emitted as N<sub>2</sub>O ranged from 0.75 to 1.2%. Lessard *et al.* (1996) found in their maize trial fertilised with dairy manure that N<sub>2</sub>O emission accounted for about 1% of the total N applied. As observed from Table 5.3, the percent of added N emitted as N<sub>2</sub>O decreased with the increasing effluent application rate, this probably results from the higher effluent loads generating more anaerobic microsites (Lowrance & Hubbard 2001) thus favouring production of N<sub>2</sub> rather than N<sub>2</sub>O (Comfort *et al.* 1990).

The soil properties (WFPS, mineral N concentration and DOC concentration in the soil) were highly correlated with the N<sub>2</sub>O emission (Table 5.6). The degree of correlation was in the order of DOC > NH<sub>4</sub><sup>+</sup> > NO<sub>3</sub><sup>-</sup> > WFPS in the soil. Lowrance and Hubbard (2001) found that although denitrification was significantly correlated with the WFPS and NH<sub>4</sub><sup>+</sup> concentration of the soil, it was poorly correlated with the soil NO<sub>3</sub><sup>-</sup> concentration. A high correlation between the denitrification potential of the soil and the C content was reported by Bijaysingh *et al.* (1988) and Abbasi & Adams (1999). On the other hand Barton & Schipper (2001) found a poor correlation of N<sub>2</sub>O emission after the DFE application to soil properties (mineral N concentration, WFPS, CO<sub>2</sub> emission and soil temperature).

Putting the data in a regression equation with forward selection, it was observed that DOC and the NH<sub>4</sub><sup>+</sup> concentrations were the two significant variables in the equation. The equation was able to explain 77% of the variability in the data (Table 5.7) indicating that the increasing addition of NH<sub>4</sub><sup>+</sup> and C substrates through increasing effluent loading caused increased N<sub>2</sub>O emission.

**Table 5.6** Correlation coefficients for relationships between N<sub>2</sub>O emission and soil properties at the experimental plots on Manawatu sandy loam. \*\*\*, \*\*, \* depicts level of significance at <0.001, <0.01 and <0.05, respectively. (N<sub>2</sub>O = kg N ha<sup>-1</sup>d<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and DOC = mg kg<sup>-1</sup> soil)

Soil properties	N <sub>2</sub> O	WFPS	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	DOC
N <sub>2</sub> O	1.00	0.56***	0.60***	0.87***	0.88***
WFPS		1.00	0.52***	0.60***	0.62***
NO <sub>3</sub> <sup>-</sup>			1.00	0.76***	0.73***
NH <sub>4</sub> <sup>+</sup>				1.00	0.96***
DOC					1.00

**Table 5.7** Results of the multiple linear regression analysis relating N<sub>2</sub>O emission with various soil properties at the experimental plots on Manawatu sandy loam. (N<sub>2</sub>O = kg N ha<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and DOC = mg kg<sup>-1</sup> soil)

Treatment	Regression Equation	No. of observations	R <sup>2</sup>
N loading	N <sub>2</sub> O = 0.0007 + 0.0006 DOC +0.0002 NH <sub>4</sub> <sup>+</sup>	408	0.77

The proportion of the applied N emitted as N<sub>2</sub>O-N decreased with the increasing rate of effluent application. With an increase in the application rate of the TFDE, the conditions were more conducive for the complete denitrification, leading to an increased N<sub>2</sub>:N<sub>2</sub>O ratio (Lowrance *et al.* 1998). Thus to reduce N<sub>2</sub>O emissions it might be worthwhile to study the effect of the suitability of land application of effluents at higher rates rather than several smaller but more frequent applications. Smaller and more frequent applications of wastewater appear to increase the amount of N loss via denitrification, by maintaining anaerobic conditions and greater NO<sub>3</sub><sup>-</sup> concentrations in more microbially active topsoil (Monnett *et al.* 1995). Applying smaller volumes of wastewater in each application probably enhances nitrification, by creating a more favourable fluctuation between anaerobic and aerobic conditions. It might be beneficial

from the nutrient leaching point of view but might not be sustainable because of increased N<sub>2</sub>O emission.

## 5.5 Conclusions

- Application of TFDE can result in a rapid increase in N<sub>2</sub>O emission due to the supply of available C, mineral N and its influence on the soil aeration status.
- The N<sub>2</sub>O emission increased with an increase in the TFDE loading rate, however, the percentage of the added N emitted as N<sub>2</sub>O decreased with the increasing rate of TFDE loading.
- The effluent loading rate affected WFPS as well as the concentration of DOC, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> in the soil; increasing with the increasing rate of TFDE application.
- Significant correlation was observed between the soil properties and the N<sub>2</sub>O emitted. The highest degree of correlation was observed between N<sub>2</sub>O emission and DOC concentration ( $r = 0.88$ ).

## Chapter 6

# Effect of farm dairy effluent on nitrous oxide emission

## 6.1 Introduction

Previous chapters have compared the effect of different types of effluents, including untreated and treated FDE and different application rates of treated FDE on  $\text{N}_2\text{O}$  emission. These were small plot studies carried out using simulated irrigation, done to examine the effect of effluent properties on  $\text{N}_2\text{O}$  emission. There have been very few comprehensive studies examining the  $\text{N}_2\text{O}$  emission from FDE irrigation application to periodically grazed paddocks as normally occurs on a commercial dairy farm. The combination of compaction caused by cattle treading (Chapter 3) during grazing and excretal deposition by the grazing cattle are additional stimulants of  $\text{N}_2\text{O}$  emission that will occur subsequent to effluent irrigation on a commercial farm. One of the main factors that influences the emission in the pasture is the grazing event (Oenema *et al.* 1997). Effluent irrigation immediately after the grazing event may enhance  $\text{N}_2\text{O}$  emission from grazed pasture.

This study was therefore undertaken to estimate the amount of  $\text{N}_2\text{O}$  emission from the freshly applied treated farm dairy effluent (TFDE) application and also to assess its residual effect on the  $\text{N}_2\text{O}$  emission from grazed pasture.

The specific objectives of this study are:

- To quantify  $\text{N}_2\text{O}$  emission from TFDE irrigation under real farming conditions.
- To examine the residual effect of FDE irrigation on  $\text{N}_2\text{O}$  emission.
- To quantify the  $\text{N}_2\text{O}$  emission immediately after a grazing event.
- To establish regression relationships between some of the soil properties affected by effluent irrigation and  $\text{N}_2\text{O}$  emission.

6.2 Material and Methods

Nitrous oxide emissions and related soil and environmental parameters (Table 6.1) were monitored for two weeks following applications of treated FDE in September 2003 (first irrigation), January (second irrigation) and February 2004 (third irrigation). The residual effect of the FDE irrigation on the N<sub>2</sub>O emissions was also monitored. The chapter also examines the grazing effect on N<sub>2</sub>O emission and other soil properties.

Table 6.1 Details of the various irrigation (fresh and residual) and grazing experiments

Experiment	Treatment	Effluent Loading	Grazing dates	Measurement period
Fresh Application				
First application (A)	Irrigated	25mm	6 <sup>th</sup> Sep. 2003	15 <sup>th</sup> to 28 <sup>th</sup> Sep,2003
	Control	–		
Second application (B)	Irrigated	21mm	26 <sup>th</sup> Jan. 2004	28 <sup>th</sup> Jan to 11 <sup>th</sup> Feb, 2004
	Control	–		
Third application (C)	Irrigated	16mm	1 <sup>st</sup> Mar. 2004	24 <sup>th</sup> Mar to 2 <sup>nd</sup> Apr 2004
	Control	–		
Residual experiment (D)	Irrigated	–	30 <sup>th</sup> May 2004	17 <sup>th</sup> Jun to 5 <sup>th</sup> Jul, 2004
	Control	–		
Grazing experiment (E)	Grazed	–	6 <sup>th</sup> Oct. 2003	7 <sup>th</sup> to 26 <sup>th</sup> Oct, 2003
	Control	–	24 <sup>th</sup> Aug. 2003	

6.2.1 Experimental site and soil characteristics

The field site, on Tokomaru silt loam, consisted of pasture grazed by dairy cows and was located on Massey University’s No. 4 Dairy Farm in the Manawatu region of New Zealand (NZMS 260, T24, 312867). The soil was classified as an Argillic-fragic Perch-gley Pallic Soil (Hewitt 1998) or a Typic Fragiaqualf (Soil Survey Staff, 1998), and was derived from loess blown from adjacent river sediments to be deposited on a deeply dissected uplifted marine terrace (Molloy, 1998). The site is located in a flat to



easy rolling landscape (~ 3% slope), which receives an average annual rainfall of ~ 1000 mm supporting a mixed pasture of perennial ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*). The characteristics of the soil at the site are presented in Table 6.2. The total rainfall and the mean air temperature distribution for the whole experimental period are shown in Figure 6.1.

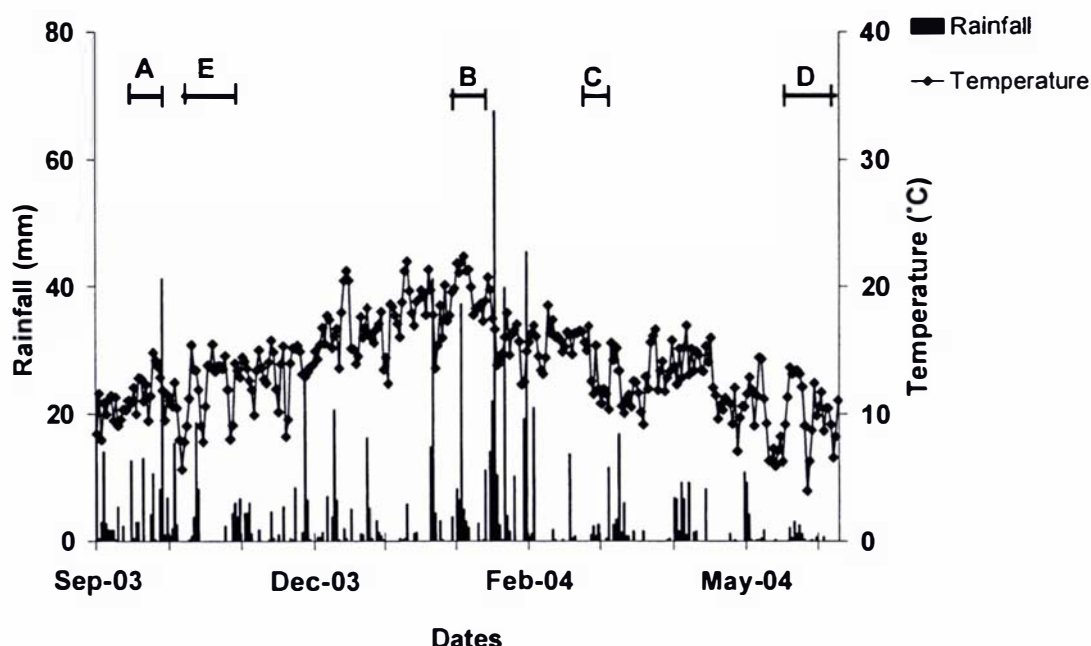
**Table 6.2 Chemical and physical properties of Tokomaru silt loam soil at the experimental site. The values in the bracket represent the standard error of mean of the four replicates**

Properties	Soil depth	
	0-5cm	5-10cm
pH	5.9 (±0.04)	6.1 (±0.07)
Bulk Density (g cm <sup>-3</sup> )	1.01 (±0.04)	1.01 (±0.06)
Total N (%)	(0.35 (±0.03)	0.22 (±0.04)
Total C (%)	3.64 (±0.52)	2.18 (±0.22)
C:N	10.4 (±0.47)	9.7 (±0.29)
CEC (cmol charge kg <sup>-1</sup> )	22.3 (±1.26)	—

The study was divided into three sections which are described below.

- The first section consists of the monitoring of the N<sub>2</sub>O emissions immediately after the application of the FDE to the pasture. This experiment will be referred to as the fresh application experiment with three irrigation events as first application (A), second application (B) and third application (C).
- The second section involves measuring N<sub>2</sub>O emissions from the field which had been irrigated with FDE two months prior to monitoring emissions. This examined the residual effect, of the effluent irrigation on the N<sub>2</sub>O emission. This experiment will be referred to as the Residual experiment (D).
- The third section of this study comprises of an experiment to examine the effect of grazing on N<sub>2</sub>O emission (E).

The details of each of the experiments are given below.



**Figure 6.1** Average rainfall and temperature distribution for September 2003 to June 2004. The line (—) denotes the monitoring duration of each experiment with A, C and D for the first, second and third fresh irrigations respectively, B for the grazing experiment and E for the residual experiment

### 6.2.1.1 Fresh application experiment

The field experiment was conducted on the effluent block of Massey University's Dairy 4 farm (Houlbrooke *et al.* 2004) have given a detailed description of the site also used for drainage water quality monitoring). Two field sites each having dimensions of 40m x 40m were selected and referred to as: irrigated and control. Three effluent irrigation events during 15<sup>th</sup> to 28<sup>th</sup> September 2003 (referred to as irrigation 1, A), 28<sup>th</sup> January to 11<sup>th</sup> February, 2004 (referred to as irrigation 2, B) and 24<sup>th</sup> March to 2<sup>nd</sup> April, 2004 (referred to as irrigation 3, C) was monitored for N<sub>2</sub>O emission, each treatment replicated 20 times. In accordance with the irrigation scheduling guideline proposed under the "Deferred Irrigation concept" (Houlbrooke *et al.* 2004) the effluent loading varied so as not to exceed the soil moisture deficit at the time of effluent irrigation. The effluent was applied at hydraulic loadings of 25mm, 21mm and 16mm for the first, second and third irrigation, respectively which resulted in N loading levels of 25.24, 21.20 and 16.16 kg ha<sup>-1</sup>, respectively. Effluent was applied with a spitfire

Mark I oscillating travelling irrigator at the rate of approximately 2.7mm min<sup>-1</sup>. The characteristics of the effluent applied are presented in Table 6.3.

### 6.2.1.2 Residual experiment

The residual effect of effluent irrigation on N<sub>2</sub>O emission and soil properties such as WFPS, mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) and dissolved organic carbon (DOC) concentrations was monitored 12 weeks after the application. The emissions were monitored for 3 weeks from the 14<sup>th</sup> June, 2004 to the 5<sup>th</sup> July, 2004. The last effluent irrigation of 16mm was applied on the 24<sup>th</sup> March, 2004.

### 6.2.1.3 Grazing experiment

The effect of grazing on N<sub>2</sub>O emission was monitored immediately (a day) after a grazing event. There are two treatments in this experiment, namely grazed and control (not recently grazed). The field was grazed according to the farm's normal management programme, i.e., with an average grazing density of approximately 80 cows ha<sup>-1</sup> for a 12 hour period. The emissions were monitored for 3 weeks from the 7<sup>th</sup> October, 2003.

A 40 x 40m plot was fenced off to avoid any grazing from taking place for a period of 6 weeks and it was used as the control plot.

The details of all the three experiments are given in Table 6.1.

## 6.2.2 Nitrous oxide measurement

The N<sub>2</sub>O emissions for the above mentioned periods for the three experiments (Table 6.1) were made using the closed chamber technique (Saggar *et al.* 2002) as described in section 3.2.2, Chapter 3. Twenty chambers were installed per treatment in a zig zag fashion to cover the spatial variability in the field. During the monitoring of N<sub>2</sub>O flux immediately after a grazing event, installing chambers directly over the dung patch was avoided. The chambers, 25 cm in diameter, were inserted about 10 cm into the soil after the effluent application. Background N<sub>2</sub>O flux was measured for the site one day before the application of the treatments. During the first week after the effluent application, measurements of the N<sub>2</sub>O emissions were made daily to capture major changes in N<sub>2</sub>O fluxes. This was followed by measurements on alternate days for rest of the experimental period till the fluxes decreased, approaching the background emission.

## 6.2.3 Analysis

### 6.2.3.1 Effluent analysis

The treated dairy effluent irrigated on the farm was from the outlet of the aerobic pond of the dairy 4 farm of Massey University. Samples of effluent were analysed for suspended solids, pH, total N, NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>, total carbon, dissolved organic carbon, chemical oxygen demand, biological oxygen demand total phosphorous and total potassium following the procedures published in standard methods (APHA 1998).

### 6.2.3.2 Soil analysis

Four soil samples were collected randomly on all days of the N<sub>2</sub>O measurement from each site from 0-5 cm and 5-10 cm depths to determine soil water content. Field moist soil samples were weighed (M<sub>i</sub>) and oven dried (105°C) to a constant mass (M<sub>s</sub>). Gravimetric soil water content (SWC) was calculated as described in equation 2 of Chapter 3 of this thesis. This was then used to calculate the WFPS (Eq. 3; Chapter 3) of the soil, for the effluent irrigated and control soil.

Soil samples (four replicates) to determine the pH, mineral N (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) and dissolved organic carbon (DOC) content for all the treatments were collected randomly from the irrigated area outside the chamber on all days of N<sub>2</sub>O measurement from 0-5 cm and 5-10 cm depths. Field moist samples were sieved (< 2mm) soon after collection. A sub-sample (5g) was extracted with a 0.5M K<sub>2</sub>SO<sub>4</sub> solution, by shaking it for 1 hr (1g soil: 4 ml extractant). The extracts were analysed for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> by standard colorimetric methods (Keeney & Nelson 1982) on an autoanalyser and for determining DOC by the dichromate oxidation (Tate *et al.* 1988) method using a spectrophotometer. Soil samples were collected from the area where the chambers had been placed at the end of the measurement period, when the chambers were removed from the ground. These samples were analysed for the above mentioned soil properties.

### 6.2.3.3 Herbage analysis

To determine the pasture growth response to applied effluent herbage was cut to a 2cm height prior to effluent application for all the three experiments. Herbage accumulation after the effluent application was recorded at the end of the measurement

period from the 30cm x 30cm plots, replicated 4 times, for all the experiments. The wet weight of herbage was recorded then oven dried at 70° C and dry matter (DM) recorded. The dry matter response was calculated by the formula given in Chapter 4.

#### **6.2.4 Oxygen diffusion rate**

The oxygen diffusion rate measurements were made to examine the difference in the diffusion rate between the irrigated/grazed and control treatments for all the three experiments by the method described in Chapter 3. The ODR was monitored on the first and the last day of the N<sub>2</sub>O measurement period for each of the three effluent irrigations as well as for the residual and the grazing experiments.

#### **6.2.5 Statistical methods**

An analysis of the variance was carried out using SAS for Windows v8 software package. The least significant differences (LSD) were calculated to estimate the differences between the treatments. The 5% confidence level is regarded as statistically significant.

A regression and correlation analysis between various soil properties and N<sub>2</sub>O emission was conducted using the SAS package.

### **6.3 Results and Discussion**

#### **6.3.1 Properties of the effluent**

Effluent characteristics applied during the three irrigation events for the fresh application is summarised in Table 6.3. The chemical composition of TFDE used for the three applications varied slightly. The total solid content and the total N content of the effluent used for all the three applications were below the range reported in the literature (Wang *et al.* 2004). About 70 - 74% of the N in the effluent was in the NH<sub>4</sub><sup>+</sup> form which is typical of the effluent N distribution values found elsewhere (Longhurst *et al.* 2000). The C: N ratio of the effluent used during all the three irrigations was 9.5.

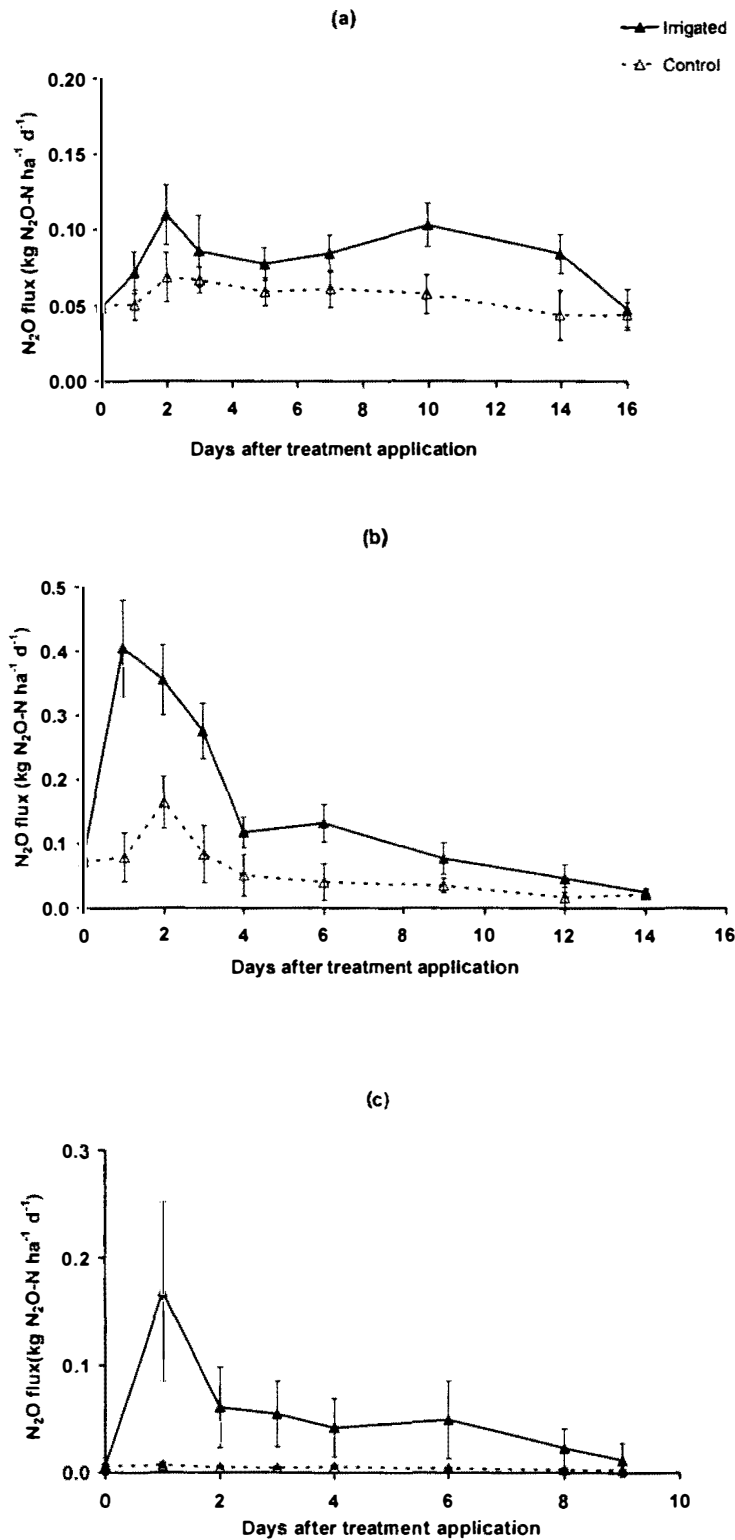
**Table 6.3      Characteristics of the farm dairy effluent applied during three applications on the Tokomaru silt loam soil**

Properties	Experiment A	Experiment B	Experiment C
Total suspended solids (mg l <sup>-1</sup> )	245.2	268.6	231.8
pH	7.6	7.8	7.6
Total N (mg l <sup>-1</sup> )	95.6	101.4	93.7
NH <sub>4</sub> <sup>+</sup> -N (mg l <sup>-1</sup> )	68.2	75.4	65.6
NO <sub>3</sub> <sup>-</sup> -N (mg l <sup>-1</sup> )	0.6	0.4	0.6
Total carbon (mg l <sup>-1</sup> )	908.2	959.2	890.3
Dissolved organic carbon (mg l <sup>-1</sup> )	18.2	19.2	17.8
C:N ratio	9.5	9.5	9.5
Chemical oxygen demand (mg l <sup>-1</sup> )	95	97	89
Biochemical oxygen demand (mg l <sup>-1</sup> )	105	112	90
Total P (mg l <sup>-1</sup> )	18.4	18.0	17.9

**6.3.2      Nitrous oxide emission**

**6.3.2.1      Fresh application experiment**

Each TFDE application (Experiments A, B and C) increased the N<sub>2</sub>O emission over the unirrigated control. The emissions peaked within a few hours of the effluent application and subsequently dropped to reach the level of emission from the control treatment within 1-2 weeks of application (Figure 6.2a, b and c). Peak emissions of 0.110, 0.404 and 0.168 kg N ha<sup>-1</sup>d<sup>-1</sup> were attained for the first, second and third application, respectively within 4-24 hours of the effluent application.



**Figure 6.2** N<sub>2</sub>O fluxes (kg N ha<sup>-1</sup> d<sup>-1</sup>) during the (a) first (experiment A) (b) second (experiment B) and (c) third (experiment C) effluent application events on Tokomaru silt loam. Each value represents a mean of twenty replicates with standard deviation shown by vertical bars. Note the difference in the scale of the Y axis.

**Table 6.4** Amount of N applied through farm dairy effluent irrigation and N<sub>2</sub>O emitted during the three fresh applications, residual irrigation and the grazing experiment on the Tokomaru silt loam

Experiment	Treatment	Emission period *	N added (kg ha <sup>-1</sup> )	Peak emission rate	N <sub>2</sub> O-N emitted (kg ha <sup>-1</sup> )	Emission factor (%) **
Fresh application						
First application (A)	Irrigated	17	23.9	0.110	1.357	2.0
	Control		Nil	0.069	0.886	–
Second application (B)	Irrigated	14	25.2	0.404	1.922	4.9
	Control		Nil	0.164	0.679	–
Third application (C)	Irrigated	9	18.0	0.168	0.487	2.5
	Control		Nil	0.007	0.038	–
Residual experiment (D)	Irrigated	19	Nil	0.1237	0.443	–
	Control		Nil	0.1033	0.390	–
Grazing experiment (E)	Grazed	23	11.6	0.044	0.537	4.0
	Control		Nil	0.007	0.077	–

\* Emission period = No. of days for emission to reach the background level

\*\*Emission factor =

$$\frac{N_2O \text{ emitted (effluent treated plot)} - N_2O \text{ emitted (control plot)}}{N \text{ added through effluent}} \times 100$$

A small second peak was observed for the first application on day 10 which was not observed for the other two irrigation events. Nitrous oxide emission from the TFDE treated pasture ranged from 0.047 to 0.110, 0.025 to 0.404 and 0.006 to 0.168 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> for the first, second and third applications respectively. The emissions then declined to the base level within 16, 14 and 9 days for the first, second and third applications, respectively. The data indicates that 44, 78 and 87% of the total emission were emitted within a week for the first, second and third irrigation, respectively.



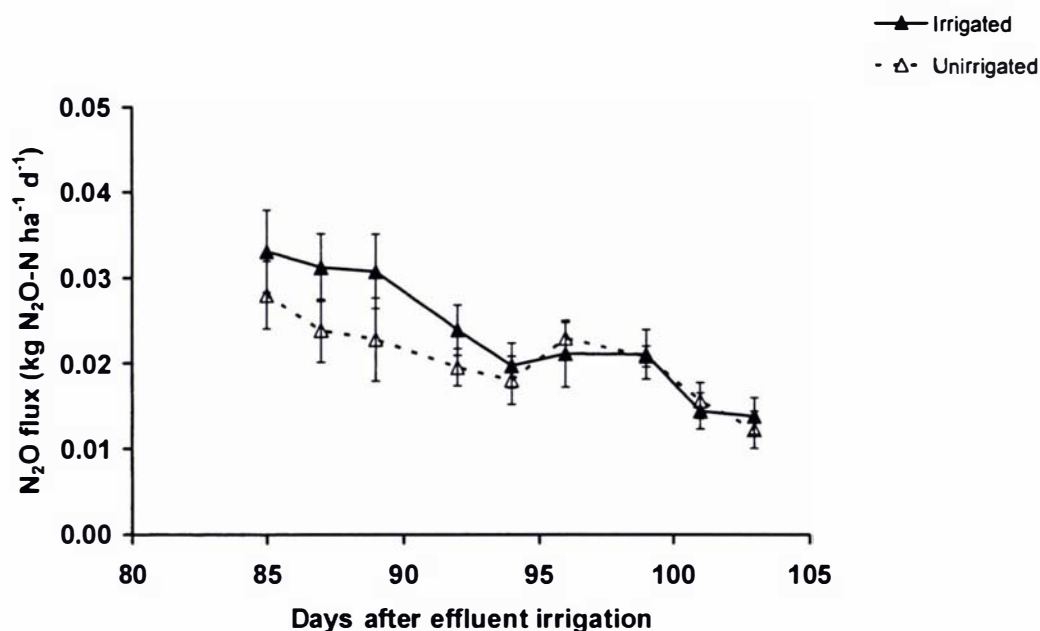
Emission from the third irrigation reached the background levels within a shorter period than for the other irrigation events. The total amounts of N<sub>2</sub>O emitted from effluent application for the first, second and third irrigation were 2%, 4.9% and 2.5% respectively, of the total N added through effluents (Table 6.4). Cumulative emissions from the irrigated site were 1.5, 2.8 and 12.6 times higher than that from the unirrigated control for respective irrigation events.

The N<sub>2</sub>O flux from the control treatment remained almost stable with daily emission ranging from 0.069 to 0.436, 0.164 to 1.212 and 0.0025 to 0.0069 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> for the first, second and third irrigations, respectively. A slight increase in the emission was observed in the second irrigation, which coincided with the rainfall event (Figure 6.2b). Among the 3 irrigations, cumulative emission from the second irrigation was higher than the other two irrigations.

### 6.3.2.2 Residual experiment

No difference in the N<sub>2</sub>O flux was observed between the irrigated and unirrigated sites two months after effluent application, suggesting there was no residual effect of the effluent irrigation on N<sub>2</sub>O emission (Figure 6.3). Overall, the daily rate of emission for the measurement period was found to range from 0.014 to 0.033 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> for irrigated and 0.012 to 0.028 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> for control. The emissions from both the irrigated and the control were found to decrease with time during the measurement period. Although the total emissions were slightly higher from the irrigated site than from the unirrigated control site, the difference was not significant.

High spatial variability was observed within the sites, which is one of the features in the measurement of N<sub>2</sub>O emission, especially under field conditions.

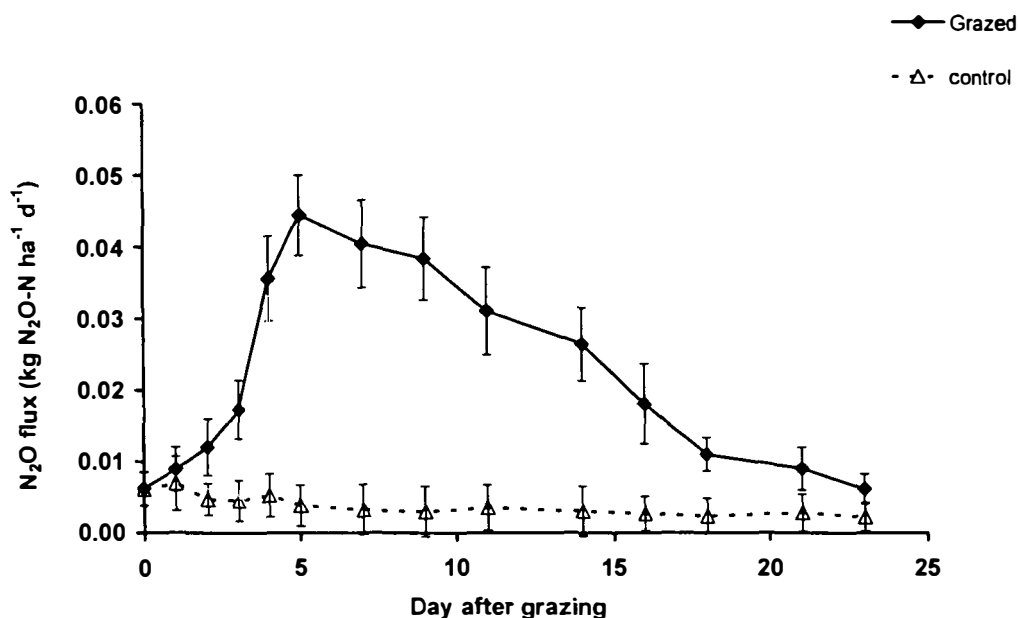


**Figure 6.3** N<sub>2</sub>O fluxes (kg N ha<sup>-1</sup> d<sup>-1</sup>) during the residual effluent application trial. Each value represents a mean of twenty replicates with standard deviation shown by vertical bars

### 6.3.2.3 Grazing experiment

Large differences in N<sub>2</sub>O emission were observed between the site that had been grazed the previous day (grazed) and the site that had not been grazed for 43 days (ungrazed) (Figure 6.4). The fluxes from the grazed sites were much higher than for the ungrazed site with the total emissions from the former site being 8 times higher than the latter site for the entire experimental period.

Prior to grazing, the background N<sub>2</sub>O emission remained low (0.0069 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup>). Emission decreased with time for the ungrazed pasture and reached 0.0052 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup>. It took almost 4 weeks for the N<sub>2</sub>O flux from the grazed pasture to return to the background level (ungrazed control) and by the end of the investigation period the difference between the two treatments was non-significant.

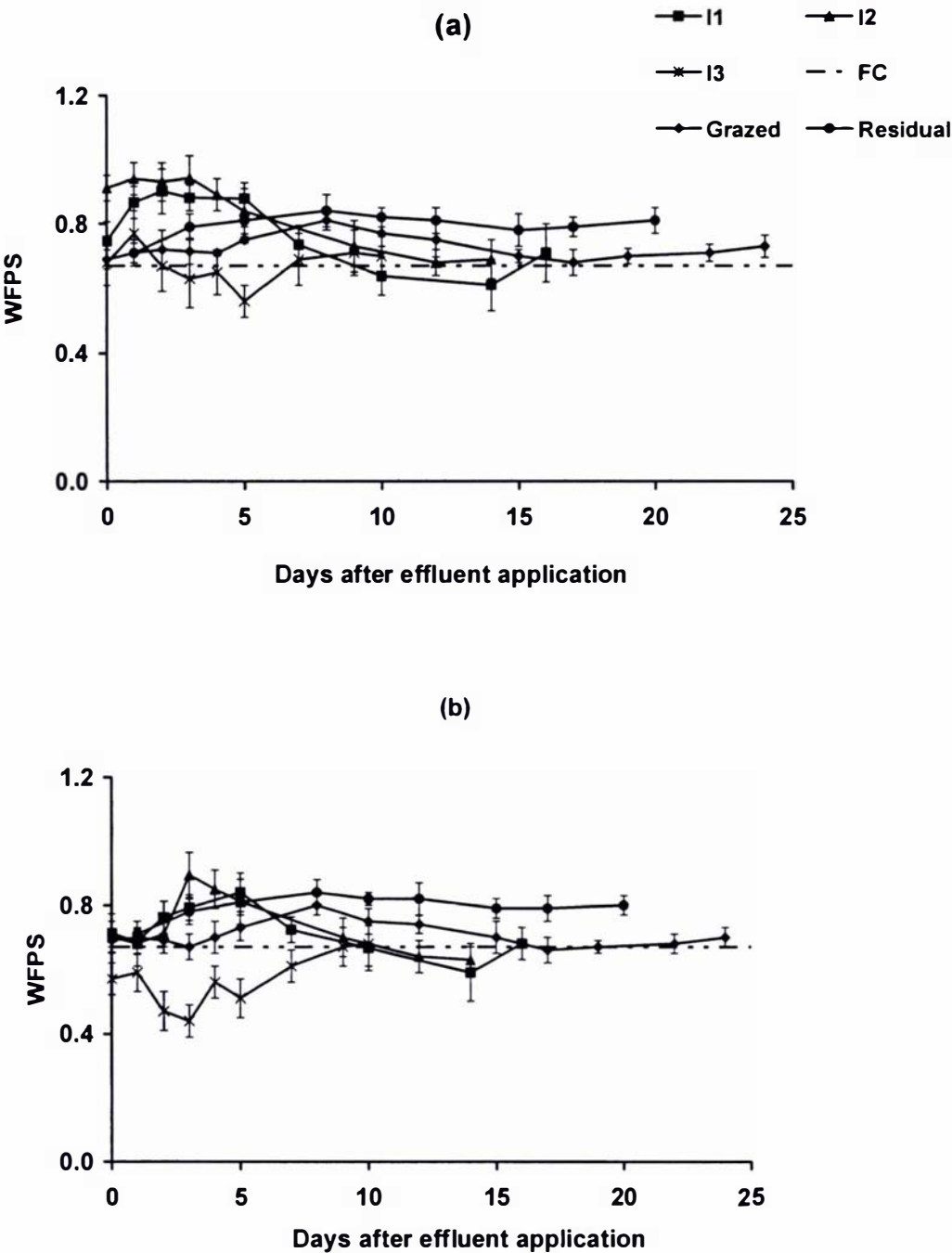


**Figure 6.4** N<sub>2</sub>O fluxes (kg N ha<sup>-1</sup> d<sup>-1</sup>) during the grazing trial. Each value represents a mean of twenty replicates with standard deviation shown by vertical bars

Assuming an N deposition rate of 290g N cow<sup>-1</sup> d<sup>-1</sup>, 11.6 kg of N ha<sup>-1</sup> would have been added in the grazing event in this experiment. Thus 4% of the added N was emitted as N<sub>2</sub>O during the entire measurement period, of which 80% was emitted within 2 weeks of the grazing event.

### 6.3.3 Water filled pore space

Water filled pore space for the irrigated, grazed and residual treatments and their respective control treatment are shown in Figure 6.5. As can be seen from the figure (Figure 6.5) the calculated WFPS during the measurement period of all three experiments was higher than the field capacity, except for the control treatment in the third irrigation event. The control treatment showed a lower WFPS than the irrigated treatment.



**Figure 6.5** WFPS distributions for (a) three freshly irrigated (experiment A, B and C), residual irrigated (experiment D) and grazed (experiment E) treatments (b) corresponding control treatment (unirrigated fresh, unirrigated residual and ungrazed) on Tokomaru silt loam. FC=Field capacity

In the case of the fresh effluent application (experiment A, B and C), the WFPS during all the three irrigation events remained above the field capacity, with the highest WFPS observed during the second irrigation (experiment B). During the third irrigation,

(experiment C) the WFPS was found to drop below the field capacity for the latter half of the measurement period. The range in WFPS values for the first, second and the third irrigation were 0.61 to 0.90, 0.69 to 0.94 and 0.56 to 0.77, respectively. The mean WFPS values for the entire measurement period for the irrigated treatment were 4.1, 5.5 and 17.5% higher than the mean value of the control treatment for the respective irrigation events. This shows that the effect of effluent application on the WFPS was highest during the third irrigation.

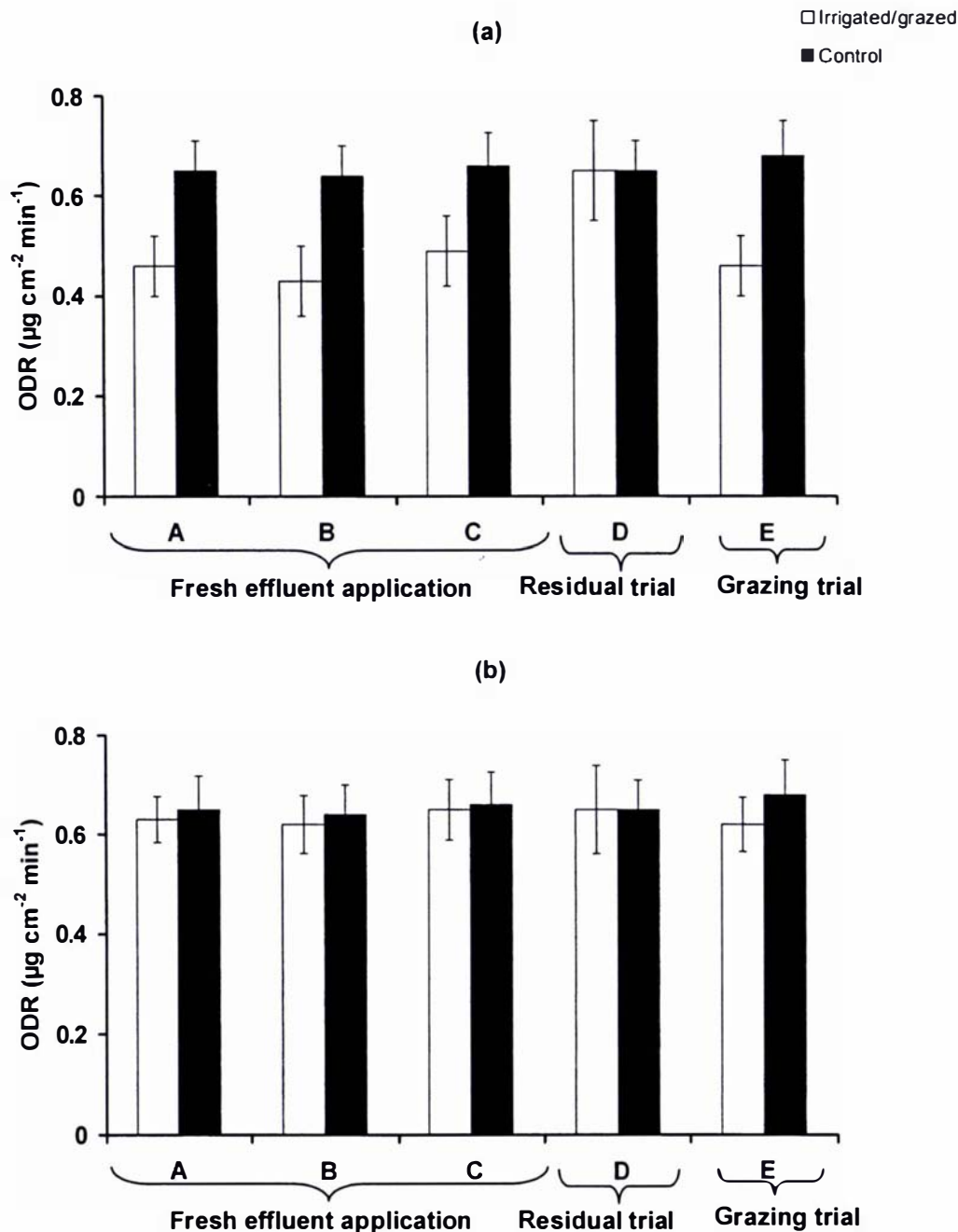
No difference in the WFPS was observed between the irrigated and the control treatments for the residual irrigation experiment (experiment D, Figure 6.5a and b). A difference between the two treatments was not expected, because any effect that the effluent irrigation had on the WFPS would have diminished by the time the measurements were made. Moreover, any difference in the moisture that the 16mm effluent application created would have been masked by the 159.8mm of rainfall that fell between the time of application of the effluent and the starting of the monitoring of the residual effect.

In the case of the grazing experiment, the effect of grazing on the WFPS was not evident (Figure 6.5a and b). WFPS was found to increase 5 days after grazing but this rise was also observed for the ungrazed site as well. Immediately after the grazing of the experimental site, the WFPS for the grazed site was higher than the ungrazed site which was due to the addition of urine by the grazing cattle or due to the compaction created by the grazing animals. The cattle dung which contains undigested particulate organic matter increases the water retention capacity of the soil (Petersen & Andersen 1996), thus increasing the WFPS of the soil as compared to the control site. Compaction of soil by the cow hooves further help in retaining higher WFPS for longer period of time under the grazed site. But the effect didn't last long and the difference in WFPS between the two treatments diminished with time.

### 6.3.4 Oxygen diffusion rate

It was observed that the ODR values fell immediately after the application of the effluent (Figure 6.6a and b). ODR values for the first, second and third irrigation fell by 29.2, 32.8 and 25.8% respectively as compared to the unirrigated control treatment immediately after the irrigation. The ODR had recovered by the end of the measurement period for all three irrigations with no significant differences observed between the

irrigated and control treatments. Among the three irrigations, ODR values were slightly lower for the second irrigation (6.5 and 12.2% lower from the first and the third irrigations) for both the irrigated and the control treatments, though the difference was not significant.



**Figure 6.6** ODR (μg cm<sup>-2</sup> min<sup>-1</sup>) for the experiments (A, B, C, D and E) during the (a) first day after treatment application and (b) last day of measurement for the respective experiments on Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

The reason for the decrease in the ODR after the effluent application has been thoroughly explained in Section 4.3.3 of Chapter 4 and the variation in ODR values observed in this series of studies are consistent with that explanation.

In the case of the experiment examining the residual effect of effluent irrigation on N<sub>2</sub>O emission no effect of the effluent irrigation on ODR was observed. The rate of oxygen diffusion was similar for both the irrigated and the control soil. Since the reduced conditions caused by the effluent irrigation are short lived (Barton & Schipper 2001; Clough & Kelliher 2005), no residual effect on ODR is anticipated 3 months after the effluent irrigation.

In the case of the grazing experiment, the ODR was found to follow the same pattern as that observed for the fresh effluent application with the diffusion rates falling immediately after the grazing event and then recovering by the end of the measurement period. The rate of oxygen diffusion was found to decrease by 32.4% as compared to the ungrazed control (Figure 6.6a). This difference in the ODR between the grazed and the ungrazed site became almost negligible by the end of the experimental period (Figure 6.6b). The initial differences are consistent with compaction (Carter *et al.* 1994) and the deposition of excreta on the soil by the grazing cattle, which provides a ready source of C to the soil microorganisms which then lead to rates of oxygen consumption exceeding the rate of supply (Comfort *et al.* 1990; Sharpe & Harper 2002; van Groenigen *et al.* 2005). See discussion Section 4.4, Chapter 4.

### 6.3.5 N transformation in soil

Soil mineral N concentration increased with the fresh TFDE application experiment as well as the grazing but no change in mineral-N was observed in the TFDE residual treatment (Figure 6.7, 6.8 & 6.9). The general pattern of increase in the concentration differed slightly between the fresh application and the grazing experiments. A slight delay in the mineralization of the N added during the grazing event was evident which was not in case of effluent application.

#### 6.3.5.1 Fresh application experiment

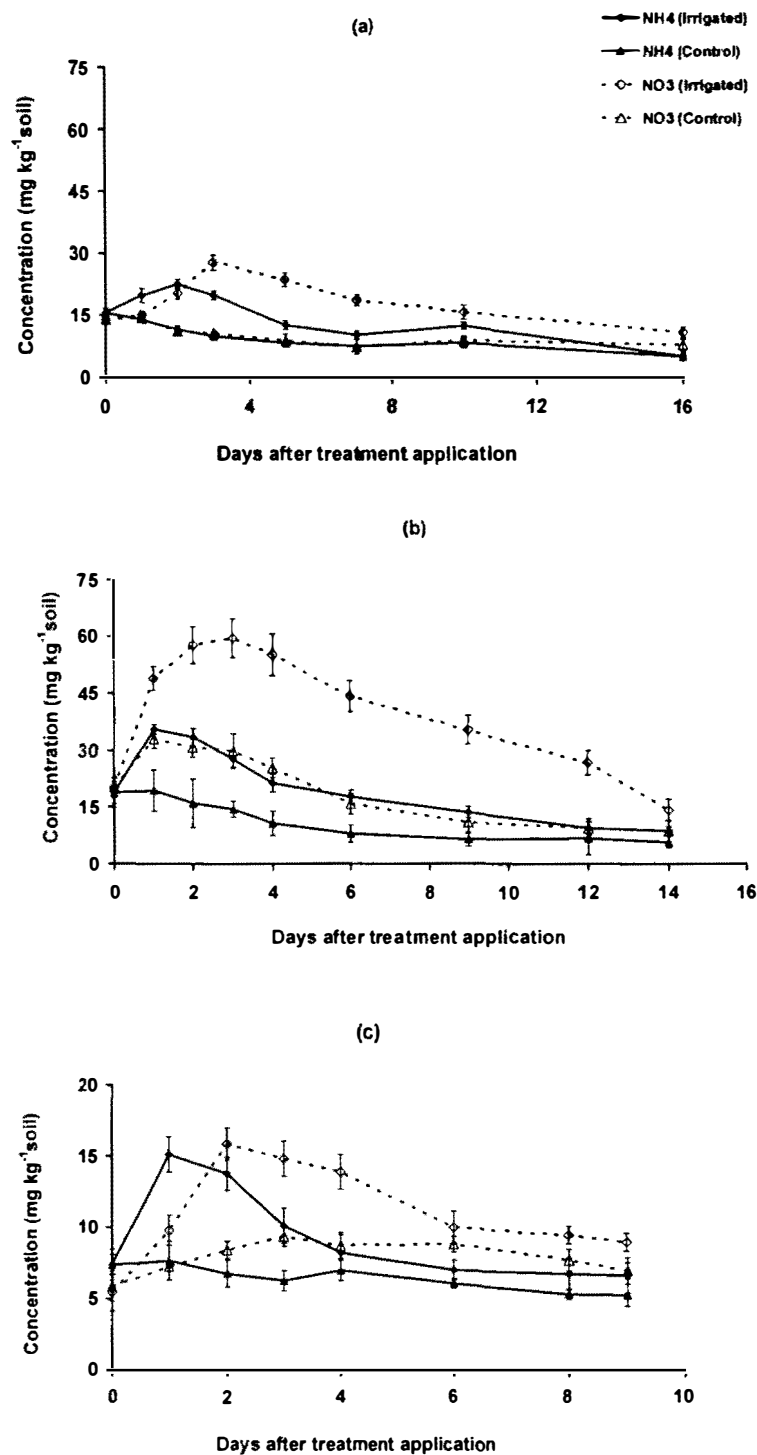
The changes in the NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentration in soil with the addition of the TFDE are shown in Figure 6.7. The general trend appears to be the same for all the

three irrigation events. Generally,  $\text{NH}_4^+$  concentration increased immediately after the application of the effluent and then decreased progressively with time. Nitrate concentration on the other hand showed an initial lag period before starting to increase. As the initial mineral N concentrations (before application of the effluent) as well as the amount of effluent-derived mineral N were different for the three irrigation events, the N mineralization rate was found to vary among the irrigation events.

The highest  $\text{NH}_4^+$  concentration of  $27.9 \text{ mg kg}^{-1}$  soil was reached within a day of the effluent application. The concentration then decreased to a minimum of  $5.1 \text{ mg kg}^{-1}$  soil on the last day of the measurement period. About 55.9% of the total added N through FDE was recovered in the form of  $\text{NH}_4^+$  in the soil during the first irrigation. The  $\text{NO}_3^-$  concentration was found to peak on the third day after the application, with concentrations ranging from 11 to  $28 \text{ mg kg}^{-1}$  soil for the three irrigations. Decreases in both the  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentration were measured from the beginning to the end of the measurement period for the control treatment. Thus the  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentration decreased from 16 to 5 and from 14 to  $7 \text{ mg kg}^{-1}$  soil, respectively. The changes in the concentrations of the mineral N in the control treatment could be attributed to the excretal input from the grazing event a week before the application of the effluent.

It can be observed that the mineral N concentration in the soil before the start of the fresh effluent application experiment was higher for the second irrigation than the first and the third irrigations. A relatively large pool of both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  existed in the area, which had been grazed a day before the application of the second irrigation. Thus a rapid transformation of the excretal N would have been ongoing in the soil when the effluent was applied, especially during the second irrigation event. The peak concentration of  $\text{NH}_4^+$  was higher for this irrigation event than in the other two irrigations. On day 1, the  $\text{NH}_4^+$  concentration in the soil for the control treatment was 1.4 and 2.5 times higher for the second irrigation than for first and the third irrigations, respectively. These differences were 1.8 and 2.4 times for the respective irrigated treatments. The highest  $\text{NH}_4^+$  concentration of  $35.6 \text{ mg kg}^{-1}$  soil was observed during the first day of the application which was 133% of the  $\text{NH}_4^+$  concentration added through the effluent.





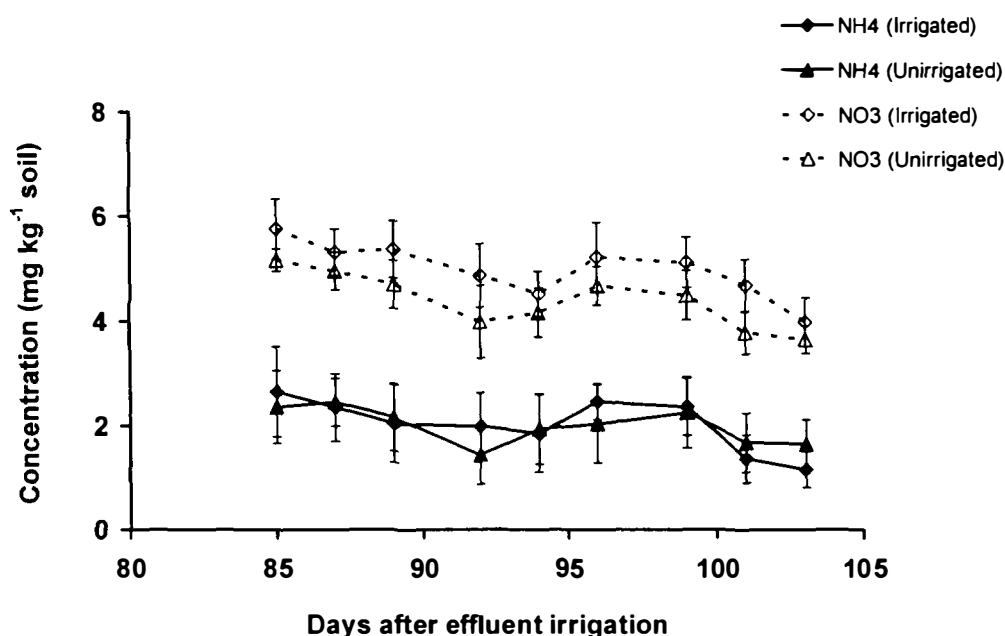
**Figure 6.7** Mineral N concentrations (mg kg<sup>-1</sup> soil) during the (a) first (experiment A) (b) second (experiment B) and (c) third (experiment C) effluent application events on Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars. Please note the difference in the scale of Y axis

This high concentration of  $\text{NH}_4^+$  in the soil is due to the combined effect of excretal N added due to grazing as well as due to the effluent application. The  $\text{NO}_3^-$  concentration also showed a similar trend with the levels being far higher than would be expected if all of the  $\text{NH}_4^+$  added mineralised. Comparing the  $\text{NO}_3^-$  concentrations in soil among the three irrigation events, it was observed that the concentration for the second irrigation was 2.3 and 4.6 times higher under the unirrigated control treatment and 3.3 and 5 times under the irrigated treatment than the first and the third irrigations, respectively. The rate of mineralization was affected by the grazing event, and a high build-up of  $\text{NO}_3^-$  was observed in the soil.

The absence of a grazing event before the application of the effluent in the third irrigation (Figure 6.7c) caused the mineral N concentrations in the soil to be lower than that found in the other two irrigations (Figure 6.7a and b). Moreover the depth of irrigation applied (and therefore the amount of added N) was also less than the other two irrigations. The range of the  $\text{NH}_4^+$  concentration for the irrigated and the control treatment were 6.7 to 15.2 mg kg<sup>-1</sup> soil and 5.3 to 7.7 mg kg<sup>-1</sup> soil, respectively. Approximately, 50% of the total added N was recovered in the soil. During the entire measurement period, the soil  $\text{NO}_3^-$  concentration from the FDE irrigated site was significantly higher than in the unirrigated control site (Figure 6.7a, b and c). The  $\text{NO}_3^-$  ranged from 5.4 to 15.9 mg kg<sup>-1</sup> soil and from 5.9 to 9.4 mg kg<sup>-1</sup> soil for the irrigated and control treatments, respectively.

#### 6.3.5.2 Residual experiment

Mineral N distribution in the grazed pasture soil receiving TFDE application 12 weeks earlier to the monitoring period was compared with the grazed pasture soil with no TFDE applied (Figure 6.8). The data showed no residual effect of the effluent application on the mineral N concentration in the soil. Although the TFDE applied soil maintained slightly higher  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations over the control treatment, the difference was not significant. The  $\text{NH}_4^+$  concentration ranged between 1.2 to 2.7 mg kg<sup>-1</sup> soil for irrigated treatment and 1.4 to 2.4 mg kg<sup>-1</sup> soil for the control treatment whereas the  $\text{NO}_3^-$  ranged between 4 to 5.76 mg kg<sup>-1</sup> soil for the irrigated treatment and 3.7 to 5.2 mg kg<sup>-1</sup> soil for the control treatment.



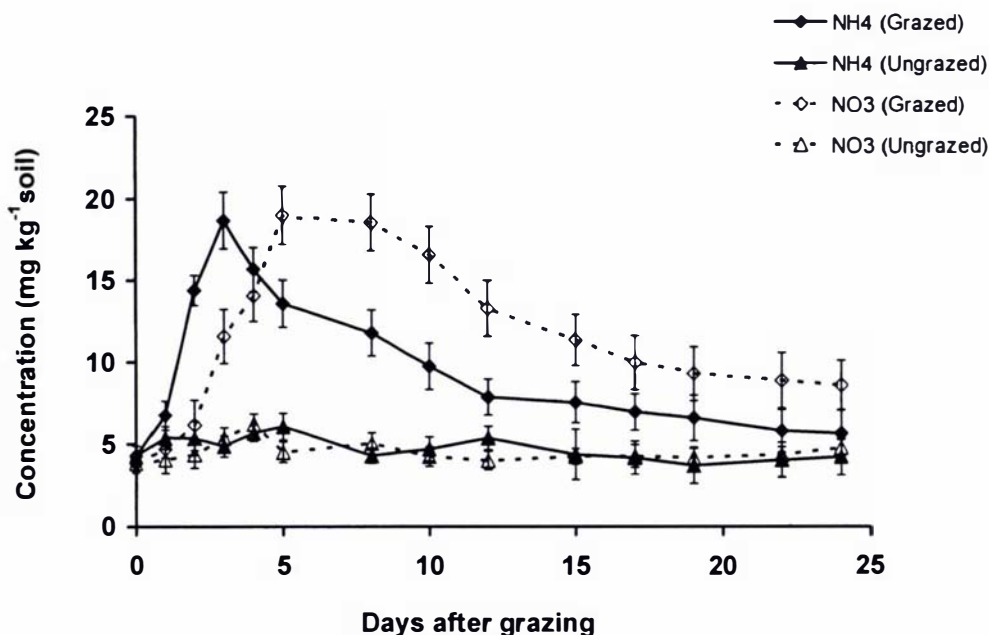
**Figure 6.8** Changes in soil mineral N concentrations (mg kg<sup>-1</sup> soil) during the monitoring period for the residual trial (Experiment D) on the Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

### 6.3.5.3 Grazing experiment

Figure 6.9 shows the trend in mineral N concentration in the pasture soil for a month following a grazing event. Overall both the NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentrations increased immediately after grazing and then decreased with time. The increase in NH<sub>4</sub><sup>+</sup> concentration from 4.26 to 18.69 mg kg<sup>-1</sup> soil occurred within 3 days after grazing. The rate of decrease was higher in the beginning but became stable 15 days after grazing. Significant differences in the concentrations were observed between the grazed and the ungrazed control treatments which lasted for 20 days after which no difference was observed. Overall the NH<sub>4</sub><sup>+</sup> concentrations ranged from 3.69 to 6.06 mg kg<sup>-1</sup> soil under the ungrazed control treatment.

The nitrate build-up started within a day after grazing. The rate of increase in NO<sub>3</sub><sup>-</sup> concentration was slow in the beginning but it increased after 3 days when the highest rate of increase of 5.42 mg kg<sup>-1</sup> soil d<sup>-1</sup> was observed. Peak NO<sub>3</sub><sup>-</sup> concentration of 19 mg kg<sup>-1</sup> soil was observed in the soil which was 3.1 times higher than the peak concentration under the control treatment. The concentration of NO<sub>3</sub><sup>-</sup> in the soil ranged

from 3.8 to 6.2 mg kg<sup>-1</sup> soil for the control treatment. NO<sub>3</sub><sup>-</sup> concentration from the grazed soil was significantly different from the control treatment for the whole of the measurement period.



**Figure 6.9** Changes in mineral N concentrations (mg kg<sup>-1</sup> soil) during the monitoring period for the grazing trial (experiment E) on Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

### 6.3.6 Dissolved organic carbon

Increases in the DOC concentration of the soil occurred with fresh effluent application and grazing (Figure 6.10, 6.11 & 6.12). This was as anticipated, because both the addition of the FDE and the excretal deposition after grazing are known to add large quantities of soluble carbon to the soil. However, there was no change in the DOC concentration in the residual irrigation experiment. The increase in the DOC concentrations varied among the three irrigations as well as after the grazing event.

#### 6.3.6.1 Fresh application experiment

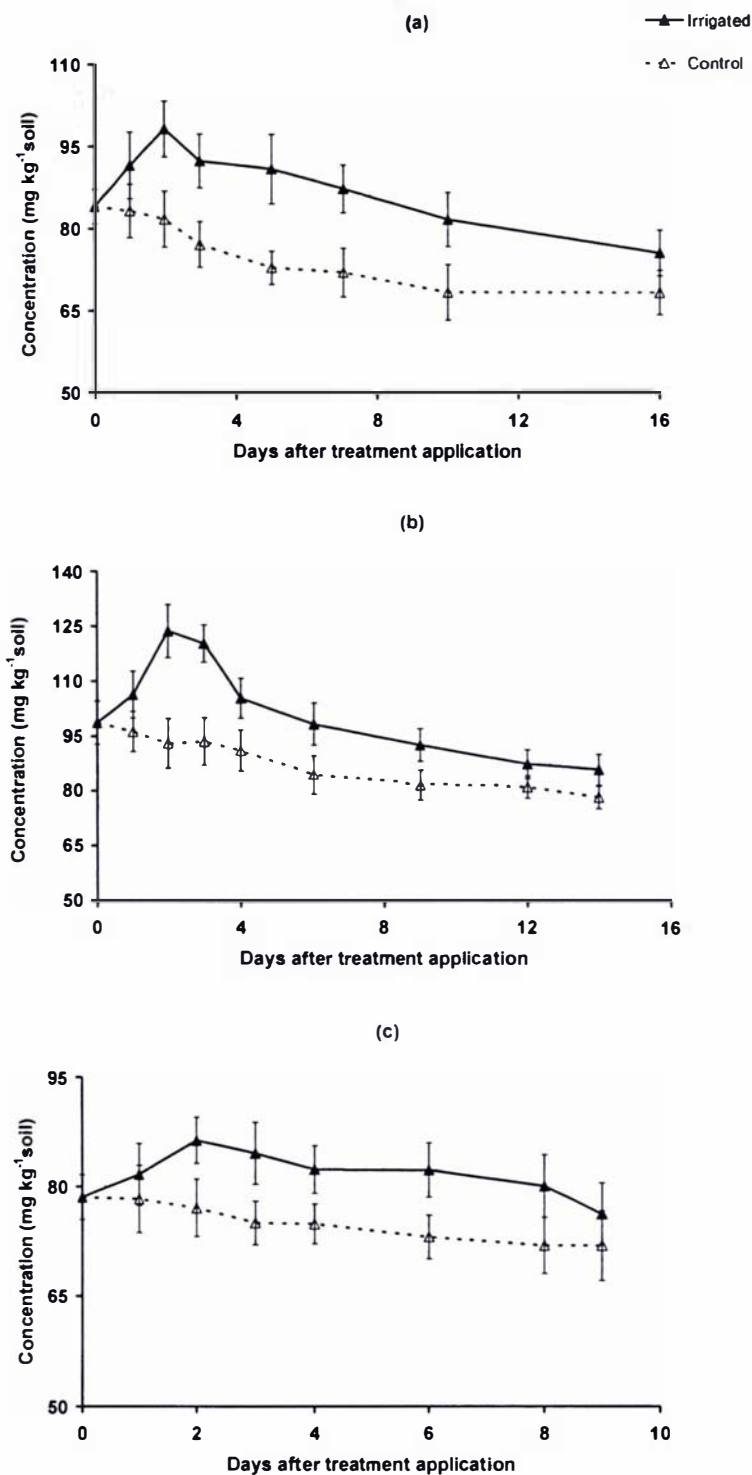
The trends in increase in the soil DOC levels immediately after the irrigations are shown in Figure 6.10a, b and c. For all the three applications, TFDE caused an

initial increase within a day of the application followed by a gradual decrease with time. Though the general trend was the same for all the three irrigations, some differences among the three events could be observed.

After the application of the first irrigation, DOC levels were found to increase rapidly within two days to the peak level of 98.3 mg kg<sup>-1</sup> soil, which was 1.2 times greater than the highest concentration observed under the control treatment. The concentration then started to decline immediately, reaching 75.6 mg kg<sup>-1</sup> soil after 16 days of the FDE application. The DOC concentration in the soil under the control treatment was found to fluctuate with time and an 18.7% decrease in the concentration was observed between the first and the last day of the measurement period. The effect of effluent was observed throughout the measurement period with significant differences observed between the two treatments.

The DOC concentrations measured during the second irrigation were higher than the other two irrigations. The concentration on day 1 of this irrigation was 25.9 and 43.2% higher than the first and the third irrigations, respectively. The concentrations during the entire measurement period ranged from 85.7 to 123.7 mg kg<sup>-1</sup> soil for irrigated and 78.1 to 98.7 mg kg<sup>-1</sup> soil for the control. The peak concentration for the irrigated treatment was 4.4 times higher than the total added DOC through effluent irrigation, indicating that effluent irrigation induced the mobilization of some of the native soil carbon. Also the excretal input from the grazing event occurring a day before the TFDE application added to the DOC concentration of the soil. By the end of the two weeks 87.7 mg kg<sup>-1</sup> soil of the DOC remained in the soil which was still significantly higher than that remaining in the control.

The third irrigation had the lowest concentration of DOC in the soil as can be seen from Figure 6.10c. Over the entire measurement period the values under the irrigated treatment ranged from 76.2 to 86.4 mg kg<sup>-1</sup> soil and 71.9 to 78.3 mg kg<sup>-1</sup> soil for the control treatment. The effect of FDE application on DOC concentration in the soil was observed for a week after the effluent application, after which the effect diminished.

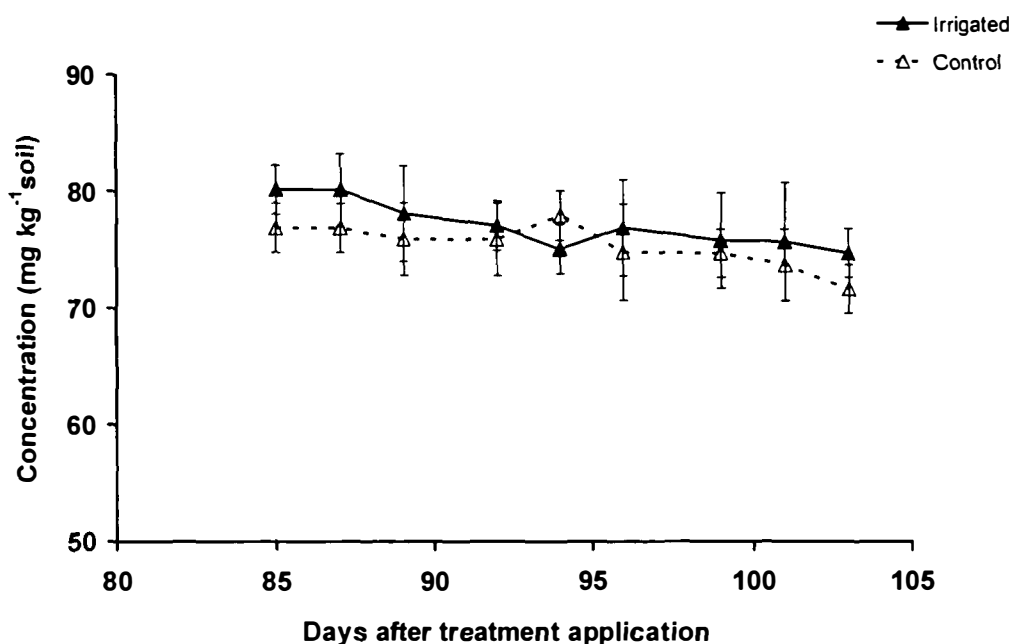


**Figure 6.10** Changes in soil DOC concentration (mg kg<sup>-1</sup> soil d<sup>-1</sup>) during the monitoring period for the (a) first (Experiment A) (b) second (Experiment B) and (c) third (Experiment C) effluent application event on Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars. Note the difference in the scale of Y axis

### 6.3.6.2 Residual experiment

The residual effect of the FDE irrigation on DOC was monitored 12 weeks after the application of the effluent (Figure 6.11). No residual effect of TFDE application was observed on the DOC concentration, while the irrigated and the unirrigated control site was having similar DOC concentrations. The DOC concentration from the irrigated site ranged from 74.7 to 80.1 mg kg<sup>-1</sup> soil whereas that from the control treatment ranged from 71.7 to 76.9 mg kg<sup>-1</sup> soil.

Overall, the DOC concentrations for both the irrigated and the control were found to decrease with time, the average rate of decrease being higher for irrigated (0.29 mg kg<sup>-1</sup> soil d<sup>-1</sup>) than control (0.04 mg kg<sup>-1</sup> soil d<sup>-1</sup>). The percent decrease in the concentrations from the first to the last measurement day was 6.8% for both the irrigated and the control sites.

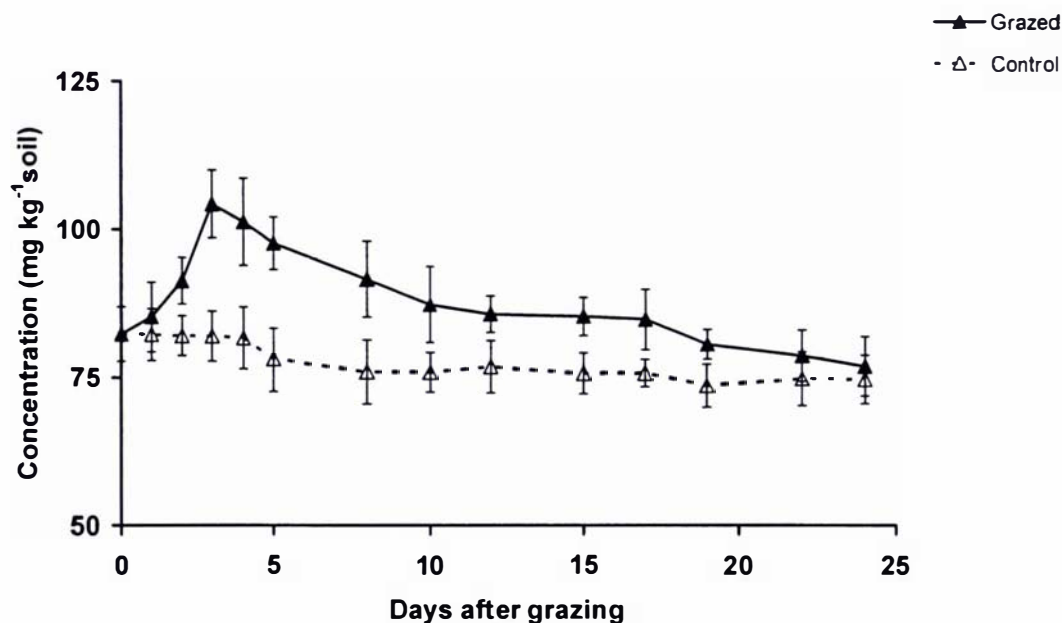


**Figure 6.11** Changes in soil DOC concentration (mg kg<sup>-1</sup> soil d<sup>-1</sup>) during the monitoring period for the residual trial (experiment D) on Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars

### 6.3.6.3 Grazing experiment

The effect of the grazing event on the DOC concentration in the soil is shown in Figure 6.12. A rapid increase in the DOC concentrations was observed after the grazing event with the highest concentration of 104.3 mg kg<sup>-1</sup> soil was attained 3 days after the grazing. Thereafter the concentration started to decrease with 76.9 mg kg<sup>-1</sup> soil DOC concentration remaining by the end of the experiment. The rate of decrease in the DOC concentration was higher for the grazed site (0.28 mg kg<sup>-1</sup> soil d<sup>-1</sup>) than that for the ungrazed control site (0.15 mg kg<sup>-1</sup> soil d<sup>-1</sup>). The DOC concentration ranged between 76.9 to 104.3 mg kg<sup>-1</sup> soil and 74.7 to 82.4 mg kg<sup>-1</sup> soil for the irrigated and the control treatment. The peak DOC concentration in the soil that had been grazed was 1.3 times higher than that of the control soil.

A large amount of carbon is added through the excreta of the grazing animals which causes an increase in the DOC levels in the soil (Petersen *et al.* 1996). However, high variability was observed in the grazed site while measuring the DOC concentrations which was due to the uneven distribution of the animal excreta during grazing.



**Figure 6.12** Changes in soil DOC concentration (mg kg<sup>-1</sup> soil d<sup>-1</sup>) during the monitoring period for the grazing trial (experiment E) on the Tokomaru silt loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars



### 6.3.7 Dry matter yield

Table 6.5 shows the pasture DM response to the three FDE irrigations and to the grazing event. It is evident that both the effluent irrigation and the grazing increased the DM yield of the pasture, though the increase was not significant for the third effluent irrigation trial and the grazing trial. For the rest of the experiments, the effect of the addition of nutrients through the animal excreta in the form of effluent or directly through grazing cattle could be seen in an increase in pasture growth. The yield response, expressed as kg DM kg<sup>-1</sup> N was the highest for the second irrigation. The DM yields for the three irrigations were 2, 2.2 and 1.9 times higher than the DM obtained from the respective unirrigated controls.

**Table 6.5** Total DM yield, percent of added N in DM and DM response to the added N for the experiments. The values in the bracket represent the standard error of mean of the four replicates

Experiment	Treatment	Monitoring period (Days)	Total DM (kg ha <sup>-1</sup> )	N added (kg ha <sup>-1</sup> )	DM response (kg DM kg <sup>-1</sup> N)
Fresh application					
First	Irrigated	14	204 (±45)	23.9	4.4
	Control	14	102 (±35)	Nil	—
Second	Irrigated	15	251 (±56)	25.2	5.5
	Control	15	113 (±51)	Nil	—
Third	Irrigated	10	135 (±30)	18.0	3.6
	Control	10	70 (±33)	Nil	—
Residual	Irrigated	19	131 (±42)	Nil	—
Experiment	Control	19	112 (±37)	Nil	—
Grazing	Grazed	23	173 (±87)	11.6	3.3
Experiment	Control	23	135 (±56)	Nil	—

No significant difference was observed between the DM yields of the irrigated and the control treatments of the residual experiment. Although the irrigated field maintained a higher DM compared to the control site, as the difference was not

significant, we can say that no residual effect of the effluent irrigation was observed on the DM yield of the pasture.

In the grazing experiment the increase in DM yield from the grazed site was 1.3 times that of the ungrazed control though the two treatments were not significantly different from each other. The variability (as observed from the SE bars) for the grazed pasture was higher than that observed in the control site. This high variability can be attributed to the uneven distribution of the animal excreta during the time of the grazing. The yield response to the excretal deposition during the grazing event was less than that observed from the irrigated site (average of the effluent three irrigations) (Table 6.5).

Farm effluent application commonly increases pasture yield (Bolan *et al.* 2004a; Wang *et al.* 2004), although the response may be influenced by factors such as application rate, application method, application time (season), soil fertility and climatic conditions (Ball & Field 1982; Lowe 1993; Di *et al.* 1998). For example, Goold (1980) recorded 43% increase in the pasture yield when irrigated with FDE (irrigated at 12 mm depth after every 27 days) with a total of 156 kg N ha<sup>-1</sup> year<sup>-1</sup>. The increase in the dry matter yield with the application of the effluent can be attributed to the addition of both the water and the nutrients through effluent irrigation. Since we did not include a control water treatment, it was not possible to isolate the effect of water on the DM yield in the pasture. However, the DM yield response to effluent irrigation has often been attributed to the supply of both the nutrients, especially N and water (Cameron *et al.* 1997).

The non significant increase in the DM yield from the grazed pasture could be attributed to the treading effect of the grazing cattle. Treading plays an important role in reducing pasture production with pasture productivity getting reduced by 30% to as high as 90% (Singleton & Addison 1999).

## 6.4 General Discussion

The addition of the FDE to dairy pastures, under normal farming conditions, caused significant increases in the N<sub>2</sub>O emissions for all the three irrigation events. A 1.5, 2.8 and 12.6 fold increase in the emission was observed during the first, second and third application compared to the unirrigated site. Similar increases in N<sub>2</sub>O emissions with the application of animal wastes have been reported in other studies as well

(Lowrance *et al.* 1998; Arcara *et al.* 1999; Chadwick *et al.* 2000; Barton & Schipper 2001). Barton & Schipper (2001) attributed FDE-induced increases in N<sub>2</sub>O to the supply of C, N and water. In our experiment we have found that although the SWC prior to effluent irrigation varied among the irrigation events, the WFPS of the 0-5 cm soil depth was above the field capacity for most of the measurement periods after all the three irrigations (Figure 6.3a and b). Denitrification typically is thought to proceed at optimal rates above 60% WFPS (Linn & Doran 1984). Over the entire measurement period, WFPS exceeded 60% for all the three effluent applications. This shows that most of the N<sub>2</sub>O emission might have been derived from the denitrification process rather than the nitrification process.

In the first two irrigations the WFPS of the unirrigated control was > 0.70 and thus the addition of the water through FDE would not have caused any significant effect on the N<sub>2</sub>O emission. During the third irrigation the WFPS was slightly lower (0.68 - 0.77) than the other two irrigations. A significantly higher rate of denitrification at higher soil moisture levels has been observed in soils amended with liquid manure (Loro *et al.* 1997). We can interpret from the results that moisture content played a greater role in the third irrigation than the other two irrigations. Hence, during the third irrigation an increase in N<sub>2</sub>O was due to the combined effect of the water, N and DOC inputs in the FDE, which has been discussed thoroughly in Section 4.4 of Chapter 4.

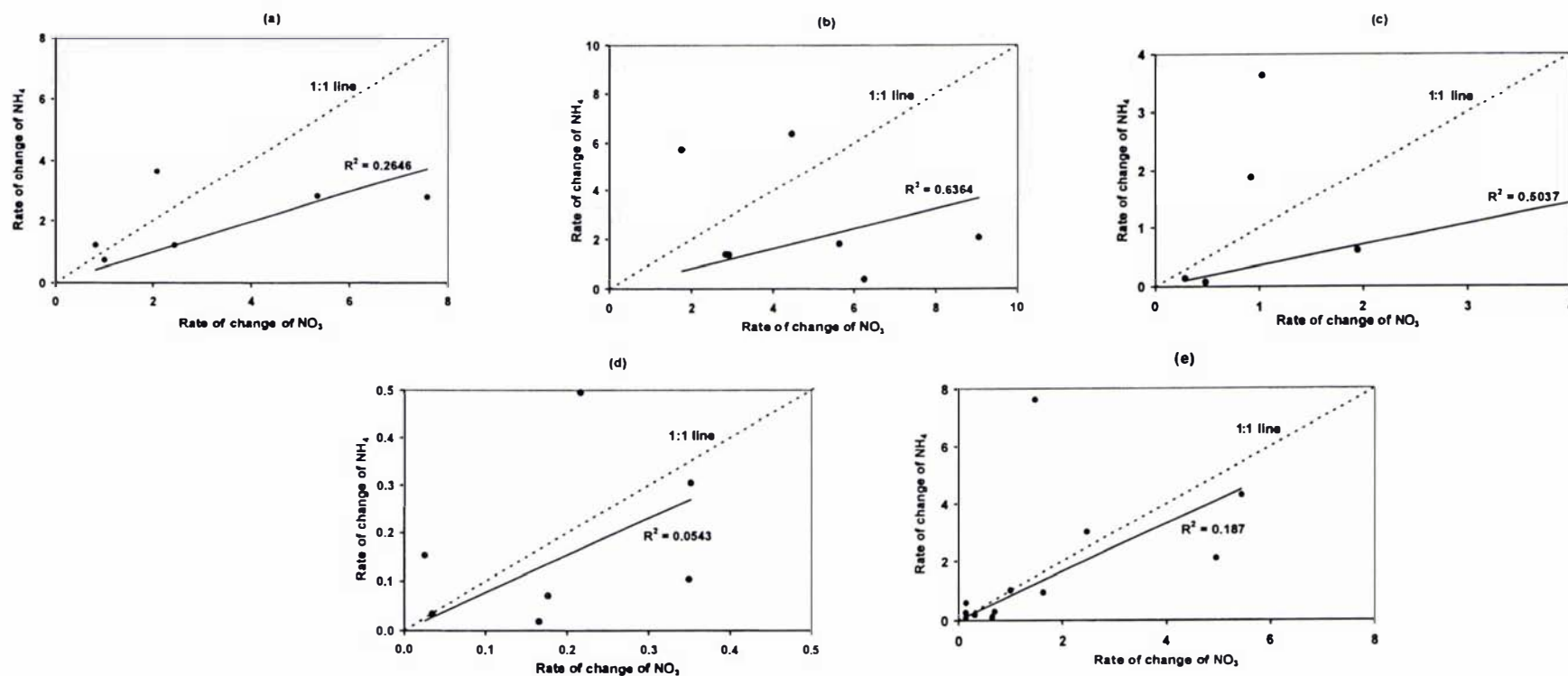
The N<sub>2</sub>O emissions from TFDE application to the soils are highly dynamic. They vary with effluent quality and the time of effluent application (Sommer *et al.* 1996) and also with the time after application. The emissions are highest immediately after the application and then decrease with time (Watanabe *et al.* 1997), which is consistent with the post TFDE application N<sub>2</sub>O emission rates reported in this Chapter.

Comfort *et al.* (1990) found that the emission of N<sub>2</sub>O was greater immediately after the FDE application followed by a shift to N<sub>2</sub>. Previous work found that FDE application increased N<sub>2</sub>O fluxes for only a short duration, with the flux returning to the background level within 3 to 48 hrs of the FDE application (Barton & Schipper 2001). However Clough & Kelliher (2005) observed no increase in N<sub>2</sub>O emission with the FDE application, which they attributed to the low level of the N application (1.5 kg ha<sup>-1</sup>).

Comparing the emission from the three effluent applications, it was observed that the emission from the second irrigation was higher than that from the other two

applications. Since the composition of the fresh TFDE was more or less similar for all the three applications, the difference in the N<sub>2</sub>O emissions could be attributed to the difference in the effluent loading and other management and climatic factors preceding and during the effluent irrigation events. A grazing event preceded the second effluent application and the excretal deposition and the compaction caused by the grazing cattle could have led to increased emission. This could have increased the relative concentrations of inorganic N in the soil for denitrification. The concentration of the mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) was higher in both the control and the irrigated treatments for the second irrigation than for the other two irrigation events. The combined effect of TFDE-borne and grazing animal excretal-borne substrates (C and N) and the mobilization of these substrates from the soil resulting from TFDE application and excretal deposition, must have led to an increase in the emission. The difference in the N<sub>2</sub>O emissions between the first and the third effluent applications could also be explained on this basis as first effluent application took place a week after the paddock had been grazed.

An examination of the graphs relating to the rate of change of the NH<sub>4</sub><sup>+</sup> with that of NO<sub>3</sub><sup>-</sup> after effluent application (Figure 6.13a, b and c) indicates that the build up of NO<sub>3</sub><sup>-</sup> was higher than the change in the concentration of NH<sub>4</sub><sup>+</sup>. The excretal N that had been added in the soil during the grazing must have undergone mineralization by the time the effluent was added. The priming effect of urine and dung addition during grazing could have led to the mineralization of some of the organic N present in the soil, leading to the addition in the NO<sub>3</sub><sup>-</sup> pool. The regression line relating the rates of change in the mineral concentration of the third application was close to the 1:1 line showing that no source other than the effluent was affecting the N<sub>2</sub>O emission. This observation further substantiates that the soil N priming effect occurred in the first two effluent applications. Clough & Kelliher (2005), while examining the combined effect of the FDE and cattle urine application on the N<sub>2</sub>O emission, observed that there was a large scale priming effect in the soil for both N and C, and attributed it to either the solubilisation of the soil organic matter due to increased pH from the hydrolysis of the urine urea (Sen & Chalk 1993), or due to the N applied in the urine itself (Clough & Kelliher 2005).



**Figure 6.13** Relationship between rate of change of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentration (absolute values) ( $\text{mg N kg}^{-1} \text{ soil d}^{-1}$ ) during the monitoring period for the (a) first (b) second and (c) third fresh effluent application event (d) residual trial and (e) grazing trial on Tokomaru silt loam (For the purpose of clarity all the data points are not shown in some of the figures)

It remains unclear, however, why the effect of grazing was not observed in the first application though the site had been grazed a week before the effluent application. Although the cumulative emission from the first application was higher than the third application (not been grazed) the percent of added N emitted was higher for the latter. Clough & Kelliher (2005) in their study observed that the FDE applied a week after the urine addition produced higher N<sub>2</sub>O emissions than the treatment where FDE had been applied alone. A similar observation can be made where the emissions from the first irrigation (which had been grazed a week earlier) were higher than the third irrigation (no grazing) though these differences cannot be attributed only to the grazing effect as other soil (WFPS, depth of irrigation) and environmental (rainfall, temperature) factors would have played their role in the higher emission from the first irrigation event.

The correlation between the soil properties (WFPS, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and DOC concentration in soil) and the N<sub>2</sub>O emission for the 3 applications show that the N<sub>2</sub>O emission from the second irrigation showed a high degree of correlation with all the soil properties (Table 6.6). Among the soil properties, the correlation was highest with the NH<sub>4</sub><sup>+</sup> concentration. Nitrous oxide emission showed poor correlation with most of the soil properties for the other two applications. A poor correlation between the N<sub>2</sub>O emissions and soil properties has been observed in other studies as well (Clayton *et al.* 1997; Barton & Schipper 2001) and could be attributed to the same reasons given in Section 3.4 of Chapter 3.

Comparing the N<sub>2</sub>O emissions from the effluent application to that of the grazed pasture (Table 6.4), it was observed that the emission factor for the grazing was comparable to the first and the third irrigation but was less than half of the second application. This could be because of the combined effect of the grazing and effluent application in the second application. Grazing is known to increase the N<sub>2</sub>O emission because of the addition of the excreta from the grazing animals (Yamulki *et al.* 1997; Saggarr *et al.* 2002). The high N concentration, the form of the N compounds and the subsequent N transformations, all contribute to these high losses during grazing (Oenema *et al.* 1997). There are additional effects caused by the grazing animals, such as treading and trampling, which cause compaction of the soil (Donkor *et al.* 2002) and potentially enhance N<sub>2</sub>O emissions from grasslands. This aspect has been covered in detail in Chapter 3 of this thesis.

Significant correlations were observed between the N<sub>2</sub>O emissions from the grazed pasture and the soil NO<sub>3</sub><sup>-</sup> concentration ( $p \leq 0.001$ ) and ( $p \leq 0.05$ ) (Table 6.6). This indicates that denitrification is the main mechanism by which N<sub>2</sub>O was produced in this experiment. A significantly higher correlation of N<sub>2</sub>O emission with NO<sub>3</sub><sup>-</sup> than with NH<sub>4</sub><sup>+</sup> has also been reported by Allen *et al.* (1996) during a grazing event in the autumn-winter season, although they did not observe any correlation between N<sub>2</sub>O emissions and soil mineral N during the spring and summer seasons. It has been reported that an uneven excretal distribution in the soil by the grazing animals leads to large spatial variability in N<sub>2</sub>O emission (Carran *et al.* 1995; Choudhary *et al.* 2002; Saggarr *et al.* 2004a) which will influence its correlation with the soil parameters if the different measured observations are spatially unique.

**Table 6.6** Correlation coefficients for relationships between N<sub>2</sub>O emission and soil properties for the irrigation and grazing experiments on Tokomaru silt loam. \*\*\*, \*\*, \* depicts level of significance at <0.001, <0.01 and <0.05, respectively. (N<sub>2</sub>O = kg N ha<sup>-1</sup>d<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and DOC = mg kg<sup>-1</sup> soil)

Experiment	Soil properties			
	WFPS	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	DOC
Fresh application				
First Irrigation (A)	0.49	0.43	0.60	0.59
Second Irrigation (B)	0.95**	0.73*	0.98***	0.85**
Third Irrigation (C)	0.48	-0.03	0.83*	0.72
Residual Experiment (D)	-0.54	0.94***	0.83**	0.69*
Grazing Experiment (E)	0.63*	0.93***	0.41	0.55

The absence of any residual effect of TFDE application on N<sub>2</sub>O emission in experiment D could be attributed to the lack of supply of the effluent-borne mineral N and DOC in the soil. The rate of mineralization of both the effluent derived N and C was fast, resulting in the loss of these substrates by the time monitoring for the N<sub>2</sub>O started. Comfort *et al.* (1990) observed a minimal increase in N<sub>2</sub>O emission 25 days after the liquid dairy manure application, possibly due to a limitation in readily

oxidizable C. They found that only 10 to 15 days were required for the readily oxidizable C to be metabolised. N<sub>2</sub>O emission in the residual trial (experiment D) was found to have a high degree of correlation with all the soil properties however it was negatively correlated with WFPS which may reflect the already cool wet soil conditions existing in June. The regression equation which showed NO<sub>3</sub><sup>-</sup> and DOC as the two significant parameters was able to explain 91% of the variability in the emission values.

The step up linear regression analysis for all three experiments is presented in Table 6.7. The results for the regression analysis for the fresh application of the effluent varied among the irrigation events. 96% of the variability is accounted for by the regression equation in the second application, only 69% is accounted for in the third application and the R<sup>2</sup> value is non-significant in the first application. Combining the data for the three applications together, the equation covers almost 80% of the variability, although the soil NH<sub>4</sub><sup>+</sup> concentration was the only parameter significant among all the soil properties.

**Table 6.7 Results of the multiple linear regression analysis relating N<sub>2</sub>O emission and various soil properties, for all the experiments on Tokomaru silt loam. (N<sub>2</sub>O = kg N ha<sup>-1</sup>d<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and DOC = mg kg<sup>-1</sup> soil)**

Treatment	Regression Equation	No. of observations	R <sup>2</sup>
Fresh application			
First Irrigation	N <sub>2</sub> O = 0.048 + 0.002 NH <sub>4</sub> <sup>+</sup>	112	0.41 NS
Second Irrigation	N <sub>2</sub> = 1.038 - 1.871 WFPS - 0.002 NO <sub>3</sub> <sup>-</sup> + 0.032 NH <sub>4</sub> <sup>+</sup> 0.005 DOC	128	0.96***
Third Irrigation	N <sub>2</sub> O = 0.152 - 0.018 NO <sub>3</sub> <sup>-</sup> - 0.006 NH <sub>4</sub> <sup>+</sup> + 0.029 DOC	112	0.69*
Residual Trial	N <sub>2</sub> O = -0.228 + 0.054 NO <sub>3</sub> <sup>-</sup> + 0.038 DOC	144	0.89***
Grazing Trial	N <sub>2</sub> O = -0.003 - 0.002 NO <sub>3</sub> <sup>-</sup> - 0.003 NH <sub>4</sub> <sup>+</sup> + 0.005 DOC	208	0.87***

The land irrigation of TFDE in all three irrigations led to a significant increase in N<sub>2</sub>O emission, causing significant loss of N from the soil. Such high variations in the



three fresh effluent applications in terms of the N<sub>2</sub>O emission and other soil properties could be, as discussed earlier, due to the difference in the effluent loading rates. In general, higher rates of the TFDE lead to higher N<sub>2</sub>O emission.

## 6.5 Conclusions

- Nitrous oxide emission from grazed dairy pasture was enhanced following the application of treated farm dairy effluent.
- The emission factor for the three irrigation events ranged from 2 to 4.9.
- Effluent irrigation increased N<sub>2</sub>O emissions for a short duration (9 to 16 days), and no long-term residual effect on the emissions was observed.
- High N<sub>2</sub>O emission (with an emission factor of 2) was measured after a grazing event with the effect of grazing observed for 3 weeks.
- Delaying effluent-irrigation after a grazing event could reduce emissions by reducing the levels of surplus mineral-N.

It is clear from the results obtained in various chapters of the thesis that the processes and the factors governing the N<sub>2</sub>O emission, especially from the grazed effluent irrigated pasture are complex. It would therefore require extensive site-specific measurements to be made at the field level to accurately quantify N<sub>2</sub>O fluxes at an ecosystem level. An alternative approach is the use simulation models to provide an estimate of N<sub>2</sub>O emission, and is the focus of next chapter.

## Chapter 7

# Modelling nitrous oxide emission from grazed pasture soils irrigated with farm dairy effluent

### 7.1 Introduction

The nitrous oxide exchange between the soil and the atmosphere is not difficult to measure, but high spatial and temporal variability on a field scale makes extrapolation to larger scales problematic.

The N<sub>2</sub>O emission data collected in previous chapters correlated with a range of factors such as WFPS, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> etc. but no single correlation was able to predict the emission for all the measurements because these empirical relationships do not account for the mechanisms that are involved in the production of N<sub>2</sub>O from the soil. The spatial covariation of N<sub>2</sub>O emission with soil properties is complex (Lark *et al.* 2004) as well as scale dependent (Groffman & Tiedje 1989) and hence cannot be predicted by these conventional analysis of soil characteristics (Ambus 1998). A process based approach is therefore required that accurately quantifies N<sub>2</sub>O emissions at the field level.

The use of mathematical models, which simulate the biological, physical and chemical processes governing N flows and fluxes in an ecosystem are desirable for scenario simulations for the purpose of testing mitigation options for greenhouse gases (Dalal *et al.* 2003). Such models are needed to develop regional and national scale inventories of greenhouse gases with a known level of uncertainties (Saggar *et al.* 2004a). A large number of models such as DNDC (Li *et al.* 1992), DayCent (Parton *et al.* 1996; Del Grosso *et al.* 2001), CASA (Potter *et al.* 1996), Expert-N (Engel & Priesack 1993), NCSOIL (Molina *et al.* 1983; Nicolardot & Molina 1994), DAISY (Hansen *et al.* 1990, 1991), CANDY (Franko 1995; Franko *et al.* 1995) etc have been developed to simulate N<sub>2</sub>O fluxes from natural and managed ecosystems. The process-oriented models (DNDC, CASA, DayCent) simulate the gas fluxes of N<sub>2</sub>, N<sub>2</sub>O

and NO<sub>x</sub> from nitrification and denitrification and include a detailed descriptions of the effect of various factors on N gas fluxes.

One such process based model is DNDC, which couples decomposition and denitrification processes as influenced by the soil environment, to predict emissions from agricultural soils (Li *et al.* 1992). DNDC has reasonable data requirements, using commonly available climate, soil and agricultural practice data as input and has been used for regional estimates of N<sub>2</sub>O production for the US (Li *et al.* 1996), China (Li *et al.* 2001), Canada (Smith *et al.* 2002), Germany (Butterbach-Bahl *et al.* 2001) and the UK (Brown *et al.* 2002).

Based on the comparisons of several models against selected field data sets, DNDC consistently ranked as one of the top models (Smith *et al.* 1997; Frolking *et al.* 1998). A group of Canadian researchers recently tested DNDC and CENTURY/DAYCENT focussing on N<sub>2</sub>O fluxes and adopted DNDC for their N<sub>2</sub>O inventory calculations (Smith *et al.* 2002; Grant *et al.* 2004; Smith *et al.* 2004). Similar tests were conducted in several European countries. Based on their tests, the researchers from a group of EU countries have adopted DNDC for N<sub>2</sub>O inventories (Brown *et al.* 2001b; Butterbach-Bahl *et al.* 2001; Brown *et al.* 2002). Kiese *et al.* (2005) have used it to estimate the N<sub>2</sub>O source strength of tropical rainforests in the wet tropics of Australia.

The DNDC model has been, modified to represent New Zealand grazed pastoral systems and is called the NZ-DNDC model (Andrew *et al.* 2003; Giltrap *et al.* 2004; Saggar *et al.* 2004a). Research is continuing to further adapt this model to enhance its ability to simulate the changes in N<sub>2</sub>O emissions resulting from current mitigation strategies such as the use of nitrification inhibitors.

The NZ-DNDC model however, has not been adapted to simulate the changes in N<sub>2</sub>O emission resulting from the TFDE irrigation. Increased N<sub>2</sub>O emissions have been reported from the land application of farm effluents (Russell *et al.* 1991; Whalen 2000) as is also evident from the results presented in the previous chapters in this thesis. This chapter investigates the suitability of the NZ-DNDC model for assessing the amount of N<sub>2</sub>O emission from TFDE irrigation in a dairy grazed pasture. Model simulations for the dairy grazed pasture with and without TFDE irrigation are compared with the measured emissions recorded during three irrigation events. The specific objective of this chapter is:

- To assess the ability of NZ-DNDC to simulate N<sub>2</sub>O emissions from pasture irrigated with TFDE.

## 7.2 Model Description

The denitrification decomposition (DNDC) model developed and described by Li *et al.* (1992) is a process oriented model of soil C and N biogeochemistry. The model forms a bridge between global C and N biogeochemical cycles and the basic ecological drivers of the C and N cycles in the soil (Figure 7.1).

The model consists of four sub models: thermal-hydraulic, crop growth, decomposition, and denitrification. The thermal-hydraulic sub model uses daily meteorological data to predict soil temperature and moisture profiles and to capture anaerobic microsite formation and sequential substrate reduction. The crop growth sub model simulates the growth of the crops from sowing until the harvest. The crop growth helps to calculate the transpiration losses using crop-specific water-use-efficiency parameters. The third sub-model is the decomposition sub model, which consists of four soil carbon pools- litter, labile humus, passive humus and microbial biomass; each pool having fixed decomposition rates and C:N ratio. The decomposition process leads to the addition of nitrogen to the inorganic pool, and carbon, which gets re-assimilated in the microbial biomass each day. The N entering the inorganic pool undergoes nitrification, plant uptake, leaching, ammonia volatilisation or adsorption onto clay minerals.

The denitrification sub model is responsive to available NO<sub>3</sub><sup>-</sup> and the soluble carbon provided by the decomposition sub model, rain events, changes in soil moisture and cold temperatures. Although the crop growth and decomposition sub models operate on a daily time-step, the denitrification sub model operates on an hourly time-step.

DNDC has default parameters for soil water content at field capacity and wilting point as a function of soil texture. The model uses a multi-layered soil for simulating soil water conditions. The schematic description of the sub models operating in the DNDC model and the factors influencing the operation of DNDC are shown in Figure 7.2.

## 7.3 Material and Methods

Nitrous oxide emissions and related soil (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, WFPS and soluble C) and environmental (rainfall, air temperature, soil temperature) parameters were monitored for two to three weeks following the TFDE irrigation in September 2003 (first irrigation, experiment A), January (second irrigation, experiment B) and February 2004 (third irrigation, experiment C) to quantify the effect of TFDE irrigation on N<sub>2</sub>O emission and are described in Chapter 6 of this thesis. During the first TFDE application, about 30% (8mm) of the total applied TFDE (25mm) was lost as surface runoff (Houlbrooke *et al.* 2004). However, no surface runoff occurred during the second and third applications.

There was 56.4, 63.8 and 17mm of rainfall preceding the first, second and third TFDE application, respectively. Therefore, the soil was wetter at the time of the first and second irrigations than at the time of the third irrigation. Also more rain was received during the measurement periods following first and second irrigations (96.4mm and 80.2mm) than following the third irrigation (7.2mm). The WFPS at the first and second irrigations was 0.71 and 0.68 and at the third TFDE application it was 0.57. The mean air temperatures during the first, second and third irrigations were 12.1, 19.9 and 12.8°C, respectively.

The paddock was grazed 8 days before the first irrigation by 112 cattle for 12 hours; 1 day before the second irrigation by 135 cattle for 12 hours; and 22 days before the third TFDE irrigation by 135 cattle for 12 hours.

### 7.3.1 Input parameters for NZ-DNDC model

The NZ-DNDC model was used to simulate N<sub>2</sub>O emission for the grazed pasture with and without TFDE irrigation. This is the first time that this model has been used to assess the changes in N<sub>2</sub>O emission with TFDE irrigation for a dairy grazed pasture.

The model input parameters are given in Figure 7.3. Some parameters have built in model values, e.g. the amount of excretal input by grazing animals, which is estimated from the animal type, animal number and grazing period. Also the model calculates the WFPS and infiltration values from the input parameters. For climate inputs the text files with data arranged in Julian days, mean air temperature (°C) and rainfall (mm) are used. Other input parameters describing the soil are the land use type as moist pasture; soil texture as silt loam; bulk density of 1.01 mg cm<sup>-3</sup>; soil pH of 5.9; a

field capacity soil water content of 0.60 and a soil organic C concentration of 0.036 kg C kg<sup>-1</sup>soil.

The current model does not have TFDE application as a separate input. Therefore, the TFDE input was simulated as simultaneous application of manure, fertiliser and irrigation. The TFDE used in this study contained about 75% of N as NH<sub>4</sub><sup>+</sup> and the remaining as organic N. The total N input was split accordingly into the inorganic and organic N (75:25). Inorganic N input was ammonium-N and organic N as manure. The addition of water from TFDE was irrigation input. The amount of N added as inorganic N and organic N and the irrigation for each TFDE application period is given in Table 7.1.

The model was run both for the unirrigated grazed and TFDE irrigations. The parameters used for the unirrigated and the TFDE treatments were the same except for the N and water addition. The input data files along with the climate files are presented in Appendix 2.

**Table 7.1** Amounts of N added and the rate of irrigation during the three treated farm dairy effluent application events (experiment A, B and C)

<b>Irrigation event</b>	<b>Inorganic N (kg N ha<sup>-1</sup>)</b>	<b>Organic N (kg N ha<sup>-1</sup>)</b>	<b>Total N (kg N ha<sup>-1</sup>)</b>	<b>C:N ratio</b>	<b>Irrigation depth (mm)</b>
First (15 <sup>th</sup> Sep. 2003)	18.9	6.3	23.9	9.5	25
Second (28 <sup>th</sup> Jan 2004)	15.7	5.3	25.2	9.5	21
Third (24 <sup>th</sup> Mar, 2004)	12.0	4.0	18	9.5	16

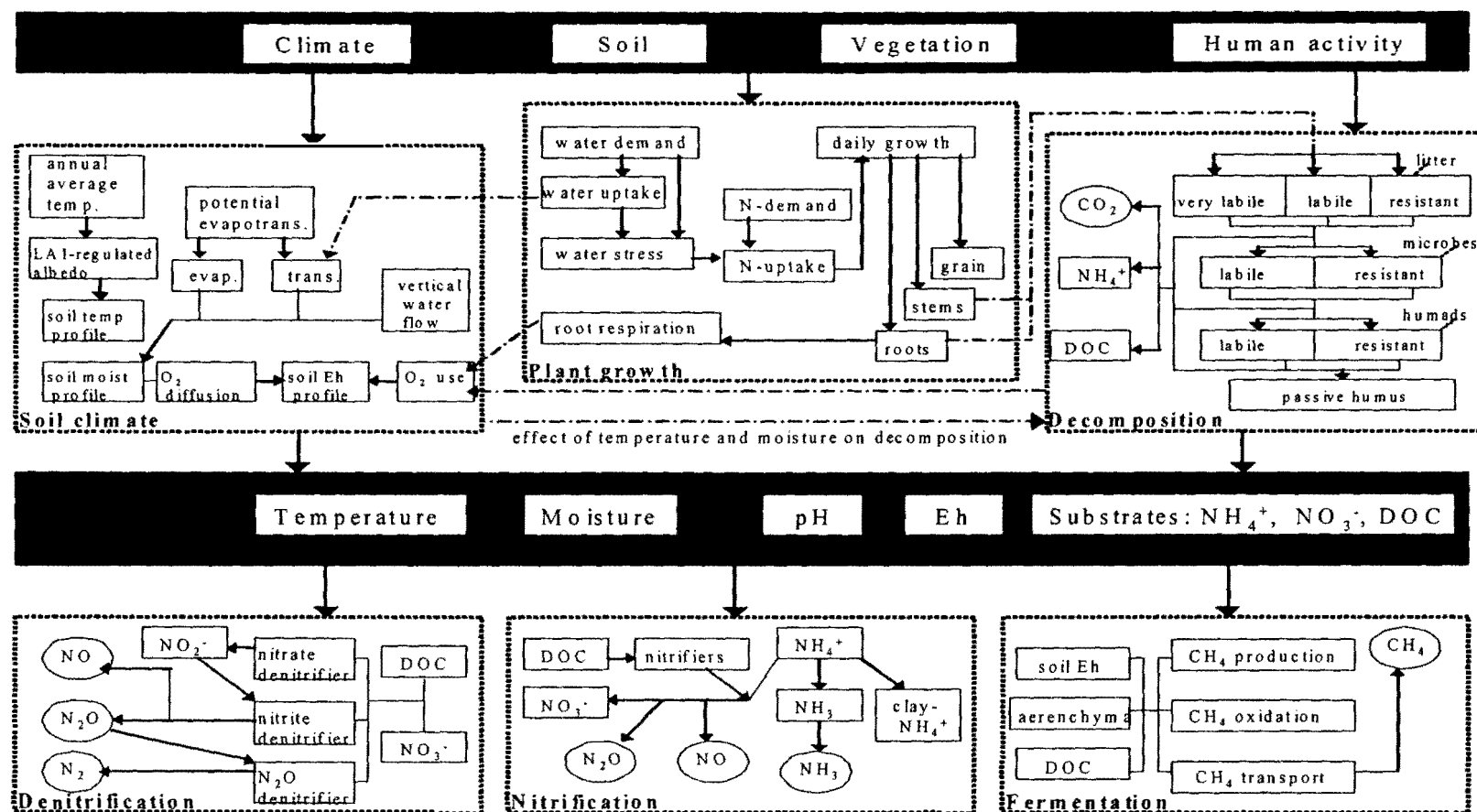
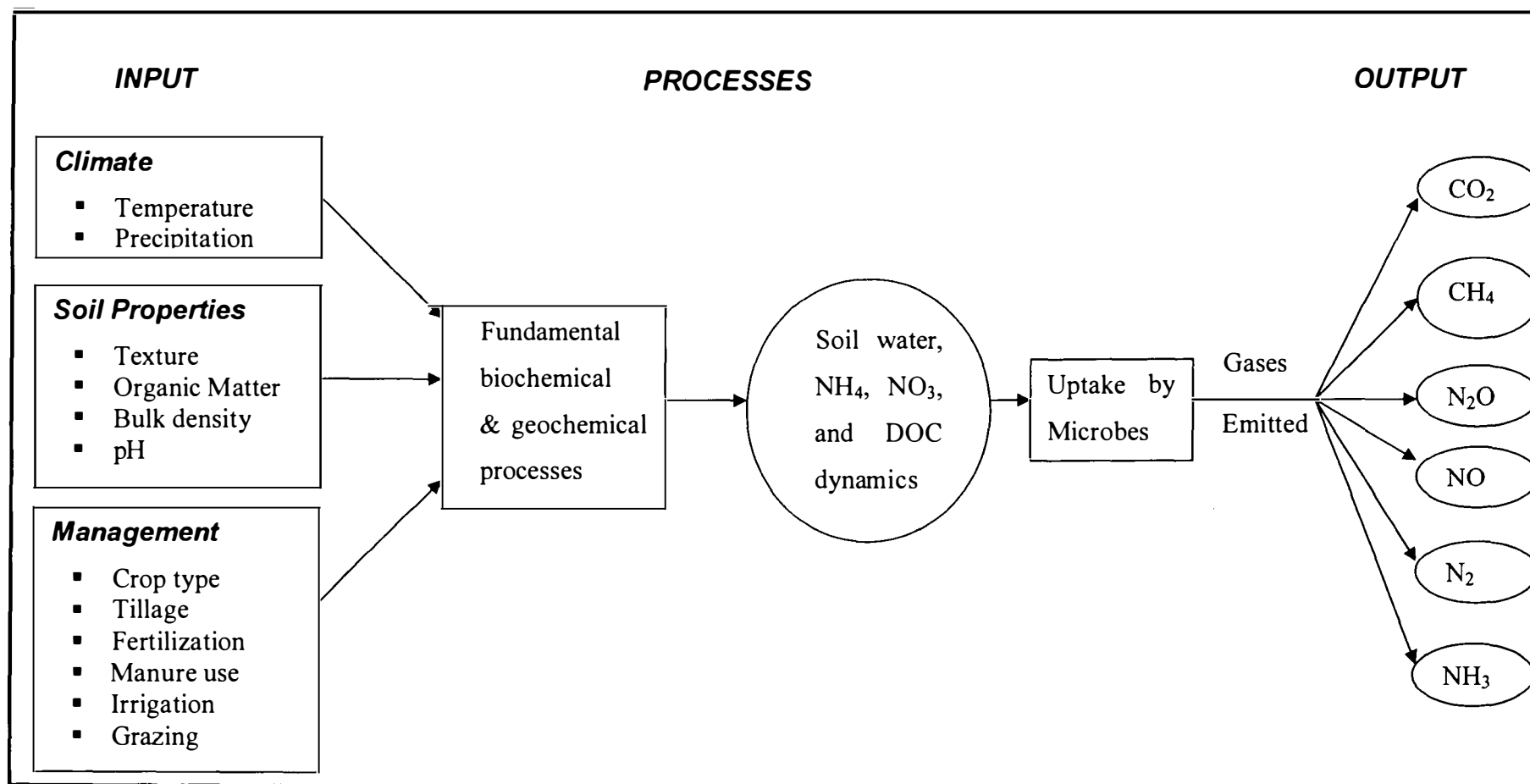
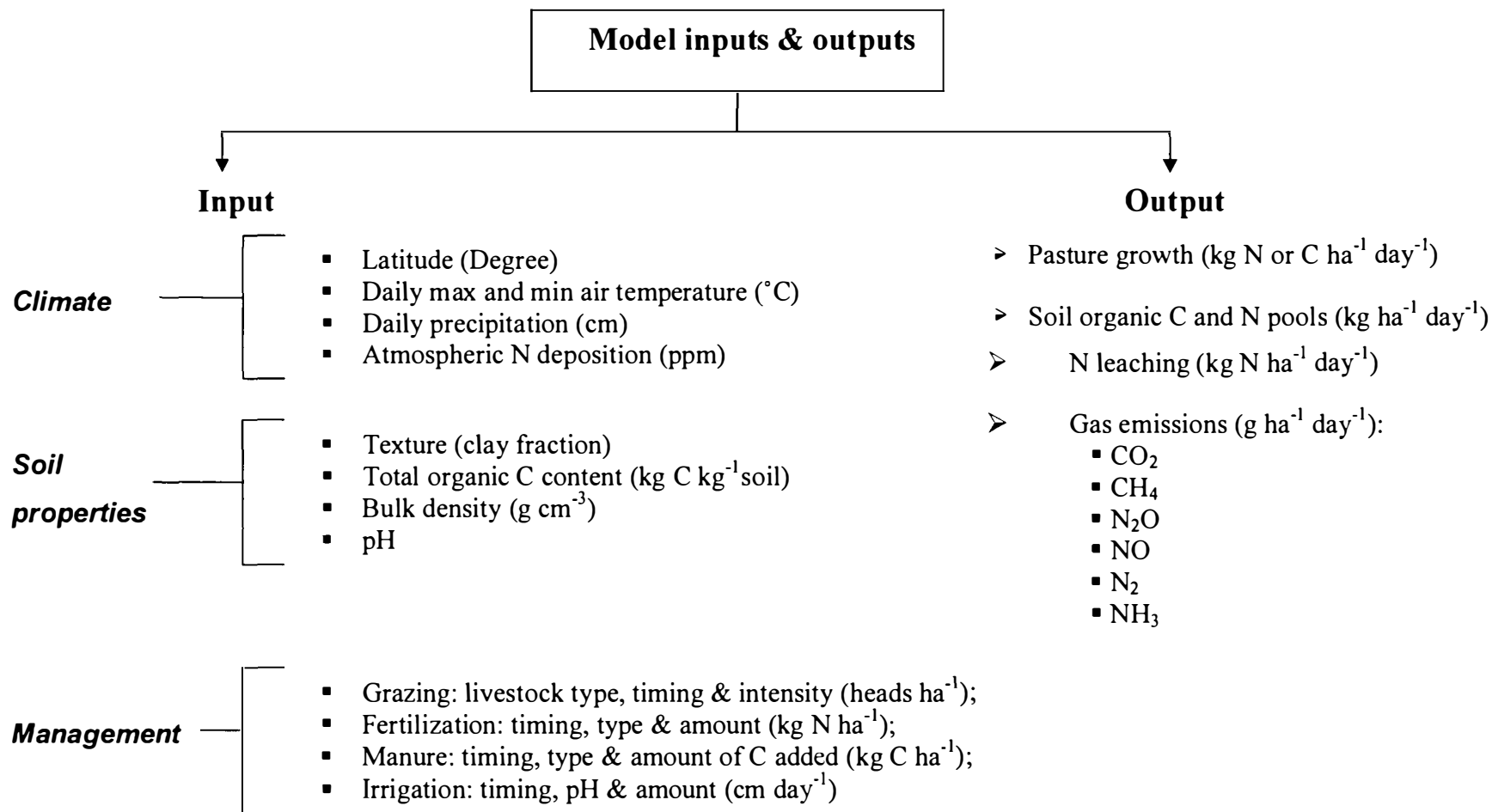


Figure 7.1 Structure of the DNDC model (Li et al. 1992).



**Figure 7.2** DNDC model - linking ecological drivers (input parameters) and soil/microbial processes to gaseous emission (output) (Salas et al. 2003)





**Figure 7.3** Input parameters required by the NZ-DNDC model and the model outputs

## 7.4 Results and Discussion

### 7.4.1 Measurements

The data on the changes in N<sub>2</sub>O emission, soil WFPS and mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) caused by TFDE irrigation have been discussed in detail in Chapter 6 of this thesis. Briefly, the total emissions from the unirrigated grazed treatments were 0.89 (± 0.09), 0.68 (± 0.17) and 0.38 (± 0.01) kg N<sub>2</sub>O-N ha<sup>-1</sup> and from the TFDE treatment were 1.36 (± 0.16), 1.92 (± 0.21) and 0.49 (± 0.10) kg N<sub>2</sub>O-N ha<sup>-1</sup> for the first (measurement period 16 days), second (measurement period 15 days) and third (measurement period 10 days) applications, respectively. The emissions were the lowest for the third measurement period for both unirrigated and TFDE treatment. For all TFDE treatments, peak emission was observed immediately after application with emission thereafter decreasing with time. Over the 2-3 weeks measurement period 2%, 4.9% and 2.5% of the total TFDE added N was emitted as N<sub>2</sub>O-N following the first, second and third TFDE application.

The WFPS in the unirrigated site was lower than the TFDE treated site following all the three applications. The range of the WFPS for the first, second and third irrigations are shown in Table 7.2. The highest difference in WFPS between the unirrigated and the TFDE treated sites was measured in the third irrigation.

**Table 7.2** Range of the WFPS, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> measured during the three treated farm dairy effluent field application events

Irrigation event	WFPS		NH <sub>4</sub> <sup>+</sup> (kg ha <sup>-1</sup> )		NO <sub>3</sub> <sup>-</sup> (kg ha <sup>-1</sup> )	
	Irrigated	Un-irrigated	Irrigated	Un-irrigated	Irrigated	Un-irrigated
First	0.61-0.90	0.59-0.84	5.1-22.7	5.0-14.0	10.9-27.9	7.3-14.3
Second	0.69-0.94	0.63-0.89	6.7-35.6	5.7-19.4	14.2-59.6	8.7-33.1
Third	0.56-0.77	0.44-0.68	6.7-15.2	5.3-7.7	9.0-15.9	7.0-9.4

Mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) concentrations were also higher for the TFDE treated sites than for the unirrigated sites for all the three applications (Table 7.2). The highest concentrations of mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) was found followed second TFDE application as compared to the other two TFDE applications.

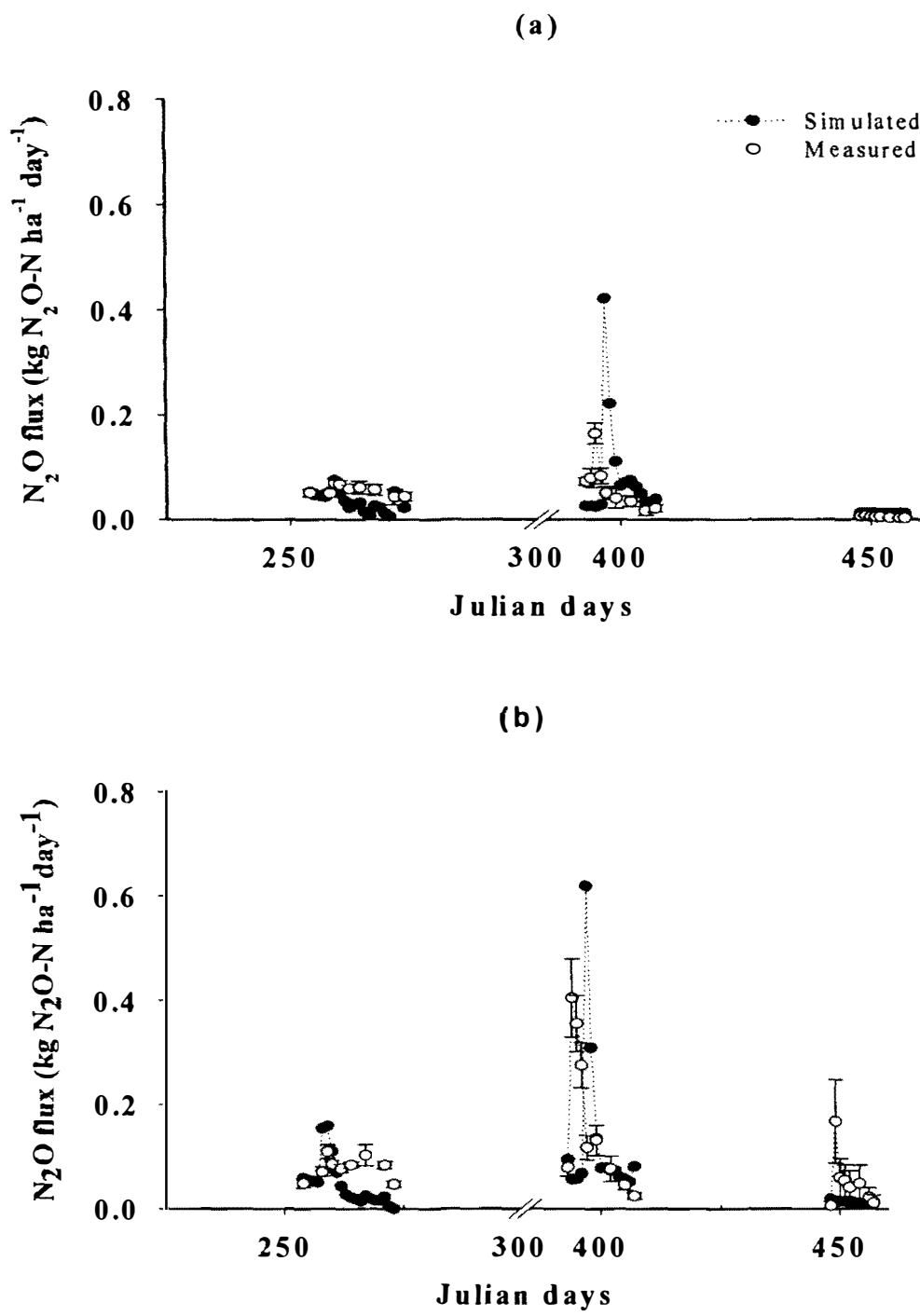
### 7.4.2 Model simulations

The NZ-DNDC simulated emissions are shown in Figure 7.4. Under the unirrigated grazing treatment, simulated emissions were 0.34, 0.79 and 0.08 kg N ha<sup>-1</sup> for the three measurement periods.

For all TFDE irrigation events, peak emissions were simulated after the application (Figure 7.4b). The emissions declined subsequently with slight fluctuations observed during the measurement period. The peak for the second TFDE application was simulated 5 days after the TFDE application. The simulated emissions over the 2-3 week simulation period were 0.38, 1.25 and 0.06 kg N ha<sup>-1</sup> from TFDE for the first, second and third treatments, respectively.

Overall, the simulated WFPS for the unirrigated treatments was lower than the TFDE irrigation treatments. The application of the effluent irrigation in the model resulted in a sharp increase in the WFPS (Figure 7.6). The model simulated that the soil remained saturated (WFPS of 0.94) for a longer period after the TFDE application for the first irrigation, compared to the other two irrigations. The WFPS fluctuated following all three TFDE irrigations (Table 7.3).

Model simulations showed an increase in the NH<sub>4</sub><sup>+</sup> concentration (Figure 7.7 b) after the TFDE irrigation but little increase in the NO<sub>3</sub><sup>-</sup> concentration was simulated (Figure 7.8a, b). The range of the simulated NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> are shown in Table 7.3. A higher increase in the NH<sub>4</sub><sup>+</sup> concentration was observed between the TFDE irrigated and unirrigated treatments



**Figure 7.4** Measured and simulated N<sub>2</sub>O emission for the (a) unirrigated and (b) irrigated treatment during the three irrigation events (experiment A, B and C). The measured values are the mean of twenty replicates. Error bars represent the standard deviation values for the measured data

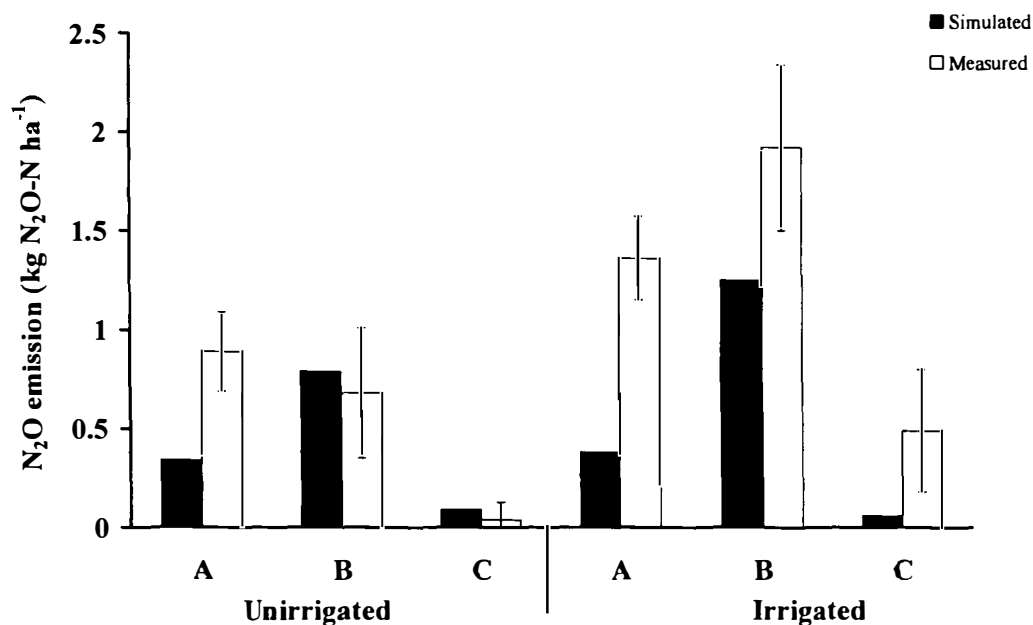
**Table 7.3** Range of the WFPS, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> simulated during the three treated farm dairy effluent application events

Irrigation event	WFPS		NH <sub>4</sub> <sup>+</sup> (kg ha <sup>-1</sup> )		NO <sub>3</sub> <sup>-</sup> (kg ha <sup>-1</sup> )	
	Irrigated	Un-irrigated	Irrigated	Un-irrigated	Irrigated	Un-irrigated
First	0.59-0.94	0.59-0.94	17.4-32.7	9.7-13.3	0.4-6.4	1.4-3.7
Second	0.45-0.93	0.38-0.93	14.2-29.5	8.7-12.7	1.9-8.9	1.8-3.8
Third	0.55-0.92	0.49-0.60	6.2-15.0	4.3-4.7	0.4-1.9	0.6-1.6

### 7.4.3 Measured vs. simulated emissions, WFPS and mineral N

The model was able to simulate the trend in the emissions as observed in the field for the unirrigated grazed pasture (Figure 7.4a). The modelled emissions were 0.11 and 0.05 kg N<sub>2</sub>O-N ha<sup>-1</sup> more than the measured emissions for the second and the third periods but 0.55 kg N<sub>2</sub>O-N ha<sup>-1</sup> lower for the first period (Figure 7.5). Overall the total measured emissions for the unirrigated grazed conditions during the three periods (1.61 kg N<sub>2</sub>O-N ha<sup>-1</sup> ± 0.62 kg N<sub>2</sub>O-N ha<sup>-1</sup>) were similar to the modelled emissions (1.21 kg N<sub>2</sub>O-N ha<sup>-1</sup>). The total simulated and the measured emissions from the unirrigated and the TFDE irrigated treatments for the three measurement periods are shown in Figure 7.5.

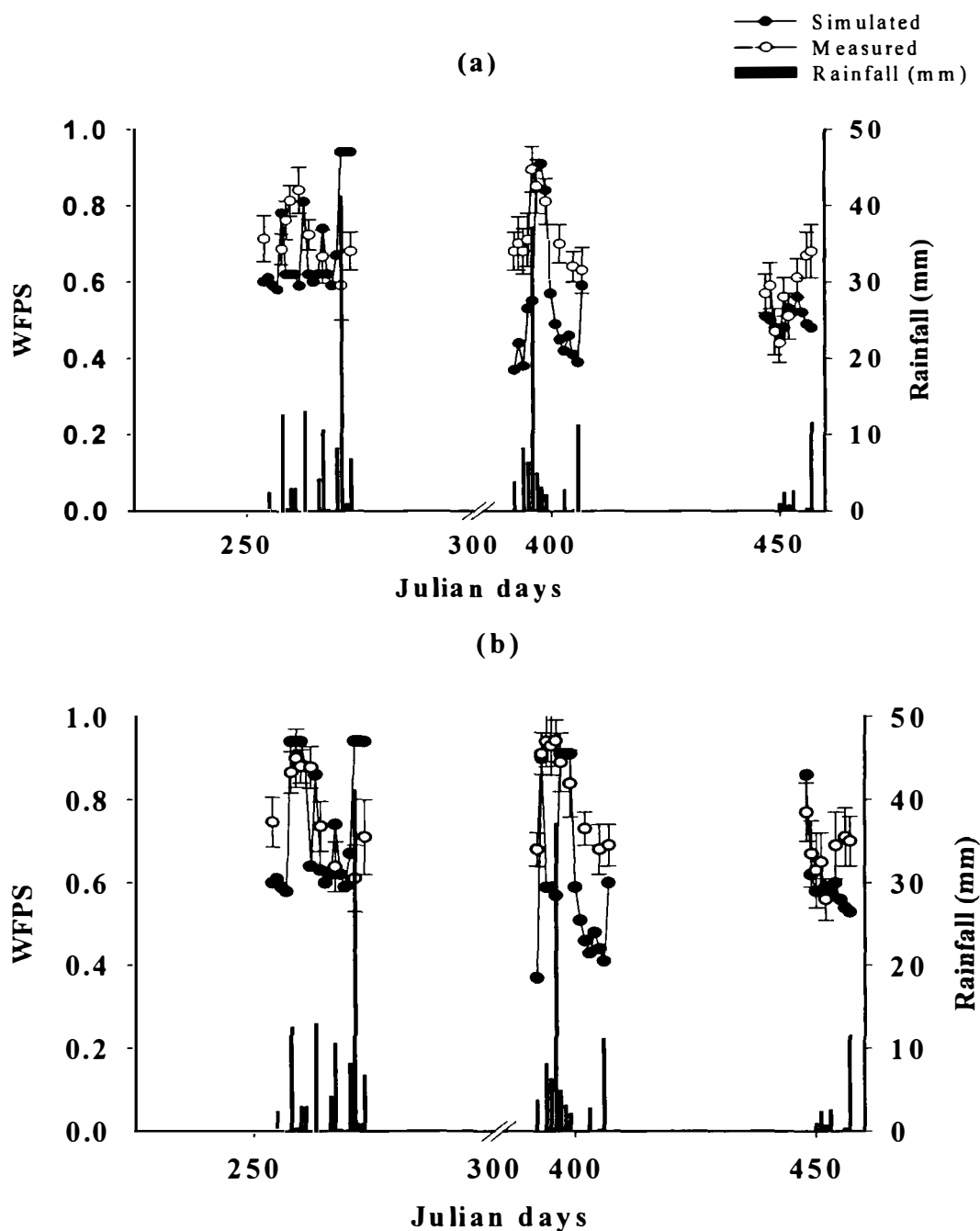
Measured and the simulated emission from TFDE application were higher for the second measurement period and lower for the other two periods (Figure 7.5). However, the measured emissions were higher than the modelled emissions. The total measured emissions for the TFDE irrigated treatments were 3.77 kg N<sub>2</sub>O-N ha<sup>-1</sup> (± 0.94 kg N<sub>2</sub>O-N ha<sup>-1</sup>) and the total modelled emissions were 1.70 kg N<sub>2</sub>O-N ha<sup>-1</sup>.



**Figure 7.5** Total simulated and measured N<sub>2</sub>O emission for the unirrigated and irrigated treatment during the three irrigation events. A, B and C represent the first, second and third irrigation event, respectively. Error bars represent the standard deviation values

The trend in emissions was similar for the measured and the modelled N<sub>2</sub>O flux for the first and second TFDE irrigations, where the model was able to predict the peaks immediately after the TFDE application, and then the emissions declined with time. However, the model was not able to simulate adequately the increase in the emission immediately after the third TFDE application (Figure 7.4b).

The model was able to predict the emission for the unirrigated grazed pasture well at the 2<sup>nd</sup> and 3<sup>rd</sup> periods but it under predicted the emission for the TFDE application. This inability of the model to simulate the emission after the TFDE application could be because of the form in which carbon is added in the TFDE. The TFDE application is known to add a lot of metabolizable carbon to the soil which enhances the N<sub>2</sub>O emission (Petersen 1999; Chadwick *et al.* 2000; Barton & Schipper 2001). As the model has not been parameterised for the effluent application, all the carbon present in the TFDE is added as organic carbon, which could lead to the under estimation of the emissions.



**Figure 7.6** Rainfall and measured and simulated WFPS for the (a) unirrigated and (b) TFDE irrigated soils during the three irrigation events (Experiment A, B and C). The measured values represent the mean of four replicates. The bars represent the rainfall measured during that day. Error bars represent the standard deviation values

The modelled WFPS readings under the unirrigated treatment were within the range of the measured values (Figure 7.6a) with the WFPS being above the field capacity for the first irrigation but being below the field capacity for most of the

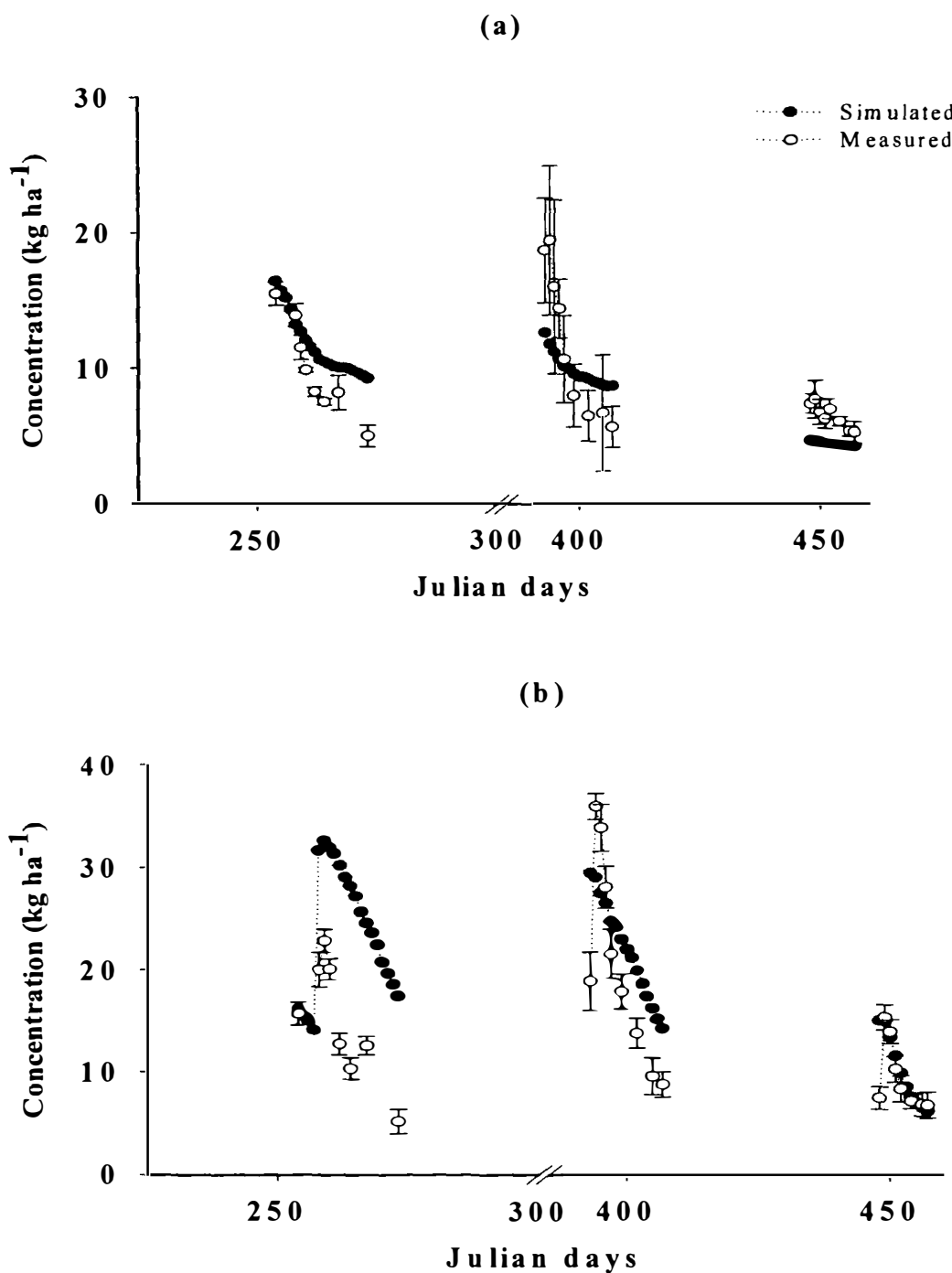
measurement period during the second and third irrigations. For the TFDE irrigated treatments, the model was able to simulate WFPS, with the same trend as had been observed for the measured values under the field conditions (Figure 7.6b). Both the measured and the simulated WFPS were found to increase immediately after the TFDE application and then gradually decrease with time, with slight fluctuations observed after the rainfall events.

The WFPS for the first and the third TFDE applications were within the measured range, but slight differences were observed for the second TFDE application. Initially, the modelled WFPS was very close to the measured WFPS, but lower simulated WFPS than the measured values were obtained towards the end of the measurement period. Saggar *et al.* (2004a) had earlier observed that the modified “NZ-DNDC” model was not so accurate in simulating changes in the WFPS compared to the measured data for the silt loam soil, where the modelled calculations resulted in much lower WFPS at the times when the top 5cm soil was almost saturated with water.

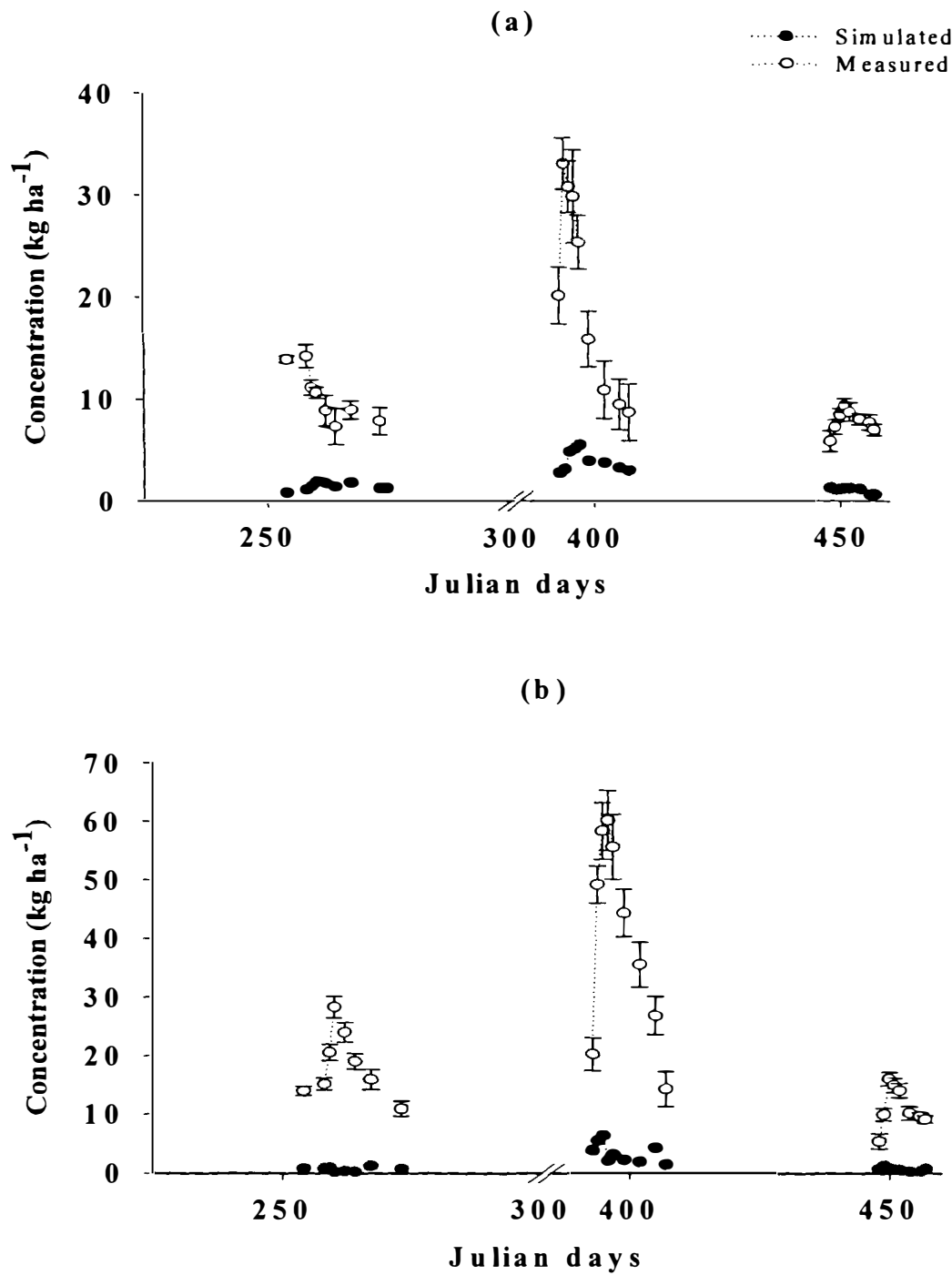
The rate of TFDE application was higher for the first event (25mm) than for the second event (21mm) and the model predicted a higher WFPS for the first TFDE application than for the second TFDE application. Moreover the amount of rainfall received during the first event was higher (96mm) than for the second event (80mm). But the measured WFPS was higher during the second application than during the first application. This may be due to 8 mm of TFDE loss through surface runoff during the first TFDE application (Houlbrooke *et al.* 2004) which DNDC simulated as drainage and not as runoff. Also the WFPS measured in the field was the mean of the four random samples taken from the paddock and may not represent the water content of the soil inside the chamber from where the daily N<sub>2</sub>O flux was measured. The difference between the simulated and measured WFPS for the second irrigation could explain the difference in the measured and simulated emissions, as the successful simulation of N<sub>2</sub>O emission depends largely on the successful simulation of soil moisture conditions (Li *et al.* 1992; Andrew *et al.* 2003).

During the TFDE application a high amount of N and C along with increased WFPS leads to conditions that are conducive for complete denitrification to take place. An increased concentration of C in the soil decreases the N<sub>2</sub>O emission because it lowers the ratio of N<sub>2</sub>O/N<sub>2</sub> produced by supplying sufficient C substrate to complete the denitrification process (Li *et al.* 1992).





**Figure 7.7** Measured and simulated  $\text{NH}_4^+$  distribution in the soil for (a) unirrigated and (b) TFDE irrigated treatment during the three irrigation events (Experiment A, B and C). The measured values represent the mean of four replicates. Error bars represent the standard deviation values



**Figure 7.8** Measured and simulated  $\text{NO}_3^-$  distribution in the soil for (a) unirrigated and (b) irrigated treatment during the three irrigation events (Experiment A, B and C). The measured values represent the mean of four replicates. Error bars represent the standard deviation values

The lower modelled values for emission could be the result of the model invoking complete denitrification and simulating N to be emitted as N<sub>2</sub> instead of N<sub>2</sub>O. The amount of N<sub>2</sub> emission predicted by the model from the first, second and third irrigation events resulting from effluent application (after subtracting the N<sub>2</sub> loss observed under the control) were 2.04, 0.63 and 0.99 kg N ha<sup>-1</sup>.

The differences observed between measured and modelled WFPS and shifts between N<sub>2</sub>O:N<sub>2</sub> emissions discussed above, however, cannot explain the lower emission observed during the third irrigation event. The WFPS around field capacity soil moisture content was not sufficient to cause complete denitrification to occur.

The model was able to simulate the NH<sub>4</sub><sup>+</sup> concentrations well (Figure 7.7) but the NO<sub>3</sub><sup>-</sup> concentrations were underestimated (Figure 7.8). This was true for both the treatments (irrigated and unirrigated) and for all the three irrigations. For the NH<sub>4</sub><sup>+</sup> concentration both the measured and the simulated curves are found to overlap each other (Figure 7.7a). As for the irrigated treatment the measured and the simulated NH<sub>4</sub><sup>+</sup> concentration for the second and the third irrigation were within the range, compared to the first irrigation where the model over predicted the values.

The model predicted NO<sub>3</sub><sup>-</sup> concentration (Figure 7.8b) was always lower compared to the measured concentration for both the unirrigated and the irrigated treatments, with the difference being more for the irrigated treatments. For the unirrigated treatment the concentration was within the range of the measured values for the first irrigation but the measured values were far higher for the other two irrigations. Comparing the DNDC simulated soil nitrate concentration for the three temperate agricultural soils with the measured data, Frohling *et al.* (1998) observed that the DNDC model generally underestimated the soil nitrate concentration, and said it was because in DNDC, hydrolysis of urea raised the soil pH, which led to increases in ammonia volatilisation and thus decreases in nitrification, thereby preventing any increase in the nitrate pool. Moreover, the soil samples for the mineral N analysis were kept in cold storage at 4°C for a few days prior to analysis. It is possible that a certain amount of nitrification might have taken place during storage and as a result the measured nitrate concentration was getting overestimated.

## 7.5 Conclusions

- The trend of the N<sub>2</sub>O emission readings simulated by the NZ-DNDC model was similar to that observed under the field measurement for both the irrigated and the control treatment.
- The model able to simulate the emission for the unirrigated grazed treatment but it underestimated emissions for the TFDE irrigated treatments.
- The modelled WFPS values were slightly higher than the measured values for the first and third TFDE applications but were slightly lower for the second TFDE irrigation.
- Partitioning of the gaseous nitrogen loss into NO, N<sub>2</sub>O and N<sub>2</sub> maybe affected by the soil WFPS. Thus accurate simulation of WFPS is important for the accurate prediction of N<sub>2</sub>O emission where WFPS is the major factor controlling emissions.
- The NZ-DNDC model needs to be parameterised specifically for effluent irrigation in order to accurately predict N<sub>2</sub>O emission from the grazed pastures irrigated with farm effluents.

## Chapter 8

# Summary & Conclusions

In this Chapter, following a brief introduction on the economic and environmental impacts of  $\text{N}_2\text{O}$  emissions, the major research findings obtained in the various small plot and field experiments, which examined the effects of grazing and effluent application on  $\text{N}_2\text{O}$  emissions from grazed pastures, are summarised. The implications of empirical and processed-based models used to predict  $\text{N}_2\text{O}$  emissions are also discussed. Finally, the future research needs in relation to the quantification and modelling of  $\text{N}_2\text{O}$  emission, and options for reducing emissions are proposed.

### 8.1 Economic and environmental impact of $\text{N}_2\text{O}$ emission

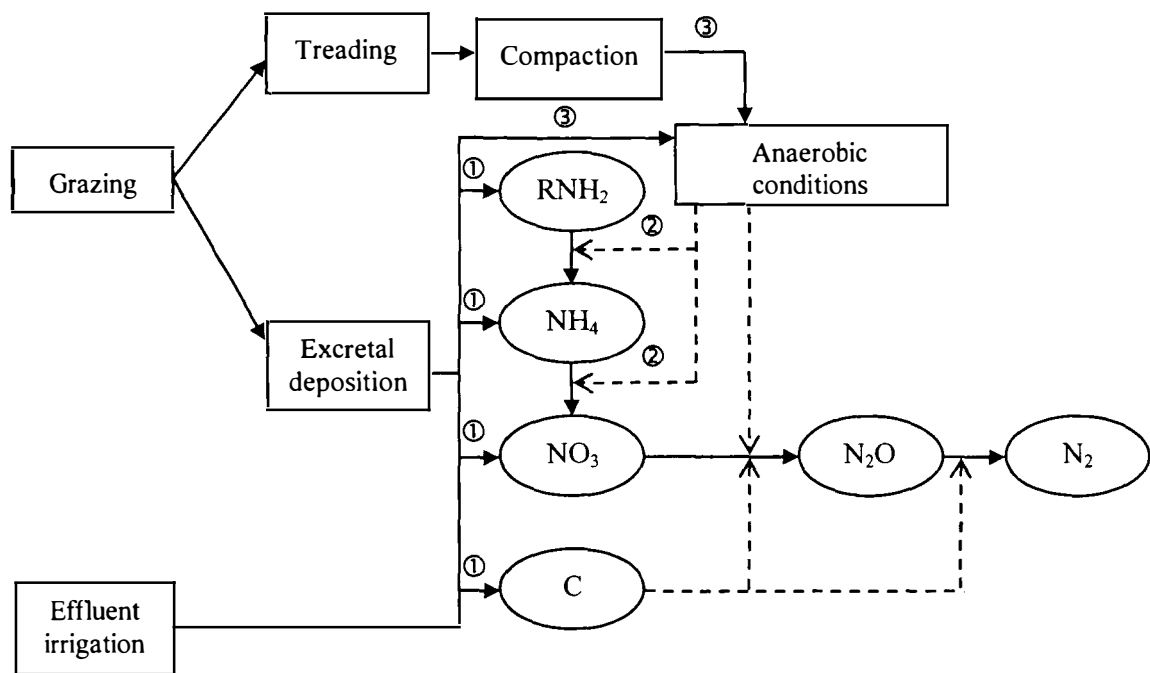
The increasing atmospheric concentration of  $\text{N}_2\text{O}$  is becoming a serious environmental concern because of its contribution to global warming. The global warming potential of  $\text{N}_2\text{O}$  is 310 times greater than that of  $\text{CO}_2$ , thus even a small increase in its concentration has a large impact on the net radiation trapped in the atmosphere (radiative forcing).  $\text{N}_2\text{O}$  gas is also known to undergo photochemical reactions in the stratosphere thus causing destruction of the stratospheric ozone shield resulting in more UV radiation to enter the earth's atmosphere. Agriculture is the main source of  $\text{N}_2\text{O}$  emission in New Zealand, with  $\text{N}_2\text{O}$  being produced as a result of the microbial processes of nitrification and denitrification occurring in the soil.

In New Zealand, of the total  $\text{N}_2\text{O}$  emission of  $40.7\text{Gg yr}^{-1}$ , about 74% comes from the direct sources i.e. from the N added from synthetic fertilisers, deposition of animal excreta, effluent irrigation, N fixation and cultivation practices. Indirect sources such as atmospheric deposition, N leaching and runoff contributing the remaining 25% of the emission. Thus the more N that is being cycled through the system, the greater the amount of  $\text{N}_2\text{O}$  released into the atmosphere. Although quantitatively  $\text{N}_2\text{O}$  emissions are less than N loss from agricultural land via N leaching and  $\text{NH}_3$

volatilisation, considering the irreparable effect N<sub>2</sub>O emission has on environmental degradation through its high global warming potential, the economic implications from the N<sub>2</sub>O emission can be higher.

## 8.2 Effects of farming practices on N<sub>2</sub>O emission

A number of farming practices affect N<sub>2</sub>O emission through their effects on the various soil physical and chemical properties (Figure 8.1). In this study the effects of soil compaction, effluent irrigation and grazing on N<sub>2</sub>O emission rates were examined. The study focussed on measuring soil factors which were likely to directly influence rates of denitrification in soil, such as the supply and transformation of N and C in the soil, and the creation of anaerobic conditions in the soil as indicated by changes in bulk density, oxygen diffusion rate and penetration resistance.



**Figure 8.1** Influence of grazing and effluent irrigation on N<sub>2</sub>O emission through their effects on: 1. Supply of C and N substrates; 2. Transformation of nitrogen; and 3. Creating anaerobic conditions

### 8.2.1      **Compaction**

The transformation and loss of N through  $\text{N}_2\text{O}$  emission from different N sources as affected by compaction treatment were measured (Chapter 3). The extent of compaction was monitored by measuring various soil physical properties such as bulk density, oxygen diffusion rate and penetration resistance.

Compaction created by both the wheel of the vehicle and cow hooves caused a significant change in the soil physical properties, thereby creating anaerobic conditions. Soil compaction and the form of N input had a significant effect on  $\text{N}_2\text{O}$  emission with compaction causing a seven fold increase in  $\text{N}_2\text{O}$  emission compared to the emission from the uncompacted soil. Among the N sources added (natural cattle urine, potassium nitrate, ammonium sulphate and urea) potassium nitrate caused significantly higher  $\text{N}_2\text{O}$  emission over the rest of the sources, with emission being 7 and 1.5 times higher for the compacted and the uncompacted soils, respectively. The  $\text{N}_2\text{O}$  emission was similar for the other N sources.

The N mineralization study showed that the rate of conversion of the amide form of N to ammonium and thus to the nitrate was faster in the absence of compaction. Thus it would be worthwhile to study further the effect the time of compaction had in relation to the N input on N dynamics in the soil and its subsequent losses through gaseous emissions. It is difficult to extrapolate these results to other sites because the level of compaction created by vehicular traffic and grazing is a function of the pressure exerted by the wheel and/or the weight of the grazing animal, soil type and its condition, particularly moisture content.

### 8.2.2      **Effluent irrigation**

With increasing cattle numbers in New Zealand, land application of the farm effluent is becoming a wide-spread and environmentally acceptable practice. The effluent applied onto land has led to increased environmental concerns like leaching of nutrients into ground water and/or gaseous emissions into the atmosphere. In this thesis we studied the effect of the types of effluent (Chapter 4) and different application rates of effluent (Chapter 5) on the  $\text{N}_2\text{O}$  emission using plot scale experiments. Treated farm dairy effluent, the most abundantly irrigated effluent on the dairy farm, was then applied

at an application rate recommended by the regional councils at the farm scale level to quantify  $\text{N}_2\text{O}$  emission under field conditions (Chapter 6).

The  $\text{N}_2\text{O}$  emissions increased immediately after the application of the effluent and then decreased with time. The emissions were affected by the type of effluent. Among the effluents, piggery effluent was found to cause the highest  $\text{N}_2\text{O}$  emissions (2.17% of the added N) during the autumn application. Meat effluent caused the highest  $\text{N}_2\text{O}$  emissions (0.84% of the added N) during the winter application. The percentage of the total added N emitted as  $\text{N}_2\text{O}$  decreased with the increasing C: N ratio of the effluent. This suggests that complete denitrification occurred as increasing levels of carbon in the effluent were added in the soil, leading to the increased production of  $\text{N}_2$  instead of  $\text{N}_2\text{O}$  emission (Figure 8.1). Besides  $\text{O}_2$ , nitrogen and carbon are the two most limiting factors controlling the overall emissions of  $\text{N}_2\text{O}$  and  $\text{N}_2$  during denitrification. The treatment of the effluent in two pond systems caused considerable reduction in the C content of the effluent. Thus the emission from the treated FDE was 14.5% lower than the emission measured from the untreated FDE. Among the two applications, the emission from the autumn application was 2-4 times higher than the winter application because of the higher N and C concentrations in the autumn-applied effluent and more favourable denitrification conditions occurring during the autumn season.

The increased application rate of treated FDE increased the amount of  $\text{N}_2\text{O}$  emission, although the percentage of the added N emitted as the  $\text{N}_2\text{O}$  decreased. Increasing the FDE loading from 25mm to 100mm resulted in a 300% increase in  $\text{N}_2\text{O}$  emission. The increased application rate resulted in higher hydraulic, and N and C loadings creating conditions conducive for the  $\text{N}_2\text{O}$  emissions. The rate of increase of the total  $\text{N}_2\text{O}$  emissions decreased with the increasing level of effluent application suggesting that effluent irrigation created conditions favourable for complete denitrification to occur in soil (Figure 8.1) and thus with increasing effluent irrigation there was a shift towards the production of  $\text{N}_2$  rather than  $\text{N}_2\text{O}$ .

The field application of the treated FDE showed a similar trend to that observed in the plot studies, with the peak emission being observed immediately after the effluent application and then returning to the background levels within 2-3 weeks. The emission from the three field irrigations resulted in different emission rates (2.0, 4.9 and 2.5% of the added N emitted), suggesting that other factors such as grazing events before effluent application, rainfall events and the mineral N and C concentration of the soil at



the time of FDE application also affected  $\text{N}_2\text{O}$  emission. Therefore, careful consideration of these factors before FDE application may help in reducing  $\text{N}_2\text{O}$  emission.

$\text{N}_2\text{O}$  emission measured 12 weeks after the effluent irrigation showed no difference in the  $\text{N}_2\text{O}$  flux between the effluent irrigated and unirrigated sites. This indicated that the residual effects of effluent irrigation on  $\text{N}_2\text{O}$  emission were negligible. No significant difference was observed in the concentration of mineral N and DOC in the irrigated and the unirrigated soils, suggesting that the C and N substrates added through effluent irrigation had been lost from the soil through leaching, volatilisation or gaseous emission prior to the monitoring of  $\text{N}_2\text{O}$  emission.

### 8.2.3 Grazing

The  $\text{N}_2\text{O}$  emissions were monitored in a field experiment at Massey University's Dairy 4 farm for 3 weeks immediately after a moderate intensity grazing event to examine the effect of grazing on  $\text{N}_2\text{O}$  emission. There were two treatments in this experiment, namely recently grazed (one day prior) and control (not grazed for 42 days). The  $\text{N}_2\text{O}$  emission from the grazed pasture was 8 times higher than that from the ungrazed area with an emission factor of 2.5%. The emission factor was calculated as the percentage of the added N through cattle excretal deposition during grazing being emitted as  $\text{N}_2\text{O}$ . The excretal N input was estimated to be 290 g of N per cow per day. The Peak emission was obtained a week after the grazing with a corresponding increase in mineral N concentration of the soil. The effect of the excretal deposition in  $\text{N}_2\text{O}$  emission was evident for the first 3 weeks, after which the emission from the grazed area was similar to that from the ungrazed area. The increase in emission immediately after the grazing event results from the combined effects of the excretal deposition, thereby providing C and N substrates as well as the compaction created due to the treading effect of the grazing cattle. Changes in soil physical properties such as bulk density, penetration resistance and ODR showed that compaction was caused by the grazing cattle (Chapter 3).

## 8.3 Modelling N<sub>2</sub>O emission

Large spatial and temporal variability exists in the measured N<sub>2</sub>O fluxes. Capturing this variability is important in order to accurately extrapolate the measured fluxes at small field scale levels to large ecosystem levels. Although chamber method is able to measure the variability at field level, it requires extensive measurement over a long period of time. On the other hand, micrometeorological techniques are good for estimating the emission on a landscape scale but are not sensitive enough to capture the variability at field levels and are also very expensive. Thus, mathematical models based on the soil and environmental characteristics which can predict the N<sub>2</sub>O emission might be a way to develop an accurate N<sub>2</sub>O inventory.

### 8.3.1 Empirical regression model

During the course of the study, regression equations for the prediction of the N<sub>2</sub>O emission for different treatments were developed to identify the effect of key soil and environmental factors regulating these emissions. No single relationship was able to predict accurately the emissions from all the treatments. For example, the multiple regression equations relating N<sub>2</sub>O emission and various soil properties were able to explain only 20% and 28% of the variation in the emissions for the compacted and the uncompacted soil even though the WFPS and the NO<sub>3</sub><sup>-</sup> concentrations were significantly correlated with the emissions (Chapter 3). Regression relationships obtained between the N<sub>2</sub>O emission from the application of different types of farm effluents and the soil properties in Chapter 4 was found to be better than that observed in Chapter 3. The equations explained 78% and 56% of the variability found in the emissions during the first and the second applications. But no one equation was able to predict the emissions for all the applications. Similarly in Chapter 6, though the individual regression equations explained the variability during the second and third irrigation events, no single equation could be developed to suit all the situations.

The production and release of N<sub>2</sub>O in soils is a complex process with many distal and proximal factors playing a major role in this process. The conditions become more complicated with grazing and effluent application, and therefore it is not possible to simulate the emission under these conditions with simple regression equations.

### 8.3.2 Process based model

A New Zealand modified process-based model called 'NZ-DNDC' was used to simulate N<sub>2</sub>O emissions from the pasture that had been irrigated with the treated FDE (Chapter 7). The model was able to simulate the N<sub>2</sub>O emissions similar to that observed during the field measurements. The emissions predicted by this model were within the range of measured values for all the three irrigation events. The model was found to over predict the WFPS in the first and the third irrigations but under predicted the WFPS values for the second irrigation event. These differences in the simulated and the measured WFPS values could be a reason for the disparity between the modelled and the measured N<sub>2</sub>O emission values.

The model was able to simulate the NH<sub>4</sub><sup>+</sup> concentrations well but the NO<sub>3</sub><sup>-</sup> concentrations were underestimated. This was true for both the irrigated and the unirrigated treatments and for all the three irrigation events.

The NZ-DNDC model does not include effluent irrigation as an input parameter and thus these irrigation events were mimicked in the model as the simultaneous occurrence of the manure, fertilisation and irrigation event. The parameterisation of an effluent irrigation event in the model may help in better simulation of the N<sub>2</sub>O emission.

## 8.4 Future research

The research work described in this thesis suggests a number of areas that require further investigation. These are:

- More long term studies are needed to find effective solutions, for reducing N<sub>2</sub>O emissions. For example, management strategies to avoid the compaction caused due to cattle treading, and the application of N fertiliser and effluent to already wet soils should be considered. Further detailed research of simultaneous nitrification and denitrification in micro and macro aggregates as affected by compaction may help in deciding the time of application of N source through fertiliser or effluent application in relation to the compaction/grazing event.

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- Investigation into the C transformations taking place in the soil from the application of different farm effluents. The role of DOC supplied by the farm effluents in  $\text{N}_2\text{O}$  emission in relation to microbial respiration and the mineralization of the C present in the soil.
  - Investigation into the simultaneous nitrification and denitrification processes occurring in the pastures irrigated with FDE and their contribution to  $\text{N}_2\text{O}$  emission. Further, a complete mass balance during  $\text{N}_2\text{O}$  measurement from effluent irrigation to determine the fractions of nitrogen lost as gaseous emissions of  $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NO}$  that might be released during the volatilisation and denitrification processes.
  - Need to examine the effect of increasing the C:N ratio of the effluent as an effective management technique to promote the return of N to the atmosphere as harmless  $\text{N}_2$  while decreasing the potential to form  $\text{N}_2\text{O}$ .
  - Modification of the NZ-DNDC model to parameterize it for simulating  $\text{N}_2\text{O}$  emission from effluent irrigation. The accuracy of the model to predict these emissions from effluent irrigation could be further improved by empirical research to study the factors affecting the emissions.
  - Further research on the management strategies to decrease  $\text{N}_2\text{O}$  emission from the farm effluents irrigated to grazed pastures especially in relation to the application rate and to integrate it with the management practices developed to reduce other environmental hazards like water pollution due to nitrate leaching.

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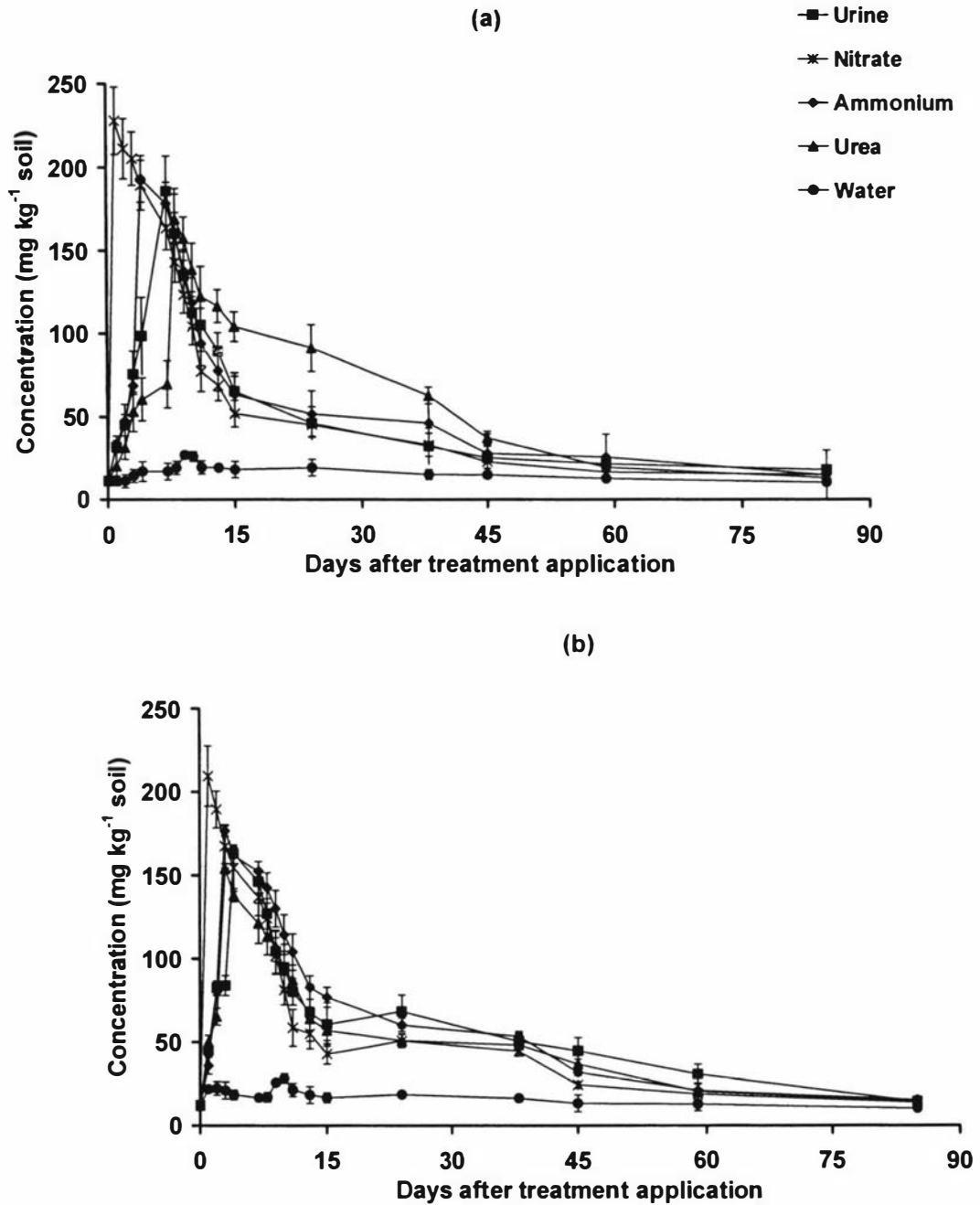


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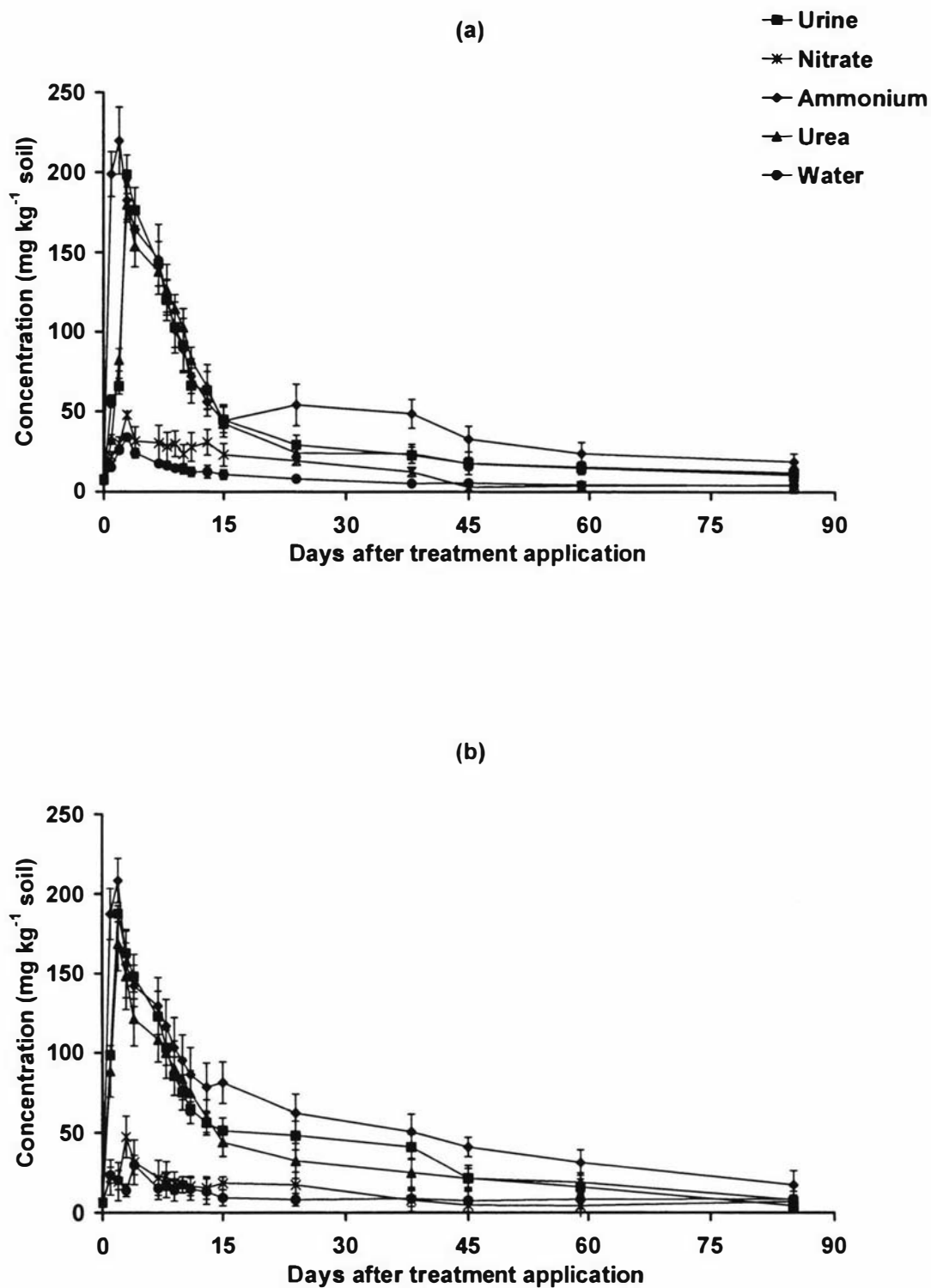
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## APPENDIX 1



**Figure 1** Distribution of  $\text{NO}_3^-$  concentration ( $\text{mg kg}^{-1}$  soil) under different treatments for (a) compacted and (b) uncompact soil at the experimental plots on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars. Day 0 represents a day before the application of treatments



**Figure 2**      Distribution of  $\text{NH}_4^+$  concentration ( $\text{mg kg}^{-1}$  soil) under different treatments for (a) compacted and (b) uncompact soil at the experimental plots on Manawatu sandy loam. Each value represents a mean of four replicates with standard deviation shown by vertical bars. Day 0 represents a day before the application of treatments

## APPENDIX 2

**Typical Input Parameters for NZ-DNDC**

This appendix provides the list of the typical input parameters that were used while running the NZ-DNDC model for the control and the irrigated treatments.

	<b>Unirigated</b>	<b>Irrigated</b>
<b>Site data</b>		
Site name	Dairy4_fert2_ctrl	Dairy4_irrig_fert2
Simulated Year	2	2
Latitude	-40.0	-40.0
Daily Record	1	1
<b>Climate data</b>		
Climate data type	0	0
NO <sub>3</sub> NH <sub>4</sub> in rainfall (mg N l <sup>-1</sup> )	0.50	0.50
NO <sub>3</sub> of atmosphere (µg N m <sup>-3</sup> )	0.06	0.06
Base CO <sub>2</sub> of atmosphere (ppm)	350.00	350.00
Climate file count	2	2
	C:\DNDC\Database\climate03.txt	C:\DNDC\Database\climate03.txt
	C:\DNDC\Database\climate04.txt	C:\DNDC\Database\climate04.txt
<b>Soil data</b>		
Soil texture	4 (Silt Loam)	4 (Silt Loam)
Land use type	3 (moist grassland/pasture)	3 (moist grassland/pasture)
Density (g cm <sup>-3</sup> )	1.01	1.01
Soil pH	5.90	5.90
SOC at surface (kg C kg <sup>-1</sup> )	0.036	0.036
Clay fraction	0.14	0.14
Bypass Flow	0	0
Litter SOC (kg C kg <sup>-1</sup> )	0.10	0.10
Humads SOC (kg C kg <sup>-1</sup> )	0.15	0.15

Humus SOC (kg C kg <sup>-1</sup> )	0.75	0.75
Soil NO <sub>3</sub> <sup>-</sup> (mg N kg <sup>-1</sup> )	10.80	10.80
Soil NH <sub>4</sub> <sup>+</sup> (mg N kg <sup>-1</sup> )	1.08	1.08
Moisture	0.40	0.40
Temperature (°C)	16.20	16.20
<b>Crop data</b>		
Rotation Number	1	1
Rotation ID	1	1
Total year	2	2
Years of a cycle	2	2
Year ID of a cycle	1	1
Crop total number	1	1
Crop ID	1	1
Crop type	12 (Perennial_grassland)	12 (Perennial_grassland)
Plant time (month d <sup>-1</sup> )	1 1	1 1
Harvest time (month d <sup>-1</sup> )	12 31	12 31
Year of harvest	1	1
Ground residue	1.0	1.0
Yield (kg DM ha <sup>-1</sup> )	1250.0	1250.0
Development rate (reproductive)	0.01	0.01
Development rate (vegetative)	0.03	0.03
Photosynthesis Efficiency	0.40	0.40
Maximum photosynthesis	60.0	60.0
Initial biomass (kg DM ha <sup>-1</sup> )	12.50	12.50
Tillage number	0	0
Fertiliser number	3	7
Fertilization ID	1-3	1-7
Month/Day/method	5 11 0 (Surface)	5 11 0 (Surface)
Depth (cm)	0.20	0.20

Nitrate	0	0
AmmBic	0	0
Urea	34.50	34.50
Anhydrous	0	0
NH <sub>4</sub> NO <sub>3</sub>	0	0
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0	18.15
NH <sub>4</sub> HPO <sub>4</sub>	0	0
Release rate	1.0	1.0
Inhibitor efficiency	0	0
Inhibitor duration	0	0
Manure number	0	4
Manure ID	NA	1
Month/day	NA	2 20
Amount (kg C/ha)	NA	230.22
C:N	NA	38.0
Type	NA	4
Weed number	0	0
Weed Problem	0	0
Flood number	0	0
Leak type	1	1
Water control	0	0
Leak rate	0	0
Irrigation Number	0	4
Irrigation type	0	0
Irrigation Index	0	0
Irrigation ID	NA	1
Irrigation Month/Day	NA	2 20
Amount of water used (cm)	NA	2.4
Irrigation water pH	NA	7.6
Grazing number	16	16

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Grazing ID	1-16	1-16
Start (month d <sup>-1</sup> )	1 3	1 3
End (month d <sup>-1</sup> )	1 3	1 3
Cattle (heads ha <sup>-1</sup> )	135	135
Horse (heads ha <sup>-1</sup> )	0	0
Sheep (heads ha <sup>-1</sup> )	0	0
Grazing hours d <sup>-1</sup>	12.0	12.0
Grass cut number	0	0
Climate file mode	0	0
Soil microbial index	1.0	1.0
Crop model approach	0	0
Depth WRL cm	2	2
Slope	0	0
Field capacity	0.6	0.6
Wilting point	0.2	0.2
CO <sub>2</sub> increase rate	0	0
SOC profile A	0.08	0.08
SOC profile B	1.40	1.40

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