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GASEOUS EMISSIONS (NH_3, N_2O and CH_4) FOLLOWING MANURE OR UREA APPLICATION TO SOIL AS INFLUENCED BY AMENDMENTS

A thesis
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Abstract

Increasing concentrations of greenhouse gases in the atmosphere may contribute to global warming. The three most important greenhouse gases are carbon dioxide (mainly from burning fossil fuels and deforestation), methane (mainly from ruminant animals and waste management) and nitrous oxide (mainly from dung, urine, and nitrogenous fertilisers). Dairy farms contribute to greenhouse gas emissions because of nitrous oxide and methane emissions (Whitehead *et al*., 2009).

Herd-homes or stand-off pads are increasingly used on dairy farms to minimise soil pugging and compaction. The manure collected from herd-home bunkers or stand-off pads, may be a source of gaseous emissions (NH_3, N_2O and CH_4). Addition of soil or sawdust to manure prior to land application of manure is a potential best farm management practice to minimise gaseous losses.

The specific objectives of the study were to:

1. Determine the optimum flow rate for measurement of ammonia emissions from manure or urea application to soil using a chamber method.
2. Quantify gaseous (NH_3, N_2O and CH_4) emissions from manure or urea after application to soil.
3. Determine the effects of addition of soil or sawdust to manure prior to land application of manure on subsequent gaseous emissions.
4. Determine the effects of surface or incorporated land application of manure or urea on gaseous emissions.

A preliminary experiment was undertaken to determine the optimum flow rate to measure ammonia emissions, from manure or urea after application to soil, using a chamber method. The flow rate experiment was set up in the glasshouse with 3 replications of 9 flow rate treatments. A flow rate of 5 L min^{-1} (1 exchange volume min^{-1}) was determined as the optimum air flow rate to use in the chamber method to measure ammonia volatilisation.

An experiment was undertaken, with 27 pots and 3 replications of 9 treatments, to investigate the effect of soil or sawdust addition to manure on gaseous emissions (NH_3, N_2O and CH_4), when applied on the land surface or incorporated. The physical and chemical properties of the soil, urine, dung, and sawdust were determined in the laboratory.

Addition of sawdust was more effective in reducing ammonia emissions, than addition of soil, to manure prior to land application. The incorporated application of all manure treatments resulted in less NH_3 volatilisation compared to surface application. Total ammonia losses were 51% of the applied N from the surface application and 2% of the applied N from incorporated application of urine and dung with soil, and 15% of the applied N from the surface application and 4% of the applied N from incorporated application of urine and dung with sawdust. Ammonia emissions followed a general pattern of rapid emission on day 2 after the application of the urine and dung to soil followed by a progressive decline over time for both the surface and incorporated application for all the manure treatments applied.

Total N_2O loss of 14% of applied N was observed with incorporated application of manure with sawdust. Most treatments had no net methane emission. Addition of soil and sawdust to manure, prior to application to soil, reduced ammonia emissions and increased nitrous oxide emissions.

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Chapter 1

Introduction

In New Zealand (NZ), dairy farming contributes 20% of export earnings but provides a challenge for the environmentally acceptable treatment of wastes from dairy farms. New Zealand dairy farms produce effluents, which contain high concentrations of nutrients such as nitrogen (N), potassium (K), and phosphorus (P), and various trace contaminants (Longhurst *et al.*, 2000). New Zealand has 5.9 million dairy cows and 4.1 million beef cattle at 30 June 2009 (Statistics New Zealand, 2010). NZ cattle excrete around 300 000 m^3 of dung and 180 million m^3 of urine every day (Saggar *et al.*, 2004a, b).

1.1 Dairy farm effluent

Bolan (2001) estimated that dairy and piggery effluents in New Zealand produce major nutrients of 8100 t N, 2500 t P, and 15 400 t K annually, worth over NZ$ 21 000 000 and which could meet the N needs of 40 500 ha of corn (*Zea mays*) or enough P for 62 500 ha of pasture. Globally farm effluents could supply enough N for 6.7 million ha of corn or enough P for 10.5 million ha of pasture. Saggar *et al.*, (2004) estimated that in New Zealand about 70 million m^3 of farm dairy effluent (FDE) were being generated annually from dairy sheds. Heatley (1996) calculated that the effluent generated by each dairy cow typically provides 5.9 kg N, 0.7 kg P, 5.4 kg K, 0.8 kg S, 2.2 kg Ca, 1 kg Mg, and 0.7 kg Na per year. Application of farm dairy effluent to pasture improves soil fertility, increases dry matter yield, and enhances the sustainability of farming systems due to the significant quantities of nutrients available (Luo *et al.*, 2004b).

1.2 Ammonia emissions from dairy farm manure

Agriculture is recognized as the major source of atmospheric ammonia (NH_3), contributing 55-56% of global NH_3 emissions (Bouwman *et al.*, 1997). Ammonia volatilisation decreases the N-nutrient value of livestock manure applied to the field (Sørensen and Amato, 2002), and contributes to the eutrophication of terrestrial ecosystems and surface waters (Roelofs, 1986), and the development of a lower tolerance to stress in woodland and forests (Nihlgard, 1985). Ammonia volatilisation also contributes to the acidification of soils that arises from the deposition of N from the atmosphere. There is a close relationship between the chemistry of the atmosphere and ammonia emissions. NH_3 reacts with sulphur dioxide (SO_2) to form particulate ammonium sulphate ($(NH_4)_2SO_4$), thus reducing the acidity of the atmosphere and reducing the distance over which sulphur (S) is transported in air (Moller and Schieferdecker, 1985). Ammonia, sulphur dioxide (SO_2) and various oxides of N (NO_x), are the three main compounds responsible for acid rain. Ammonia can react with nitrate and sulphate to form particulates, which can contribute to acidic depositions (Sommer and Hutchings, 2001).

1.3 Greenhouse gas emissions (N_2O and CH_4) from dairy farm manure

The two non-carbon dioxide greenhouse gases nitrous oxide (N_2O) and methane (CH_4) comprise 54.8% of total NZ emissions (Ministry for the Environment 2006). Recent estimates indicate New Zealand's agricultural sector produces approximately 1.165 million tonnes of CH_4 and 0.039 million tonnes of N_2O annually. New Zealand's target for 2008-2012 under the Kyoto Protocol is to reduce GHG emissions to 1990 levels. In 2004, total net emissions were about 21% higher than 1990 levels, with agricultural methane and N_2O emissions being 6.5% and 25% above 1990 levels, respectively (Ministry for the Environment 2006). Nitrous oxide has a large global warming potential (GWP), which is c. 310 times higher than that of CO_2 and NO_x has a long atmospheric lifetime of 150 years. Methane, with a GWP 21 times higher than CO_2 is also a potent greenhouse gas that can affect climate directly, through its interaction with long-wave infrared energy and indirectly, through atmospheric oxidation reactions (Whitehead *et al.*, 2009). Methane is second only to CO_2 in importance as a greenhouse gas and contributes around 18% of the greenhouse effect.

1.4 Mitigating strategies to reduce gaseous emissions

The largest single source of gaseous emissions and leaching of nitrogen in New Zealand pastures is animal excreta (de Klein *et al*., 2006). Ammonia emissions are highest when pastures are grazed during winter. There has been much research focused on reduction of gaseous losses and N leaching to develop best on-farm management practices. Winter management strategies on dairy farms, like constructing stand-off pads and herd-homes, restrict autumn/winter grazing and thereby restrict the amount of excreta N return to the pastures during winter, thus potentially reducing N leaching and gaseous emissions (de Klein and Ledgard, 2001; Luo *et al*., 2006).

Stand-off pads are constructed from C-rich materials (like wood chips and sawdust) on which animals can be held for long periods during wet weather (Luo *et al*., 2006). A herd-home is a combination of feeding platform, stand-off facility and animal shelter comprising a "greenhouse" type roof over slatted concrete floors with an under-floor bunker. Longhurst *et al*., (2006) studied different bunker media (raw manure, soil, soil + wood shavings and wood shavings) for their performance in absorption and retention of nutrients and found that topsoil was the most viable option for retaining nutrients in bunker media. Luo *et al*., (2006) observed that zeolite was better at minimising NH_3 volatilisation losses than pine bark, wood chips or soil.

A trend towards the intensification of dairy farming has contributed to increasing emissions, which poses concerns for the environment. Better management practices will help to make livestock farming more sustainable by reducing fertiliser cost, reducing environmental degradation from greenhouse gas emissions, increasing nutrient use efficiency, and protecting water resources from leaching and runoff of toxic elements.

1.5 Ammonia emissions measurement methods

Kissel *et al*. (1977) measure NH_3 volatilisation under field conditions without creating an artificial environment in the vicinity of the applied fertiliser or urine deposition using an enclosed chamber method. Black *et al*., (1985b) compared three methods of estimating NH_3 volatilisation an enclosure system with continuous air flow (EM), an unconfined micrometeorological method (integrated horizontal flux method-IHFM), and by mass balance analysis (MBA). Hoff *et al.*, (1981) showed that the enclosure technique could underestimate NH_3 loss with high winds. Bolan *et al.*, 2004 and Singh, 2007 used a chamber method to measure ammonia emissions. With the little information available on the effect of wind speed on ammonia emissions, there is a need to determine the optimum flow rate to measure ammonia emissions after manure application to land.

1.6 Objectives of the study

The overall goal of this study was to identify the best management strategy for application of cattle manure (dung and urine) to land to minimise ammonia, nitrous oxide and methane emissions to the atmosphere.

The specific objectives of the study were to:

1. Determine the optimum flow rate for measurement of ammonia emissions from manure or urea application to soil using a chamber method.
2. Quantify gaseous (NH_3, N_2O and CH_4) emissions from manure or urea after application to soil.
3. Determine the effects of addition of soil or sawdust to manure prior to land application of manure on subsequent gaseous emissions.
4. Determine the effect of surface and incorporated application of manure or urea on gaseous emissions.

Chapter 2

Literature Review

2.1 Introduction

The main objective of this literature review is to provide data on nutrient losses from cattle housing and storage systems. Manure characteristics and their composition are quantified and the nutrient losses from buildings housing livestock, animal manure storage and following manure application to land are reviewed. The literature reviewed covers the nutrient losses at different stages from excreta deposition to application to land, and the strategies to reduce losses.

2.2 Sources of cattle manure

A wide range of effluent and manure materials are generated in the dairy industry (Table 2.1). Farm dairy effluent is a mixture of faeces, urine, and water generated from wash down of the cow shed. Animal manure from animal houses is a mixture of faeces and urine plus bedding, spilt feed, spilt drinking water and water used for washing. In housing systems where livestock are tied, the excretion is separated into solid manure (FYM), mainly containing faeces and straw, and liquid manure, which is a mixture of water, urine and dissolvable faecal components. If manure is collected as farm yard manure, the bedding component is much higher than in slurry. Due to addition of washing water and little use of bedding materials (Misselbrook *et al*., 2005), slurries collected from below slatted floors (Zhang *et al*., 2005) have lower ammonia emissions than other manures.

2.3 Characteristics and composition of manure

The chemical composition varies among different effluents (Table 2.1). Only a small percentage of the total nutrient content of effluent is in a form readily available for plant uptake. Approximately 74-95% of dairy shed effluent nitrogen is in the organic form (e.g., urea, protein) (Longhurst *et al*., 2000; Singleton *et al*., 2001; Selvarajah, 1996; Barkle *et al*., 2001), and about 19% is readily available (Roach *et al*., 2001). Variations in manure composition are likely to be due to the time of milking, the age and breed of the herd, feed quality, wash water management and the time relative to lactation.

Longhurst *et al*., (2000) reported that dairy and pig farm effluent generally contains high concentrations of nutrients, particularly N, P, and K. The average composition of farm dairy effluent comprises 10% excreta, 4% teat washings and 86% wash-water plus other foreign material (Gibson, 1995). Cattle urine contributes some organic compounds and 60-90% of the total N in urine is urea, which is rapidly hydrolysed to ammonium-N and volatilises as ammonia, leaving some ammoniacal-N in the effluent (Jarvis *et al*., 1989; Selvarajah, 1995 and Bolan et al., 2004a). Warburton, 1977 and Macgregor *et al*., 1979 analysed the readily available dissolved kjeldahl-N in dairy shed effluent and found that it accounted for 55% of the total N.

Table 2. 1 Mineral composition of farm dairy effluent and manure (mg l^{-1}) - studies from both New Zealand and overseas countries

Source	**Total N**	**NH_4^+-N**	**NO_3^--N**	**Total Solids**	**pH**	**Total C**	**P**	**K**	**Mg**	**Ca**	**Na**	**References**
Dairy shed effluent	90-240	13.5-61	0.05-3.0	16-67								Warburton (1977); Macgregor (1979); Cooke *et al.*, (1979); Silva *et al.*, (1999); Singleton *et al.*, 2001
Dairy farm effluent	181-363	13-95	1-6	2400-13400	7.6-8.3	1868-3880	49-69	370-435	39	177	54	Goold (1980); O'Toole (1996); Selvarajah (1996); Trolove (1997); Bolan (1998); Di *et al.*, (1998); Longhurst *et al.*, (2000); Di and Cameron, (2002)
Dairy waste water	30-170			200-1600			15-52.5	16-170				Sweeten and wolfe(1990); Tanner *et al.*, (1995); Knight *et al.* (2000); Schaafsman *et al.*, (2000); Cameron *et al.*, (2002); Luostarinen and Rintala (2005)
Dairy factory effluent	158	24.0	6.7		7.0	4555.5					85.3	Cameron *et al.*, 2002
Milk centre waste water	55-7500			210-15000			14-280	570-3330				Loehr (1984); Wright and Graves (1990); Newman *et al.*, (2000)
2 pond system	110	95		185			24	231				Bolan *et al.*, 2004b
Pond sludge(wet)	1597	153	9			17364	168					Cameron *et al.*, 1996
Pond effluent		106		198			27					Craggs *et al.*, 2004
Manure runoff	205			720			35					Loehr (1984)
Dairy slurry	2700			5700			600	1600				Loehr (1984)
Slurry*	3.95	1.63			7.2		0.63	3.46				Husteed *et al.*, 1991
Dairy manure	2198						707	1801				Rico *et al.*, (2007)
Dairy manure		7.33			7.6		4.52	2.75				Michael Jr *et al.*, 2004
farm yard manure	6.2	1.3										Mosquera *et al.*, 2006
Fresh manure	3.5	1.4			7.2							Kaparaju and Rintala, 2008
Solid manure*	4.85	1.33			7.8		1.45	3.85				Chambers *et al.*, 1997
Deep litter*	5.2	0.9			8.6		1.4	9.7				Sommer and Christensen, 1990
Liquid manure*	2.6	2.05			8.7		0.03	4.33				Rohde and Johansson, 1996

*units are g/kg (except pH)

2.4 Nitrogen cycle

2.4.1 Overall cycle in a farm environment

Nitrogen is an essential component of DNA, RNA and proteins, the building blocks of life. All organisms require N to live and grow. For plants and animals to be able to use nitrogen, N_2 gas must first be converted to more a chemically available form such as ammonium (NH_4^+), nitrate (NO_3^-), or organic nitrogen (e.g. urea - $(NH_3)_2CO$). Nitrogen fixation, nitrogen uptake (organism growth), nitrogen mineralisation, nitrification and denitrification are the five main processes involved in the nitrogen cycle (Pidwirny, 2006) (Figure 2.1).

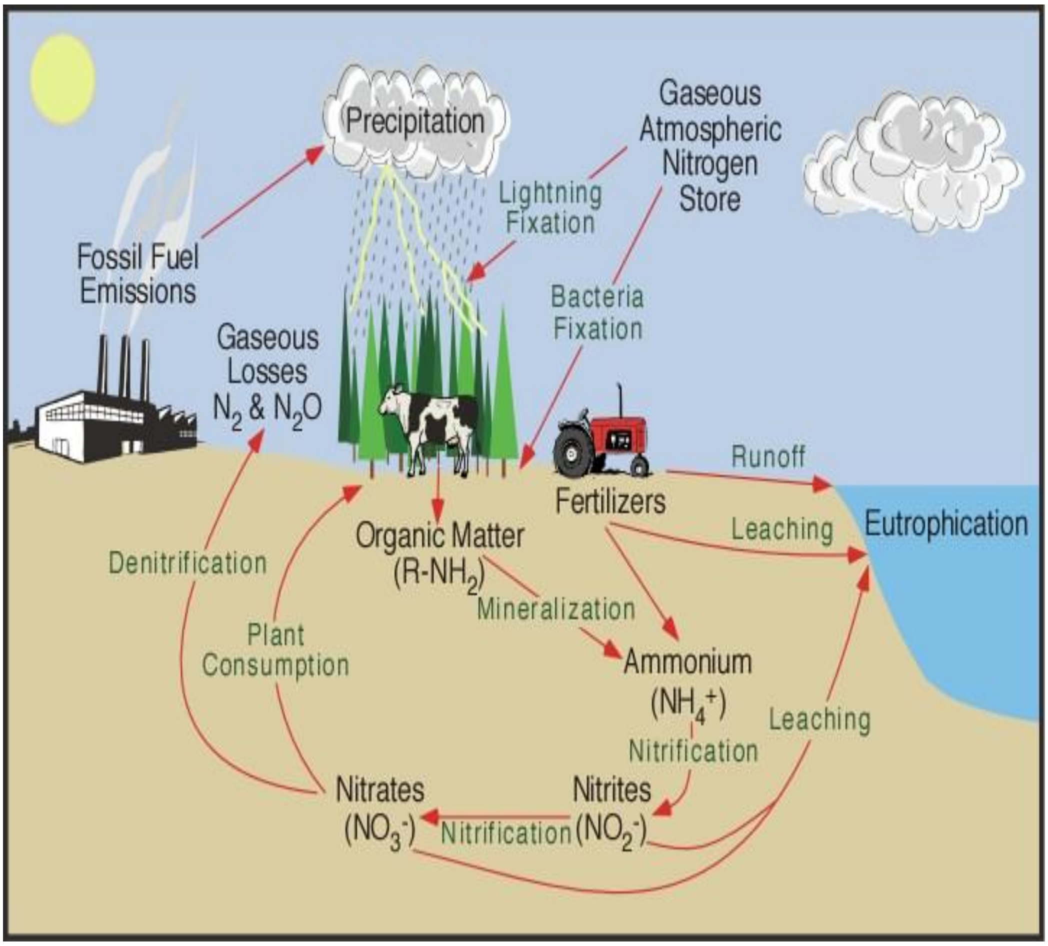

Figure 2.1 Nitrogen cycle (Pidwirny, 2006)

The reactions are as follows

Nitrogen fixation

$N_2 \rightarrow NH_4^+$

Nitrogen uptake

NH_4^+ → organic N

Nitrogen mineralisation

organic N → NH_4^+

Nitrification

$NH_4^+ \rightarrow NO_3^-$

Denitrification

$NO_3^- \rightarrow N_2 + N_2O$

2.4.2 Nitrogen fixation ($N_2 \rightarrow NH_4^+$)

Nitrogen fixation is the process whereby N_2 is converted to ammonium. Nitrogen fixation is essential because it is the only way that organisms can attain nitrogen from the atmosphere. *Rhizobium*, are the only organisms that fix nitrogen through metabolic processes (Pidwirny, M., 2006; Bolan *et al*., 2004a).

2.4.3 Nitrogen uptake (NH_4^+ →organic N)

The ammonia produced by nitrogen-fixing bacteria is usually quickly incorporated into protein and other organic nitrogen compounds, either by a host plant, the bacteria itself, or other soil organisms.

2.4.4 Nitrogen mineralisation (organic N →NH_4^+)

After nitrogen is incorporated into organic matter, it is often converted back into inorganic nitrogen by a process called nitrogen mineralisation.

Livestock effluents are typically rich in nitrogen. The majority of the excreta nitrogen at the time of excretion is in an organic form (Bolan *et al*., 2004a). The organic form has to be mineralised to plant available forms before it can be available to plants.

The concentration of urea in urine is typically around 97% (McCrory and Hobbs, 2001). After excretion, urea is rapidly hydrolysed by urease enzymes to ammonium carbonate. Ammonium carbonate disassociates to produce NH_4^+ and

CO_3^{--} and releases hydroxyl ions (Equation 2.1), causing the pH to increase (Bolan *et al.*, 2004a) through the following equation.

$$CO(NH_2)_2 \rightarrow 2NH_4^+ + 2OH^- + CO_2 \qquad \textbf{(2.1)}$$

Mineralisation of organic matter mainly occurs through the activity of heterotrophic micro-organisms that require carbon as a source of energy. Simple molecules such as amino acids and amines are released and are further metabolised by enzyme activity to yield NH_4^+ ions (Saggar *et al.*, 2004). Ammonium can be removed from the plant available pool via volatilisation, fixation to 2:1 clay minerals, immobilisation back into organic forms by soil micro-organisms or nitrification to nitrate, another plant available form. The proportion and chemical nature of organic and mineral nitrogen will vary in relation to animal type, diet and age. For instance, in raw dairy effluent, approximately 75-95% of N is present in an organic form (Longhurst *et al.*, 2000).

2.4.5 Nitrification ($NH_4^+ \rightarrow NO_3^-$)

Some of the ammonium produced by decomposition is converted to nitrate via a process called nitrification. Nitrification is the microbial oxidation of NH_3 or NH_4^+ to NO_2^- and then to NO_3^- (Equation 2.2 and 2.3). In soils, the transformation of ammonium to nitrate is primarily carried out by *Nitrospora* bacteria, however in slurries it is predominated *Nitrosomonas* bacteria (Addiscott, 2005). Nitrite is further oxidised to nitrate by *Nitrobacter* bacteria, via the following reaction

$$NH_3 + O_2 + 2H^+ + 2e^- \rightarrow NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4e^- \qquad \textbf{(2.2)}$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \qquad \textbf{(2.3)}$$

Nitrification has some important consequences. Ammonium ions are positively charged and therefore stick to negatively charged clay particles and soil organic matter. The positive charge prevents ammonium-N from being leached out of the soil by rainfall or irrigation. In contrast, the negatively charged nitrate ion is poorly held by soil particles and so can be leached through the soil profile, leading to decreased soil fertility and nitrate enrichment of downstream surface and ground waters.

The rate of effluent N nitrification in the soil is determined by four main factors: pH (optimal is between 4.5 and 7.5), available oxygen, temperature (optimal range 25-30^{0}C), and concentration of other nutrients in the effluent matrix, such as phosphate, that may limit nitrification rates.

2.4.6 Immobilisation

In contrast to mineralisation, during immobilisation mineral N is utilised by a range of soil micro-organisms for assimilating carbon during cell growth (Addiscott, 2005). Mineral N incorporated into the microbial biomass is converted into organic forms, which become unavailable for plant uptake. Once the microbial population starts to die and decompose, organic N is again mineralised and re-released back into the plant available pool.

The important factor influencing net immobilisation over net mineralisation is the C:N ratio. Immobilisation is generally favoured in soils with a carbon to nitrogen ratio in the order of 30:1. When the ratio declines below 20:1, mineralisation will take place (Bolan *et al.*, 2004a).

2.4.7 Denitrification

Denitrification losses of N can occur through two mechanisms, the most important being biological denitrification and the other chemical denitrification. Biological denitrification takes place under anaerobic conditions, where facultative anaerobic bacteria use NO_3^- as an electron acceptor, in place of oxygen, during metabolic creations. The final result is the production of gaseous nitrogen (N_2) (Equation 2.5), or one of the nitrogen oxides, which can then be lost from the soil into the atmosphere.

Aerobic conditions

$$C_2H_{12}O_6 + 6O_2 \rightarrow 6\ CO_2 + 6\ H_2O \qquad \textbf{(2.4)}$$

Anaerobic conditions

$$C_2H_{12}O_6 + 4NO_3^- \rightarrow 6CO_2 + 6H_2O + 2N_2\uparrow \qquad \textbf{(2.5)}$$

The reduction of NO_3^- proceeds in a series of steps (Equation 2.6), with the progressive loss of oxygen producing, in turn, nitrite, nitric oxide, nitrous oxide and finally dinitrogen (N_2).

$$\begin{array}{ccccccccc} & & & & \multicolumn{5}{c}{\text{Gaseous losses}} \\ & & & & \Uparrow & & \Uparrow & & \Uparrow \\ 2NO_3^- & \rightarrow & 2NO_2^- & \rightarrow & 2NO & \rightarrow & N_2O & \rightarrow & N_2 \\ \text{(Nitrate)} & & \text{(Nitrite)} & & \text{(Nitric Oxide)} & & \text{(Nitrous Oxide)} & & \text{(Di-nitrogen gas)} \end{array} \qquad \textbf{(2.6)}$$

The rate of denitrification depends on a number of factors and is enhanced by a source of available C. Thus the incorporation of straw or manure into the soil results in denitrification losses if the soil becomes wet and anaerobic over winter. Soil pH can influence the rate of denitrification. In acid soils with a pH less than 5, the denitrification rate is very slow compared with neutral or high pH soil. Soil temperature also has a pronounced influence on denitrification rates (Bolan *et al.*, 2004a). At temperatures below 10^0C the rate is slow and at temperatures below 2^0C denitrification almost stops.

High N and C contents provide optimum conditions for nitrification, the oxidation of NH_4^+ to NO_3^- (Poth and Focht, 1985) and denitrification.

During storage and composting of livestock solid manure the high C:N ratio may enhance immobilisation and thereby reduce nitrification and denitrification (Kirchmann, 1985). During composting of cattle and pig farm yard manure Petersen *et al.*, (1998) observed denitrification losses of 13% and 33%, respectively.

Luo *et al.*, (2000) observed that when rainfall is prolonged in winter and evapotranspiration is low, the soil moisture regime is favourable for denitrification and N_2O emission. According to Oenema *et al.*, 2001 during nitrification or denitrification, all NH_4^+-N will be converted into NO_3 and N may be lost as N_2O, NO, or N_2.

2.5 Ammonia (NH_3) volatilisation

2.5.1 Overview

Ammonia is formed by the breakdown of nitrogen in the form of urea in the urine of the animals. Ammonia formation is catalyzed by the enzyme urease; first urea is converted into the ammonium ion in a liquid layer. The ammonium ion concentration is in equilibrium with the concentration of molecular ammonia (NH_3) in the liquid layer. Release of ammonia from the liquid layer (volatilisation) takes place at the air-liquid layer boundary. The rate of volatilisation of ammonia depends on the reaction mechanisms, the concentrations of ammonia in the liquid and the air, and the transfer processes from the liquid to the gaseous phase (Monteny *et al.*, 1998).

There are three steps involved in the process of emission of ammonia, namely: production, volatilisation and emission. The breakdown of urea is as follows (Equation 2.7):

$$\text{Urea} \rightarrow NH_4^+ \rightarrow NH_{3\,(aq)} \rightarrow NH_{3\,(g)\,(\text{inside air})} \rightarrow NH_{3\,(g)\,(\text{outside air})} \qquad \textbf{(2.7)}$$

The equilibrium between ammonium ions and ammonia in the manure solution is regulated by pH. If the pH value is decreased, the equilibrium is displaced towards ammonium and less ammonia is formed (Kirchmann and Witter, 1989). The most important soil properties controlling NH_3 volatilisation are pH and cation exchange capacity (CEC). The pH of the soil and effluent affects the equilibrium between NH_4^+ and NH_3. At higher pH the equilibrium between ions moves in favour of NH_3, however, at lower pH NH_4^+ is favoured.

Henry *et al.*, (1999) described the relative concentration of NH_3 increasing from 0.1% at pH 6 to 1% at pH 7, 10% at pH 8, and 50% at pH 9, thus, NH_3 volatilisation is negligible from acid-forming fertilisers. Similarly, high ammonia volatilisation was reported when the pH was also high (Bolan *et al.*, 2004; Chadwick *et al.*, 2001; Saggar *et al.*, 2004). Moreover, by reducing slurry pH from 8.0 to 5.5 using sulphuric acid, a dramatic reduction in NH_3 volatilisation was observed (Pain *et al.*, 1990). The rate of ammonia emission to the atmosphere will depend on factors affecting the equillibria between NH_3 and NH_4^+ in solution and between dissolved and gaseous NH_3. Mean annual ammonia emission from United Kingdom (UK) livestock manure storage and spreading are presented in Table 2.2.

Table 2.2 Annual NH_3 emissions from UK livestock production

Source	Mean NH_3 emission (t x10^6)	
	Pain *et al.*, 1998	Webb and Misselbrook, 2004
Hard standings	27.3	39.2
Hard standings		17.7
Buildings	17.1	10.0
Spreading	49.0	51.6
Grazing	5.0	9.4
Total	98.7	127.9

The animal excreta degraded biologically in grazed pastures can lead to formation of NH_4^+ ions and NH_3 in the soil in a ratio dependent on the pH, NH_3 will then volatilize to the atmosphere. Total concentration of ammoniacal nitrogen (TAN = NH_4 + NH_3), pH and dry matter content are the important characteristics which determine NH_3 volatilisation (Jarvis and Pain, 1990; Sommer and Husted, 1995).

The amount of NH_3 volatilized increases with increasing temperature, and the effect of mixing on NH_3 volatilisation depends on the temperature at which the manure slurry is stored. The reduction in NH_3 volatilisation at low temperature caused by disturbing the microbial communities by mixing will be small compared to the release of entrapped NH_3 and so mixing will result in a net increase in NH_3 emissions. At higher temperature, the contribution of microbial activity to NH_3 volatilisation is much higher and so NH_3 volatilisation will be much more affected by exposure to oxygen caused by mixing (Van der Stelt *et al.*, 2007).

The CEC of soil influences the NH_3 concentration through the reaction of NH_4^+ ions with the negatively charged cation exchange sites. Soils with low CEC are more prone to NH_3 volatilisation than the soils with high CEC (Saggar *et al.*, 2004a). There is an inverse relationship between NH_3 loss and CEC, and the relationship is stronger for urine than for urea (Whitehead and Raistrick, 1990).

About 4 to 46% of urine N from urine patches will be lost as NH_3. Hot, dry, summer conditions favor losses, whereas cool, moist, winter conditions minimise losses. Thus, measured mean urine patch volatilisation losses of 22% in summer, 25% in autumn, but only 12% in winter were reported by (Sherlock and Goh, 1984). Vallis *et al*., (1985) found losses as high as 46% in the tropical dry season. Ryden *et al*., (1987) estimated losses of urine N of 22% at a mean air temperature of 16°C, and losses of only 10% at a mean air temperatures of 8°C. Denmead *et al*., (2004) summarised a number of published emission rates (Table 2.3) for dairy cattle and compared the results with his study and found that emissions were greater in summer than in winter.

Table 2.3 Daily emissions of NH_3-N from pastures during grazing by dairy cattle.

Country	g N animal^{-1} d^{-1}	References
UK	16.9	Misselbrook *et a*l., (2000)
Europe	17.5	Bouwman *et al*., (1997)
New Zealand	30.1	Ledgard *et a*l., (1999)
Netherlands	39.8	Bussink (1992)
USA	43.8	Mosier *et al*., (1998)
Australia	39.8	Eckard *et al*., (2003)
Australia(winter)	3.4	Denmead *et al*., (2004)
Australia(summer)	47.1	Denmead *et al*., (2004)

2.5.2 NH_3 emissions during excreta deposition

Usually in New Zealand dairy cows spend most of their time grazing pasture outside. With intensification of dairy farming in recent years, some of the dairy farms are using partial housing during winter to minimise nutrient losses and to maximise productivity (de Klein and Ledgard, 2001). The frequency of manure removal varies from several times a day, up to monthly intervals. The manure removal system (e.g., type of channel, removal frequency) is more important than the housing system from an NH_3 emissions point of view. The mean NH_3 emissions from different yard types and housing systems are summarised and presented in (Table 2.4).

Seasonal differences in emission rates were found from a dairy cow collecting yard in which measurements were made in late summer and winter (Misselbrook *et al*., 1998). Misselbrook *et al*., 2001 observed that ammonia emissions from a collecting yard were lower than from the feeding yard. Similarly, Keck (1997) also observed the effect of temperature on NH_3 emissions from urine and feces.

Table 2.4 Mean NH_3 emissions from different yard types and housing systems

Yard type/Housing	Cleaning method	Mean NH_3 emission rates (mg NH_3-N m^{-2} h^{-1})	Measuring method	References
dairy cow collecting yard	daily	280	equilibrium concentration technique	Misselbrook *et al.*, 2001
dairy cow feeding yard	daily in winter, weekly in summer	690	closed chambers	Misselbrook *et al.*, 2001
beef feeding/ loafing area	weekly in summer	220	closed chambers	Misselbrook *et al.*, 2001
deep litter barn		13.9 kg NH_3/cow/yr		Mosquera *et al.*, 2006
outdoor storage		7.9 kg NH_3/cow/yr		Mosquera *et al.*, 2006
Straw bedded		3.7 kg NH_3 500 kg^{-1} $90d^{-1}$		Demmers *et al.*, 1998
slurry with scraped floor		6.0 kg NH_3 500 kg^{-1} $90d^{-1}$		Vant'Ooster, 1994
slurry with slats		8.3 kg NH_3 500 kg^{-1} $90d^{-1}$		Vander Hock, 1993
slurry		8.8 kg NH_3 500 kg^{-1} $90d^{-1}$		Vander Hock, 1993

2.5.2.1 Slatted floor

Slatted floors were primarily developed to reduce the amount of daily labour required to clean manure and as a means to passively transfer liquid manure directly to a storage or gravity collection gutter located immediately below the slatted floor. Braam and Swierstra, (1999) reported that about 40% of the NH_3

emissions in a slatted floor housing system are generated from slurry stored in the pit below the slatted floor and the balance 60% is generated from urea deposited on the slats.

Zhang *et al.*, (2005) found that in a naturally ventilated building with different floor types and manure handling systems, ammonia emissions increased with temperature (Table 2.5), but the increase was mostly dependent on floor type and manure system. In their study, the emission rate is given as g HPU^{-1} d^{-1} where HPU (Heat production unit) is defined as 1000W total heat produced by the livestock at an environmental temperature of 20°C.

Table 2.5 Mean NH_3 emissions from different floor types and handling systems related to temperature-Zhang *et al.*, 2005

Floor type	manure handling system	emissions (g HPU^{-1} d^{-1})			Indoor temperature °C
		NH_3	CH_4	N_2O	
Solid concrete floor	delta scraper	76	399	0.2	21.7
		26	244	0.5	7.0
Hot rolled asphalt	scraper & drain	23	230	0.0	17.4
		14	289	3.3	6.2
Pre-manufactured concrete elements (grooves)	scraper & drain	24	218	1.0	19.9
		11	236	0.2	6.1
Pre-manufactured concrete elements (profiles)	scraper & drain	20	248	2.2	15.7
		9	217	0.0	3.6
Slatted floor	scraper	14	244	1.5	9.6
		27	339	0.8	19.0
Slatted floor	back flushing	68	343	0.1	22.4
		18	283	1.4	5.8
Slatted floor	circulation without additive	36	277	3.7	17.3
		20	279	3.1	6.3
Slatted floor	circulation with additive	22	285	2.8	8.9

NH_3 emissions from cows in tie stalls were 35% less than those kept in cubicles (Monteny and Erisman, 1998), because of a reduction in area of floor covered by feces and urine and slurry pit surfaces. Braam and Swierstra, (1999) and Oosthoek *et al.*, (1991) found that scraping of smooth floor may reduce emission by up to

Table 2.6 Ammonia emission factors for cattle buildings

Building design	Pen design	Emission factor (% of total-N)	Emission factor (kg NH_3-N per kg TAN)	Country	References
Tie stalls	slurry	3.0	0.6	Austria	Amon *et al.*, (2001)
Cubicle	partly slatted floor, 0.4 m deep slurry Channel	6.0	0.12	Northern Europe	Groot Koerkamp *et al.*, (1998)
Cubicle	partly slatted floor, 1.2 m deep slurry Channel	8.0	0.17	Netherland	Kroodsma *et al.*, (1993)
Cubicle	slatted floor	2-15	20 and 45 g NH_3-N cow^{-1} day^{-1}	Netherland	Monteny and Erisman, 1998
Tie stalls	slatted floor		5-21 g NH_3-N cow^{-1} day^{-1}		
	slatted floor, slurry	8.0		Denmark	Poulsen *et al.*, (2001)
Solid	floor deep litter	6.0	0.12	Denmark	Rom and Henriksen (2000)

30%, but may be harmful to animal welfare. Water spraying after scraping solid floors may reduce emission by 65% (Braam *et al.*, 1997; Swierstra and Braam, 1999; Swierstra *et al.*, 1995). Scraping and spraying the floor with formalin, thereby reducing urease activity, may reduce NH_3 emission by 50% (Ogink and Kroodsma, 1996) in slatted floors. Ammonia emission factors for cattle buildings were summarised from the recent studies and showed that 2-15% of total-N was emitted from various buildings with differing floors (Table 2.6).

2.5.2.2 Deep litter

Deep litter is a housing system where manure is stored together with bedding material in a thick layer on the floor. The amount of bedding material added to the litter should be sufficient to absorb the manure and create a relatively dry bedded area for the animal. The most common bedding material used in deep litter housing is straw, long or chopped wood shavings, sawdust and peat.

Sommer (2001) found that, during composting of deep litter, N losses due to leaching, NH_3 emission and denitrification were between 12 and 28% of the initial N. Chambers *et al.*, (2003) compared NH_3 emissions between beef cattle on straw-bedded systems and cattle in slurry-based systems. Their study showed that the straw-bedded system resulted in significantly less NH_3 emission ($p<0.10$) than the slurry system (20.1 kg compared with 29.6 kg NH_3-N per 500 kg live weight gain, equating to 33 and 49 g NH_3 cow^{-1} day^{-1}, respectively). Karlson and Jeppsson, (1995) and Petersen *et al.*, (1998) reported losses of 25-30% of the total-N in stored pig manure and cattle deep litter, even though low emissions of 1-10% were measured by Amon *et al.*, (2001) and Chadwick (2005).

In deep litter systems the decomposition of manure and bedding material is complex. The oxygen level decreases with depth in deep litter (Groenestein and Van fassen, 1996). Deep litter degradation is a slow-composting process and the rate and efficiency of the composting process is influenced by several factors like temperature, moisture content, C/N ratio, pH level, oxygen level and the physical structure of the organic material (Crawford, 1985). The amount of nitrogen that can be immobilized during the decomposition depends on the carbon content in the deep litter. Adding carbon-rich organic materials to the manure means that more ammonium can be biologically immobilized during decomposition (Kirchmann, 1985; 1989).

Poincelot (1974) found that the excess nitrogen is lost to the atmosphere as ammonia if the C/N ratio is below 26. According to Kirchmann (1985) at C/N ratios above 50, no ammonia nitrogen losses occur. The ammonia volatilized from manure is less when the ratio between available carbon and nitrogen is higher. In the deep litter system, the manure is mixed with bedding material of a higher C/N ratio. The C/N ratio in urine is about 1, in fresh cattle feces is around 23 (Kirchmann, 1985). A range of high C/N ratio materials have been used in deep litter systems. In wood waste, the C/N ratio is about 600 and in peat (*Sphagnum fuscum*) about 91. Kirchmann and Witter, (1989) found that the adsorption capacity of peat was 23.4 mg NH_3-N/g dry matter. Jeppson (1999) estimated that the average ammonia emission rate (Table 2.7) from the different beds was between 319 and 747 mg m^{-2} h^{-1}. The mixture of peat and chopped straw was estimated to reduce the ammonia emission by 57% compared with long straw, because peat has high capacity to adsorb ammonia, low pH value, high C/N ratio and a high capacity to absorb water, all of which affects the mechanisms that reduce ammonia losses during decomposition.

Table 2.7 Mean ammonia emission rates of the four deep litters and the manure alley (Jeppson, 1999)

Bedding material/manure alley	Ammonia emission rate (mg m^{-2} h^{-1})
Long straw	747
Chopped straw	547
Chopped straw with additive	552
Peat and chopped straw	319
Manure alley	297

2.5.2.3 Stand-off pads

Stand-off pads are built with a drained loafing area to hold cattle for longer periods when the conditions are not suitable to keep them in pasture, and also to reduce NO_3 leaching losses, and prevent soil and sward damage (Luo *et al.*, 2007a). The strategic use of stand-off pads or feed pads during wetter periods is increasingly being encouraged on New Zealand dairy farms to minimise soil and pasture damage and to reduce the risk of environmental losses (de Klein and Ledgard, 2001; Chadwick *et al*., 2002). By using a stand-off pad there is a decrease in autumn grazing which reduces both N_2O emissions and NO_3^- leaching losses from grazed pasture by about 40% (de Klein *et al*., 2006).

Improved winter management systems reduce animal excreta deposition on wet soils and reduce pugging damage due to grazing (Luo *et al*., 2006; Luo *et al*., 2007a). Luo *et al*., (2007b) with an increase in NH_4^+-N (2.03-6.51 mg N kg ha^{-1}) emissions and NO_3-N leaching, but the increase was higher in NO_3-N concentration because rapid transformations of excreta-N take place in soil after application of effluent.

2.5.3 NH_3 emissions during manure storage

The proportion of the total manure produced in the form of liquid manure/slurry and solid manure varies considerably between countries (Burton and Turner, 2003; Menzi, 2002). For animal welfare reasons there is a trend toward more solid manure systems in many countries. Until manure can be transported to the field for spreading, the collected animal manure in housing systems must be stored for some time inside or outside the housing. The emission from stored solid manure depends on composting of manure. Water content, porosity (density) and C content in the manure influences composting. Manure composition and climate influences the NH_3 emission from stored manure. Emission from the stored manure will be affected by mineralisation and immobilisation, which will change the organic N and total ammoniacal N.

Protejoie *et al*., (2003) showed that around 50% of ammonia emissions were from housing and storage with the other 50% emitted from surface application of slurry to land. Kulling *et al*., (2003) found total-N losses were 11% with farm yard manure, 19% for liquid manure and 30% for slurry during 5-7 weeks storage. Misselbrook *et al*., (1998) and Pain *et al*., (1998) measured ammonia emissions for cattle during housing, storage and spreading and observed more emissions during spreading than housing and storage (Table 2.8).

Table 2.8 Emission of ammonia from dairy cows (kg N cow^{-1} yr^{-1})

Grazing	Land spreading	Housing	Collecting yard	Storage	Total	References
0.96	10.46	5.86	0	3.45	20.73	Pain *et al*., 1998
0.96	10.46	5.20	3.03	3.45	23.10	Misselbrook *et al*., 1998

2.5.3.1 Slurry storage

In Netherlands, Ireland and Norway, slurry stores may be partly below the slatted floor of the animal building and partly outside in slurry tanks (Burton and Turner, 2003; Menzi, 2002). Most of liquid manure/slurry is stored in tanks made with concrete outside the livestock houses.

Ammonia emission from slurry in open tanks, silos, and lagoons ranges from 1.44 to 2.33 kg NH_3-N m^{-2} $year^{-1}$ which contributes between 6 and 30% of the total N in stored slurry. Due to higher pH and TAN content in fermented slurry, emissions from in slurry that has been fermented in a biogas plant tends to be double those from untreated slurry (Sommer *et al*., 1993; Sommer, 1997).

Amon *et al*., (2006) found that slurry separation increased net total NH_3 emissions due to composting of the solids. They also reported that covering the slurry store with a layer of chopped straw instead of a wooden cover increased NH_3 emissions during storage and after field application (Table 2.9).

Table 2.9 NH_3, CH_4, N_2O and greenhouse gas (GHG) emissions during storage and after field application of dairy cattle slurry

Source	NH_3 g m^{-3}	CH_4 g m^{-3}	N_2O g m^{-3}	GHG kg CO_2 eq. m^{-3}
Untreated	226.7	4046.9	23.9	92.40
Separated(solid and liquid)	402.8	2363.3	28.6	58.51
Anaerobically digested	229.9	1344.5	31.2	37.90
Straw cover	320.4	4926.2	52.5	119.73
Slurry separation	422.6	1739.3	54.2	53.32

Significant decreases of NH_3 losses were found in covered slurries (Sommer, 1997; Sommer *et al.*, 1993; Hornig *et al.*, 1999; Portejoie *et al.*, 2003; Misselbrook *et al.*, 2005a). The cover may be a natural surface crust, a cover of straw, peat or floating expanded clay particles, or a roof. Crusting will take place on stores with a slurry dry matter content of < 2%. Generally cattle slurries form crusts more rapidly than pig slurries. NH_3 volatilisation is reduced by reducing the pH in the surface of the slurry with a cover of straw (Xue *et al.*, 1999; Clemens *et al.*, 2002). Verboon *et al.*, (2000) observed that the reduction in ammonia emissions when slurry was covered with a tent cover averaged 71% in winter and 84% in summer. For a straw crust emissions were reduced to 65% in winter and 70% in summer.

2.5.3.2 Solid manure storage

NH_3 losses during storage of solid manure were reduced by 50% following addition of straw (25 kg per cow daily) (Kirchmann and Witter, 1989). According to Amon *et al.*, (2001) and Chadwick (2005) rain will reduce NH_3 volatilisation by leaching TAN into lower sections. Dewes (1996) found reduction of emissions from 43% of total N to 22% of total-N with increasing straw addition from 2.5 to 15 kg straw LU^{-1} day^{-1}. Covering the heap with a tarpaulin or compaction of the litter may reduce losses up to 50-90% by decreasing passage of air through the heap (Chadwick, 2005 and Sommer, 2001). The mean ammonia emissions from cattle farm yard manure and deep litter ranged from 2.2-4.9% and 2.3-15 % of total N respectively. The nitrate leaching from stored farm yard manure varied between 2-4% of total N (Table 2.10). The ammonia emissions from stacked solid manure were reviewed and are presented in table 2.11.

Table 2.10 Estimates of N losses by leaching from stored farm yard manure

Manure	% lost by leaching		References
	N	TAN*	
Cattle	2-4	8-16	Amon *et al*., (1997)
Beef cattle	3	12	Eghball *et al*., (1997)
Cattle and pig	2-4	4-16	Petersen *et al*., (1998)
Cattle and pig	2-4	8-16	Sommer (2001)

*Estimated assuming TAN in fresh farm yard manure is 25% of total N.

Table 2.11 Ammonia emissions from stacked solid manure

Animal	Manure	Temperature >50^{o}C	Mean emission of NH_3 (kg NH_3-N t^{-1})	Mean emission of NH_3 (NH_3-N % of Total-N)	References
Cattle	FYM	No	0.1	2.2	Amon *et al*., 2001
Cattle	FYM	Yes	0.4	4.9	Chadwick, 2005
Pig	FYM	Yes	2.8	23.5	Sommer, 2001
Dairy cow	Deep litter mixed at start	Yes	0.2	2.3	Sommer and Dahl 1999
Dairy cow	Deep litter	Yes	1.3	15.5	Lammers *et al*., 1997
Pig	Deep litter	Yes	2.4	30.2	Takashi *et al*., 2001

2.5.3.3 Anaerobic lagoons

Smith *et al.*, (2000, 2001) demonstrated that lagoons and lined ponds are the major storage systems for manure in North America, the United Kingdom, and some Southern and Eastern European countries. In the absence of oxygen, organic wastes are biologically degraded into CO_2, CH_4, N_2 and H_2S during anaerobic fermentation. Urine N is a prime source for NH_3 and N_2O emissions, and anaerobic decomposition of dung leads the emission of CH_4.

Harper *et al.*, (2004) found much smaller NH_3 emissions from animal housing (7%), lagoons (8%) and fields (2%). They also observed the conversion of significant quantities of NH_4^+ to N_2 in lagoons (Equation 2.8), with the emission rate largely dependent on NH_4^+ concentrations.

$$NH_4^+ + NH_3 + O_2 \rightarrow N_2O \rightarrow N_2 \qquad \mathbf{(2.8)}$$

Conversion of NH_4^+ to N_2 in lagoons through chemical denitrification accounted for the greatest loss component of the N entering the farms (43% as N_2) with small amounts lost as N_2O (0.1%).

2.5.3.4 Composting

Composting is an alternative to conventional management of agricultural wastes which involves natural biological breakdown of dung into more stable organic substances. During the composting process and storage, ammonia emissions increase gradually. Amon *et al.*, (1997a) found greater losses from composted than from uncomposted manure. During composting, fresh air from the atmosphere enters through the lower section of the heap and an upward airflow takes place. Composting increases the pH, which causes interim increases in the NH_3 fraction of NH_4^+, so that the volatilisation of NH_3 from composting solid manure and deep litter may be high.

Osada *et al.*, (2001) found that composting of deep litter caused an initial increase in temperature of between 60 and 70^{o}C and then declined slowly to 25-30^{o}C after 10-12 days. They also reported that 23% of the total-N content in the stored deep litter was volatilized as ammonia. Martins and Dewes (1992) observed most leaching (>70%) within the first 10 days of the composting period and found that between 9·6 and 19·6% of the initial total nitrogen was lost as leachates during the composting period. The major proportion of nitrogen in the leachate (76·5-

97·8%) was ammonium-N. They also reported that between 46·8 and 77·4% of the initial total nitrogen content was emitted as NH_3 with small amounts (<5%) of Kn_{ox}. During the composting, addition of amendments, such as woodchips, elemental sulphur (S) and zeolite decreased NH_3 volatilisation (Mahimairaja *et al.*, 1994).

2.5.4 NH_3 volatilisation during and after application of manure to land

Ammonia emissions from manure during and after application depend on:

- The rate of conversion of NH_4^+ to NH_3 gas,
- Transfer of NH_3 gas between the soil solution and the atmosphere,
- Soil properties such as pH, cation exchange capacity (CEC), water content and porosity,
- Spreading techniques and surface exposure of the manure,
- Climatic conditions including temperature, rainfall and wind speed,
- Method and rate of application of manures and
- Height and density of the crop.

The majority of soil nitrogen is relatively immobile, however, nitrate because of its negative charge, is repelled by cation exchange sites and is therefore readily leached when water drains through the soil. In New Zealand, NO_3^- leaching mainly occurs in late autumn, winter and early spring, when there is an excess of rainfall over evapotranspiration and the soil is at or near field capacity. During this period plant uptake of nitrogen is low and therefore nitrate may be present in significant quantities in the soil solution. A considerable amount of N is lost from intensively grazed pastures due to leaching from animal urine patches in New Zealand.

Cameron and Di (2004) summarised and compare the data (Table 2.12) on nitrate leaching losses from farm effluent and waste experiments conducted on Templeton soil lysimeters, with a range of farm effluents and wastes, including pig slurry, dairy pond sludge, farm-dairy effluent, and cow urine. The leaching losses decreased in the following order: cow urine>pig slurry>farm-dairy effluent>dairy pond sludge.

Table 2.12 Nitrate leaching from cattle manure applied to pasture soils in New Zealand (adapted from Cameron *et al*., 2004)

Source	Soil type	Rate (kg N ha^{-1} yr^{-1})	Irrigation method	Application frequency per year (mm)	Leaching loss (kg N ha^{-1} yr^{-1})	References
Dairy shed effluent	fine sandy loam	200	flood (6x100mm)	4x50	6	Silva *et al*., 1999
		400	flood (6x100mm)	4x100	10	Silva *et al*., 1999
		400	flood (6x50mm)	2x200	25	Di *et al*., 1998
		400	flood (6x100mm)	2x200	13	Di *et al*., 1998
Dairy pond sludge	fine sandy loam	300	surface	1	<1	Cameron *et al*., 1996
		300	injected (25mm)	1	5	
Dairy farm effluent	brown loam	100	spray	8x12.5	18	Roach *et al*., 2001
		200	spray	8x25	20	
		400	spray	8x50	50	
Urine patch	fine sandy loam	500	flood (6x100mm)	1	40	Fraser *et al*., 1994
		1000	flood (6x100mm)	1	124	Silva *et al*., 1999
		1000	flood (6x100mm)	1	77	Di *et al*., 2002

Nitrate is most susceptible to leaching, followed by ammonium and organic forms of N. Split application of effluent at different times and reducing the overall rate from 400 to 200 kg N/ha, reduced the overall quantity of nitrate leached by c.

30%. Studies by Bierman *et al.*, (1999) found nitrogen lost in runoff was 5 to 19% of N excreted and 10 to 16% leached into soil. Contrary to this, relatively low loss of nitrogen through leaching was found in solid storage systems (less than 5% of N excreted), but greater loss could also occur (Rotz, 2004).

In addition to the potential for nitrate-N leaching, many studies report that total soil N increases with effluent irrigation (Magesan *et al*., 1999; Barkle *et al*., 2000; Degens *et al*., 2000; Peacock *et al*., 2001; Cameron *et al*., 2002; Hawke & Summers 2003), contrary to this some researchers have shown that effluent irrigation can decrease total soil N (Falkiner & Smith 1997; Sparling *et al*., 2001), or result in no change (Schipper *et al*., 1996; Sparling *et al*., 2001). Saggar *et al*., (2004) summarised selected references on NH_3 volatilisation from cattle wastes applied to pasture soils (Table 2.13).

Table 2.13 Ammonia emission from animal manure applied to the soil

Manure source	Soil type	Manure rate (m^3 ha^{-1})	measurement method	Ammonia emission rate kg N ha^{-1}	Country	References
Cattle slurry	sandy loam	15	mass balance	16.6	Netherlands	Pain *et al*., 1990
Cattle slurry		60	wind tunnel	33.2	United Kingdom	Thompson *et al*.,1990
		20-120	wind tunnel	16.5-73	United Kingdom	Thompson *et al*.,1991
Dairy manure	fine sandy loam to silt loam	75	theoretical profile shape	23-106	Canada	Gordon *et al*., 2000
		18-64		4.5-20	Canada	Gordon *et al*., 2000
Cattle slurry	sandy	30	wind tunnel	33.3-82.9%	Denmark	Sommer and Olsen, 1991

Surface broadcasting is a rapid and inexpensive method of slurry application but may damage the crop (Christie, 1987). If applying slurry on perennial forages in stony or hard soils, where it is difficult to inject the slurry then surface banding (applying manure in strips on the soil surface) is the best available technology. Also, surface banding decreases slurry contact with residues and the standing crop and increases contact with soil, further reducing air flow over the manure (Sommer and Hutchings, 2001). Thus, banding reduces ammonia emissions compared to broadcasting by minimising the surface area exposed to the atmosphere.

Bolan *et al*., (2004a) also observed changes in pasture growth rates and nutrient concentration, when farm dairy effluent was applied to a high fertility perennial rye grass (*Lolium perenne*) and white clover (*Trifolium repens*) pasture (Olsen P 25-30 mg P ml^{-1}). farm dairy effluent (aerobic pond) with N, P, K, Ca, and Mg concentrations of 135, 22.1, 231, 15.2, and 11.5 mg l^{-1}, respectively, was applied at the rate of 0, 150, and 200 kg N ha^{-1} and measured pasture dry matter yield increased with an increasing rate of farm dairy effluent application. The concentration of N and K also increased with an increasing rate of farm dairy effluent application. Increasing rate of effluent application decreased the content of exchangeable Ca and Mg in the soil, due to the high K loading and leaching of anions. Usually farm dairy effluent is alkaline and most New Zealand soils are acidic. Most of the recent studies have shown that farm dairy effluent irrigation increases soil pH (Menzies *et al*., 1999; Barkle *et al*., 2000; Redding 2001; Sparling *et al*., 2001). An additional application of N has been shown to reduce the clover component of a white clover/rye grass pasture (Bolan *et al*., 2004a; Wang *et al*., 2004; Monaghan *et al*., 2005).

Pain *et al*., (1989) reported that NH_3 losses were less than 1% of the applied ammonium with conventional spreaders, trail hose application and a cable driven irrigator. However, by using an irrigation device having a spreading length of 25-30 m (Philips *et al*., 1991; Gronauer *et al*., 1994), the losses were up to 10% of applied TAN. During sprinkler application of dairy waste, 18% of the total ammoniacal nitrogen entering from the sprinkler pump volatilized before it reached the ground (Rumburg *et al*., 2006). Similarly, Sharpe and Harper (1997) also found that during sprinkler application of swine effluent, 13% of the NH_4-N volatilized during application. They also reported that overall sprinkler waste application emissions for each cow per annum was 34 kg. Huijsmans, (1999) studied and compared different methods of application (Table 2.14) to land and observed that injection and closed slots resulted in less TAN losses than surface application or surface banding.

Table 2.14 Cumulative loss of NH_3 after application to land by using different methods and site types

Application method	Site type	% of TAN lost
Surface spreading	grass	68.0
Injection, closed slot	grass	1.0
Narrow band spreading	grass	10.2
Trail hose	grass	25.6
Injection	arable land	9.0
Surface spread and subsequently ploughed with in 2 h	arable land	19.7

Longhurst *et al.*, (1999) applied raw farm dairy effluent at different N loading rates to grazed pastures and found that the pasture yield over a year increased by up to 24% compared to the control. The efficiency of N use decreased with increasing farm dairy effluent loading rates. Ammonia emissions from surface application of farm yard manure to the field at different times (ranged from 19 to 65% of the total-N) are presented in Table 2.15.

Table 2.15 Ammonia emission from solid animal manure (FYM) applied to the field

Manure source	Application method	Ammonia emission, % of Total-N applied				Country	References
		0-6 hrs	0-24 hrs	0-36 hrs	> 6 days		
Cattle and pigs	Surface applied	22	32.5		65	United Kingdom	(Chambers *et al*., 1997)
Cattle	Surface applied			60		Europe	(Menzi *et al*., 1997)
Cattle	Surface applied	11	22		37	Denmark	(Sommer and Christensen, 1990)
Pigs	Surface applied	6	10		19	Denmark	(Sommer and Christensen, 1990)

Rodhe *et al*., (2006) observed that shallow injection in closed slots was a promising technique to reduce negative environmental impacts from NH_3 emissions with a limited release of N_2O and CH_4. With shallow injectors the ammonia losses were 20-75% lower than after band spreading on sandy soils (Hansen *et al*., 2003). Apparent NH_4-N recovery values for injected slurry ranged from 23 to 50%, whereas that of broadcast and band-spread slurries was ranged from 16 to 33% and 17 to 38%, respectively (Mattila *et al*., 2003).

High losses of ammonia and deterioration of fodder quality was observed in spreading of manure into ley crops (Rodhe and Rammer, 2002). To reduce ammonia losses after spreading, incorporation of slurry into the soil is the most efficient method (Misselbrook *et al*., 2002; Mattila & Joki-Tokola, 2003). Slurry incorporation reduces odour problems (Phillips *et al*., 1991) and improved fodder quality (Rodhe and Rammer, 2002).

Application of manure by trail hose and injection was found to be effective in reducing farm GHG emissions on average by 0.7 and 3.2% compared to broadcasting (Weiske *et al*., 2006). The use of a free stall barn, bottom-loaded slurry storage and direct injection of manure into the soil reduced NH_3 emissions by 33% to 50% compared to other commonly used dairy housing and manure handling systems in the north eastern United States (Rotz *et al*., 2006). Rodhe *et al*., (1996) studied and compared application of manure using different methods of application (Table 2.16) and found that trial hose application resulted in lower emissions than other methods.

Table 2.16 Ammonia emission from cattle and pig slurry or liquid manure applied by different methods

Manure source	Crop	Ammonia emission, % of Total-N applied			Country	References
		Broad spreading	Trail hose application	Injection to 2 cm		
Pig	Barley	10	5		Sweden	Rohde and Johansson (1996)
Cattle	Ley	40	29	39	Sweden	Rohde and Johansson (1996)
Cattle	Ley	67	31	42	Sweden	Rohde and Johansson (1996)
Cattle	Ley	9			Norway	Morken (1992)
Pig	Ley	8			Norway	Morken (1992)

2.6 Nitrous oxide (N_2O) emissions from manure

2.6.1 Overview

Grazing pasture is a major system of livestock production in many countries including New Zealand and it has been identified as an important source of N_2O (Ministry for Environment, 2006). Nitrous oxide emissions from grazed pastures in New Zealand are generally high, reaching up to 150 g N_2O-N ha^{-1} day^{-1} in winter when soil is wet, and the emissions increase soon after grazing due to N in the dung and urine excreted by grazing animals (Luo *et al*., 2008a; Saggar *et al*., 2004a, 2007a).

De Klein *et al*., 2003 reported that most of the N_2O is generated from mineral-N originating from animal dung and urine, biologically fixed N_2 and mineralisation of soil organic-N. More than half New Zealand's N_2O emissions originate directly from uneven deposition of excretal N in grazed pastoral soils, while another 30% are from indirect emissions from leached and volatilized excretal-N. New Zealand N_2O emissions increased by 25% between 1990 and 2004 (Ministry for Environment, 2006), mainly due to a sharp increase in fertiliser-N use and associated excretal-N inputs.

2.6.2 N_2O emissions during manure deposition

N_2O emissions from animal excreta occurs from cattle urine patches deposited under wet soil conditions in autumn and winter (Ledgard *et al*., 1996; de Klein *et al*., 2003, 2004). Emissions from agricultural soils and livestock housing amount to 3.9 Tg yr^{-1} N_2O-N. According to Freibauer and Kaltschmitt (2001) animal houses (6%), manure storage (2%), and grazing (13%) contribute 21% of N_2O emissions from the agriculture sector.

Table 2.17 Mean N_2O and CH_4 emissions from different yard types and housing systems

Cleaning method	Mean N_2O emission rates (mg N_2O-N m $^{-2}$ h $^{-1}$)	Mean CH_4 emission rates (mg CH_4-C m $^{-2}$ h $^{-1}$)	Measuring method	References
Scraped daily	7.5	0.43	equilibrium concentration technique	Misselbrook *et al*., 2001
Scraped daily in winter, weekly in summer	18.6	0.36	closed chambers	Misselbrook *et al*., 2001
Scraped weekly in summer	10.2	0.59	closed chambers	Misselbrook *et al*., 2001
		1.3 kg CH_4/cow/yr	Integrated horizontal flux approach	Mosquera *et al*., 2006

2.6.3 N_2O emissions during manure storage

The emission of N_2O from manure during storage and treatment depends on the nitrogen and carbon content of the manure and on the duration of the storage and type of treatment (Amon *et al*., 2006). Nitrification (the oxidation of ammonia to nitrate) is a necessary prerequisite for the emission of N_2O from stored animal manures. In stored animal manures, provided with sufficient supply of oxygen nitrification occurs. Nitrification does not occur under anaerobic conditions. Under anaerobic conditions, denitrification is more likely to occur, transforming nitrites and nitrates to N_2O and dinitrogen (N_2) (Robertson and Tiedje, 1987). The ratio of N_2O to N_2 increases with increasing acidity, nitrate concentration and reduced moisture. NO_x (sum of NO and NO_2) promotes ozone formation in the troposphere and N_2O is a greenhouse gas and contributes to stratospheric ozone depletion (Crutzen, 1976).

Lovell & Jarvis (1996) measured significant emissions of N_2O following urine application (417 g N_2O-N ha^{-1} day^{-1}). Chadwick *et al.*, (2000) reported N_2O

emissions from dairy slurry were 10 times greater in summer than in winter. NH_3 volatilisation can be reduced by reducing the pH in the surface of the slurry with a cover of straw (Xue *et al.*, 1999; Clemens *et al.*, 2002). However, straw can increase emissions of methane and nitrous oxide. Nitrous oxide emissions are mainly caused creation of anaerobic conditions when encrustation of the surface of the slurry occurs or cover material is applied. The total content and the nature of the slurry solids influence crust formation. A combination of covering the slurry and acidification also reduces pH values below 6.0, which results in a reduction of methane and nitrous oxide emissions (Berg *et al.*, 2006). Liquid manure storage facilities are sources of methane, nitrous oxide and ammonia emissions. Lowering the pH value of the slurry can reduce both methane and nitrous oxide emissions.

De Klein & van Logtestijn (1994) found that denitrification was the main source of N_2O immediately after urine application and also measured denitrification and N_2O emissions from urine application to grasslands. Overall, urine significantly increased N_2O emissions up to 14 days after application up to 6 kg N ha^{-1} day^{-1}. Lovell & Jarvis (1996) also measured significant emissions of N_2O following urine application (417 g N_2O-N ha^{-1} day^{-1}). Mogge *et al.*, (1999) reported that the denitrification losses increased with temperature in pastures treated with cattle slurry, while N-losses from pastures treated with farmyard manure were unaffected by temperature. N_2O emissions from the dung (9.9 mg N_2O-N $patch^{-1}$) were equal to those from the urine (9.5 mg N_2O-N $patch^{-1}$) and the average emission factor from the urine (0.56%) was much higher than from the dung (0.19%).

2.6.3.1 Stand-off pads

Stand-off pads are built with a drained loafing area to house cattle for longer periods when the conditions are not suitable for stay them in pasture, and also to reduce NO_3^- leaching losses, and prevent soil and sward damage (Luo *et al.*, 2007a). By using a stand-off pad there is a decrease in autumn grazing which reduces both N_2O emissions and NO_3^- leaching losses from grazed pasture by about 40% (de Klein *et al.*, 2006).

Improved winter management systems reduced animal excreta deposition on wet soils and reduced pugging damage due to grazing (Luo *et al*., 2006; Luo *et al*., 2007a). Luo *et al*., (2007b) estimated that the use of stand-off pads, resulted in emission of 0.054 kg N_2O-N. Nitrous oxide emissions increase gradually after application of cattle manure to land and only 0.01-0.03% of the N applied in the effluent was emitted as N_2O (Luo *et al*., 2007b).

Work by Luo *et al*., (2004), suggests that restricted winter grazing reduces excreta deposition on to wet soil and minimises the potential N_2O emissions and nitrate leaching after application. Excreta collected from the stand-off pads was stored and returned to the pastures during dry periods when the soil water filled pore space was not suitable for N_2O emissions. Delaying effluent application after grazing may reduce emissions by decreasing the surplus mineral-N levels (Luo *et al*., 2007b).

De Klein and Clark (2002) estimated that, if fully implemented for all dairy and beef farms, restricted grazing management during wet weather for dairy and beef cattle could reduce total agricultural N_2O emissions in New Zealand by about 6%. Chadwick *et al*., (2002) estimated that, where grazing animals were kept on pads for 60 days during winter, but were allowed to graze for 4 hours per day during that period, reduced N_2O emissions from the farm reduced by about 6% compared to year-round grazing.

2.6.3.2 Herd-homes

Nutrient leaching and gaseous emissions of N_2O from animal excreta mostly occur during wet periods in late autumn and winter (Luo *et al*., 2000; Ledgard *et al*., 2006). Under wet conditions animal grazing can lead to degradation of soil structure and can effect pasture production and quality (Singleton *et al*., 2000), and transfer of microorganisms to waterways (Muirhead *et al*., 2005). Some dairy farmers in New Zealand are moving cows out of paddocks to hold them temporarily in herd-homes (Longhurst *et al*., 2006; Luo *et al*., 2006) to protect the soils from damage and to prevent nutrient losses and faecal contamination. This reduction of N may be due to adsorption and/or immobilisation of N and sulphur (S) by the C-rich bark material.

When soil and sawdust were used as bunker media in a herd-home, the soil bunker showed the greatest reduction in moisture content, followed by soil mixed with sawdust, sawdust then raw manure. The bunker with soil as the absorbent material showed the most effective nutrient conservation with the lowest decline (10-34%) in the total amount of nutrients over 9 months. The highest decline was observed in raw manure bunker (70%N and 33%S) (Qiu *et al*., 2007).

2.6.4 N_2O emissions from manure applied to soil

Jarvis & Pain (1994) observed that the ratios of N_2O emissions to total denitrification are variable and previous studies indicated that N_2-N/N_2O-N ratios after manure slurry additions were in the range of 3:1 to nearly 1:1 (Jarvis *et al*., 1994). Thompson *et al*., (1987) measured denitrification losses of 12 and 21% from surface application or injection of dairy cattle slurry into a grassland soil in winter. Bhandral *et al*., (2003a, b) estimated N_2O emissions during summer application and found that 0.7% of the total added N was emitted within 13 weeks; whereas 0.6% of the total added N was emitted in 7 weeks during winter.

Barton and Schipper (2001) observed a significant increase in denitrification rates immediately after dairy-farm effluent irrigation, peaking at 24 h, and then decreasing to pre-irrigation rates after 3 days. They also found higher N_2O emissions from dairy-farm effluent than from inorganic N fertiliser, because of enhanced denitrification activity resulting from increased C availability and/or from decreased soil aeration following increased respiration. Lowering the C content of slurry decreased N_2O emissions (Petersen 1999; Bhandral *et al*., 2004; Saggar *et al*., 2004c).

Chadwick (1997) also found that the proportion of N input emitted as N_2O increased with increasing time after effluent application, and was higher in the soil with surface-applied effluent than with injected effluent. Comfort *et al*., (1990) observed that the greatest emission of N_2O occurred initially after the injection of liquid dairy-cattle manure, this was followed by a shift to N_2.

Saggar *et al*., (2004) summarised selected references on NH_3 volatilisation and N_2O emissions from cattle wastes applied to pasture soils (Table 2.18)

Table 2.18 Nitrous oxide emission from animal wastes applied to pasture soils

Soil type	Country	N source	N input (kg ha^{-1})	N_2O emission (kg N ha^{-1})	References
Silty clay loam	England	Cattle slurry surface	45	0.004	Ellis *et al*., (1998)
Silty clay loam	England	injected	45	0.081	Ellis *et al*., (1998)
Sandy soil	Netherlands	Cattle slurry	0	0.9	de Klein *et al*., (1996)
			365	13.7	
	Japan	Cattle slurry	230	0.195	Watanabe *et al*., (1997)
Poorly drained, sandy soil	Netherlands	Cattle slurry surface	45	0.1	Velthof *et al*., (1996)
		injected	45	0.1	
Typic Haploboroll	Canada	Solid feedlot manure	0	0.7	Chang *et al*., (1998)
			268	11	
			537	23	
			806	56	
Gleyed Melanic Brunisol	Canada	Liquid dairy cattle manure	0	<0.5	Paul *et al*., (1993)
			136	0.5	
			340	1.5	
			680	16	
Well-drained medium textured	Canada	Dairy cattle slurry	0	3.28	Paul & Zebarth (1997)
			600	52.2	
		Manure	0	36	
			600	156	
Coarse textured	Canada	Dairy cattle slurry	0	0.73	
			600	9.49	
		Manure	0	37	
			600	95	
	United Kingdom	Dairy cattle slurry	264	46	Thompson (1989)
Sandy loam	Denmark	Cattle slurry	0	0.24	Christensen (1983)
			492	7.70	
	United States	Liquid dairy manure	0	6.39	Comfort *et al*., (1990)
			174	16.4-20.8	
Silty clay loam	England	Dung	25	0.059	Yamulki *et al*., (1998)
		Urine	78	0.341	

The nitrous oxide emissions from manure applied to soil measured with different methods are presented in table 2.19.

Table 2.19 N_2O emissions measured from different animal manures applied to field

Source	Measuring method	N_2O emissions	Country	References
Dung heap	static chamber method	51 g N_2O-N m^{-3} d^{-1}	United Kingdom	Skiba *et al.*,2006
Dung heap	Dynamic chamber method	315 g N_2O-N m^{-3} d^{-1}	United Kingdom	Skiba *et al.*,2006
Dung heap	SF6 tracer ratio method	5.3 g N_2O-N m^{-3} d^{-1}	United Kingdom	Skiba *et al.*,2006
Dung heap	Gaussian plume method	14.4 g N_2O-N m^{-3} d^{-1}	United Kingdom	Skiba *et al.*,2006
Solid cattle manure		0.7 g N_2O-N $m^{-3}d^{-1}$	United Kingdom	Chadwick *et al.*, 1999
Solid dairy manure	Mass balance	0.4 g N_2O-N m^{-2} d^{-1}	United Kingdom	Brown *et al.*, 2002
Beef cattle FYM		0.003- 0.078 kg N_2O-N t^{-1}	United Kingdom	Chadwick and Webb, 2001
Dairy cow FYM		0.024- 0.056 kg N_2O-N t^{-1}	Austria	Amon *et al.*, 2001
Dairy effluent		1.2 kg N_2O ha^{-1} yr^{-1}	New Zealand	Khan, 1999
Dairy slurry-surface application		1.51 kg N_2O ha^{-1} yr^{-1}	United Kingdom	Chadwick *et al.*, 2000
Cattle slurry-soil incorporation		36.7 kg N_2O ha^{-1} yr^{-1}	Netherlands	Velthof *et al.*, 2003

2.7 Methane (CH_4) emissions from manure

2.7.1 Overview

Livestock manure is a significant source of atmospheric methane in many countries. It has been estimated that the total global CH_4 emissions from manure can account for approximately 35.2 Tg yr^{-1}, i.e., c. 9% of the total biogenic source (Steed and Hashimoto, 1994).

2.7.2 Methane emissions during manure storage

Emission of CH_4 from animal excreta will depend on several parameters including the amount of faecal matter excreted, the physical form of the deposit (shape, size), excretal form (solid, slurry or effluent), climatic and soil conditions, and the length of time the deposits remain intact before being decomposed. Holter (1997) estimated that the total CH_4 emissions from dung produced by a cow was only 0.8-4.0% of the emission likely to result from the same dung stored over the same period as liquid manure. Husted (1994) revealed that solid manure produces higher emission 11% compared to 4% from the slurry (Table 2.20).

Table 2.20 Methane emissions from dung stored in different ways

Storage	A (kg CH_4)	B (kg CH_4)
Slurry	11.0	15.5
Solid manure	3.7	5.3
Pasture dung(low emission)	0.09	ND
Pasture dung(high emission)	0.42	ND

A: emission from dung produced during the grazing season
B: emission from the annual dung production (Husted, 1994).

Production of CH_4 by methanogenic bacteria is limited to strictly anaerobic conditions (Tiedje *et al.*, 1984), but CH_4 emissions may also be affected by the physical characteristics of farm yard manure that enhance the escape efficiency of the gas (Yamulki and Jarvis, 2002). Osada *et al.*, (2001) reported methane emissions of 50.7 g C t^{-1} (DM) from the compost heap, which was 0.01% of the total C in the compost. Similar trends were observed by Hellman *et al*., (1997). Cattle urine will infiltrate into the deep layers thus, reducing the surface area of deep litter (sawdust or straw) in contact with the air. A study by Sommer *et al*., (2004) indicated that daily flushing of slurry from cattle houses would reduce total annual CH_4+N_2O emissions by 35% (CO_2 eq.).

Composting of deep litter during storage may cause emission losses of ammonia, N_2O and methane. During composting, the emission of N_2O was 0.1-0.3% of total-N and CH_4 emission was 0.01-0.03% of total-C (Sommer 2001).

2.7.3 CH_4 emissions from manure applied to soil

Methane emissions during storage from different manures were summarised and presented in table 2.21.

Table 2.21 Methane emissions during storage from different cattle manures

Manure source	Emission rate	Country	References
compost	0.113 kg CH_4-C t^{-1}	Austria	Amon *et al*., 1997
solid manure	1.12 kg CH_4-C t^{-1}	Austria	Amon *et al*., 1997
beef cattle FYM	1.53-2.55 kg CH_4-C t^{-1}	United kingdom	Chadwick and Webb, 2001
dairy cows	274 g CH_4 d^{-1} $animal^{-1}$	Netherlands	van Amstel *et al*., 2003
young cows	170 g CH_4 d^{-1} $animal^{-1}$	Netherlands	van Amstel *et al*., 2003
calves	48 g CH_4 d^{-1} $animal^{-1}$	Netherlands	van Amstel *et al*., 2003
conventional dairy farms	500 g CH_4 d^{-1} $animal^{-1}$	Netherlands	Huisin't veld and Monteny, 2003
conventional dairy farms	700 g CH_4 d^{-1} $animal^{-1}$	Netherlands	Hensen *et al*., 2006
cow house with straw bedding	1000 g CH_4 d^{-1} $animal^{-1}$	Netherlands	Huisin't veld and Monteny, 2003
cow house with straw bedding	1400 g CH_4 d^{-1} $animal^{-1}$	Netherlands	Hensen *et al*., 2006
cow house with straw bedding	230 g CH_4 d^{-1} LU^{-1}	Germany	Jungbluth *et al*., 2001
cow house with straw bedding	190 g CH_4 d^{-1} LU^{-1}	Austria	Amon *et al*., 2001
Manure (slurry)	53 g CH_4 m^{-3} d^{-1}	France	Sneath *et al*., 2006
FYM	40 g CH_4 m^{-3} d^{-1}	France	Sneath *et al*., 2006
Manure (slurry)	11 g CH_4 m^{-3} d^{-1}	Netherlands	Hensen *et al*., 2006
dung pats on pasture	2.268 kg CH_4 kg dung-C^{-1})x10^{-3}	New Zealand	Sherlock *et al*., (2003)
In situ on pasture	2.567 kg CH_4 kg dung-C^{-1})x10^{-3}	New Zealand	Saggar *et al*., (2003)

2.8 Other nutrients losses

2.8.1 Carbon

During composting of deep litter, reduction of C content was between 40 and 49% of the initial C content (Sommer, 2001) and these are similar to previous measurements (Sommer and Dahl, 1999). Stockpiling or thermophilic composting of cattle manure resulted in significant carbon losses of 17% and 26.4% (Atallah, 1995) and relative nitrogen gains of 25% and 32.7% for stockpiled and composted manure, respectively. With increasing time of storage or composting the C/N ratio will decrease.

2.8.2 Phosphorus

Application of farm effluent to the soil in long run, based on N loading, leads to P and heavy metal accumulation in the soil. Effluent P accumulates in soils, so that the fate and movement of P in the effluent has become an important issue. Runoff of P can enter waterways and leads to surface water eutrophication (Sharpley, 1995; Chardon *et al.*, 1997). During composting of deep litter, leaching losses of P were less than 2.4% (Sommer, 2001) of the initial content, because P precipitates as solids that are not easily dissolvable. The concentration of P increased during composting as a consequence of the low losses of P and a reduction in the amount of deep litter.

In general, New Zealand soils have a high capacity to absorb P and hence effluent irrigation has been observed to increase soil total P (Redding, 2001; Hawke and Summers, 2003). In one of the few New Zealand studies on the effects of farm dairy effluent application on soil P, Toor *et al.*, (2004) outlined the results from lysimeter and field experiments to draw conclusions about impacts of P inputs on soil P amounts and forms. While the applied farm dairy effluent was high in inorganic P (86% versus 9.6% organic P), the leachate collected contained mainly organic P (85-88%). Their study suggested that the inorganic P applied in farm dairy effluent was adsorbed because of the high P fixation capacity of Lismore subsoil.

2.8.3 Potassium

Bolan *et al.,* (2004a) showed that application of farm effluent based on N loading leads to greater concentrations of potassium (K) in effluent which can contribute to pasture nutrient imbalance and induce problems for animal health.

During composting of deep litter potassium leaching was 8-16% (Sommer, 2001) of the initial K content, similar to a study by Petersen *et al*., (1998). Due to high mobility of K salts, it was easily dissolved in water and leads to leaching. Compaction and covering with tarpaulin reduced leaching losses to 8-11% as compared to 14-16% of K from the untreated and mixed composts. Lower infiltration of water into the heap may cause the lower leaching losses from these heaps.

Most studies have shown that effluent irrigation can increase soil cation exchange capacity and/or exchangeable cations (K, Na, Ca, and Mg) (Menzies *et al*., 1999; Hawke & Summers, 2003). Hawke & Summers (2003) noticed an increase in CEC and exchangeable cations following farm dairy effluent application. This has been attributed to the typically high concentrations of K in animal manure, inducing the leaching loss of other exchangeable bases due to the competition with K (Bolan *et al*., 2004a). Increased K concentrations can detrimentally affect soil physical properties because high levels of K may disperse clays. Aarons *et al*., (2004a, b) attributed changes in soil nutrient concentrations due to dung decomposition to the solubility of the individual nutrients; hence, whereas most P was physically incorporated, K was leached into the soil. Changes in the balance between K, Ca, and Mg concentrations in the soil can also affect pasture composition and animal health.

2.9 Measurement methods for NH_3 volatilisation

Ammonia volatilisation has been estimated indirectly using a mass balance approach and directly by measuring NH_3 gas emission. Measuring ammonia volatilisation in the field poses several problems. Direct measurement of NH_3 emission gives an accurate estimate of volatilisation losses. A number of methods have been used to measure NH_3 emission in pasture soils, including enclosure methods, micrometeorological methods and wind tunnel measurements

(Jayaweera and Mikkelsen, 1991; Harrison and Webb, 2001). Enclosure methods are most commonly used in NH_3 volatilisation measurements (Denmead, 1982). A variety of enclosure designs are used to measure NH_3 losses (Harrison and Webb, 2001). These methods are simple and convenient, and can be used successfully to evaluate NH_3 losses under a variety of experimental variables.

Kissel *et al*., (1977) designed and tested an automated device that could be used to measure NH_3 volatilisation under field conditions without creating an artificial environment in the vicinity of the applied fertiliser or urine deposition. The system of Kissel *et al*., (1977) consisted of a vacuum pump, a chemical trap to capture NH_3, and a volatilisation chamber. The enclosure chamber method is a direct measurement of ammonia volatilisation by enclosing volume of air above the soil surface, and passing air rapidly through the chambers to collect the ammonia from the air with acid. The chemical trap generally consists of boric acid, sulphuric acid, or oxalic acid (Schjoerring *et al*., 1992). Sherlock and Goh (1984) used the enclosure technique to measure NH_3 volatilisation losses from pasture in New Zealand receiving either sheep urine or aqueous urea.

Black *et al*., (1985b) compared three methods of estimating NH_3 volatilisation from urea broadcast (100 kg N ha^{-1}) on to pasture: an enclosure system with continuous air flow (EM), an unconfined micrometeorological method (integrated horizontal flux method-IHFM), and by mass balance analysis (MBA). The cumulative loss after 96 h measured by the three methods was 24, 25 and 30%, respectively, of the N applied. The slightly higher estimated loss by the MBA was attributed mainly to microbial immobilisation of applied N, which was not accounted for in the mass balance.

Hoff *et al*., (1981) showed the intermittent enclosure technique could greatly underestimate NH_3 loss when high winds prevailed between periods of lid closure. Enclosure technique should be used only when ambient wind speeds are low (e.g., greenhouse experiments), or where wind speed is known to have little effect, or where other suitable precautions are taken. Lightner *et al*., (1990) carried out field measurements of NH_3 volatilisation from fertilised plots using ventilated chambers in spring and summer over 2 years. Ammonia volatilisation ranged from 27 to 41% of applied N in spring and from 12 to 27% in summer from fertilised plots.

Micrometeorological methods have been developed for making accurate measurements of NH_3 volatilisation in the field (Denmead, 1982; Sherlock *et al.*, 1995; Wood *et al.*, 2000). Micrometeorological techniques have an advantage in that they do not disturb the natural environmental conditions that influence NH_3 volatilisation; rather they provide an average integrated flux over a large area, which minimises the sampling variability. Micrometeorological techniques, however, are difficult to use in practice, as they are costly in instrumentation, laborious, site-specific and weather-dependent in their application to the experimental area. Moreover, a micrometeorological method needs more area for experiments, and also requires several micrometeorological variables including air temperature, vapour pressure, and atmospheric pressure to get accurate determination of ammonia.

Sherlock *et al.*, (1989) showed that the losses measured with this sampler at the ZINST height were quite close to those measured with the full profile, mass-balance micrometeorological reference method (11.6% loss with the sampler versus 13.4% loss with the full-profile method). Fox *et al.*, (1996) and Prasertsak *et al.*, (2001) used a simplified micrometeorological method to successively estimate NH_3 volatilisation losses from a number of fertilisers applied to pasture soils. Zhu *et al.*, (2000) investigated the feasibility of using denuder tubes with the relaxed eddy-accumulation (REA) technique to measure NH_3 fluxes. The denuder tubes, coated with oxalic acid, were used at the inlet of the REA system to trap NH_3 in air.

Lockyer (1984) developed a system of small wind tunnels to study NH_3 volatilisation losses under field conditions from grassland without inducing marked changes in the microclimate of the sward. Weerden *et al.*, (1996) obtained a recovery of 86 and 90% NH_3 for two systems of small wind tunnels commonly used for studying NH_3 volatilisation losses from grassland. Sommer *et al.*, (1991) measured NH_3 losses from surface-applied cattle slurry under field conditions using a wind-tunnel system that allowed variables affecting NH_3 loss to be examined under controlled conditions. The experiments were carried out on a sandy soil with seven different surface covers. The NH_3 loss rate increased when wind speeds increased up to 2.5 m s^{-1}. Thompson *et al.*, (1990) conducted three experiments to examine the influence of slurry application rate, wind speed and applying slurry in narrow bands on NH_3 volatilisation from cattle slurry surface applied to grassland. The experiments were conducted in the field using a system of small wind tunnels to measure NH_3 loss. There was an inverse relationship between slurry application rate and the proportion of NH_4^+-N volatilized. Sommer and Jensen (1994) used the wind tunnel technique to measure NH_3 volatilisation from various N fertilisers applied to a sandy soil.

2.10 Conclusion

About half (49.4%) of total greenhouse gas emissions in New Zealand come from the agriculture sector, of which N_2O accounts for one third (Ministry for Environment, 2008). In New Zealand, nitrogen losses in the form of NH_3 and N_2O from grazed pastures may contribute to eutrification of streams and acidification of soils, and N_2O is a GHG, which causes stratospheric ozone depletion and global warming.

The literature review in this thesis covers the gaseous emissions ($NH_{3,}$ N_2O and CH_4) from dairy farms and mitigation options. Limited work has been carried out previously to investigate the gaseous emissions following addition of soil or sawdust to manure prior to application of manure to land.

Many studies have examined the nitrous oxide and methane losses from manure deposition, storage and application to land and their reducing strategies. With the little information available on mitigation strategies, it was difficult to find the inter-relations of gaseous emissions. The effectiveness of some natural materials (pine bark, soil and sawdust) addition to manure was reviewed and observed these C-rich materials retain N in the manure, and reduce ammonia emissions due to adsorption and/or immobilisation of N.

Among all the manure application methods, incorporation of manure into the soil was found to be the efficient method in reducing gaseous emissions following manure application to land (Misselbrook *et al*., 2002).

Nitrous oxide emissions are more likely occur under anaerobic conditions during manure storage or application to land. Under anaerobic conditions, denitrification takes place and it transforms nitrites and nitrates to N_2O andN_2. Lowering the C-content of materials reduces N_2O emissions (Bhandral *et al*., 2004) and also observed reduction of methane and nitrous oxide emissions by lowering the pH of the manure (Berg *et al*., 2006). There has been a limited research with natural material addition to manure application methods all over the world. Thus, in my research I will test the effects of addition of carbon source (sawdust or soil) to manure prior to land application, and surface and incorporated application on gaseous emissions in New Zealand conditions.

Ammonia emissions measurement methods (Enclosure method, wind tunnel method and micrometeorological methods) were reviewed in this chapter and observed limited data available to measure gaseous emissions from manure applied to soil using chamber method with different air flow rates through chambers. A chamber method was used in most of the studies and some studies observed that ammonia emissions increased with increasing wind speed and some studies found ammonia emissions were not increased with wind speed. Thus in this thesis an effort will be made to determine the optimum flow rate to measure ammonia emissions using a chamber method.

Chapter 3

Determination of optimum chamber air flow rate to measure ammonia volatilisation from urine or urea applied to soil

3.1 Introduction

The main aim of this chapter was to determine the optimum flow rate for measurement of ammonia emissions from manure or urea application to soil using a chamber method.

Ammonia volatilisation has been estimated indirectly using a mass balance approach and directly by measuring NH_3 gas emission. Direct measurement of NH_3 emission gives an accurate estimate of volatilisation losses. Various methods including enclosure methods, micrometeorological methods and wind tunnel measurements (Jayaweera and Mikkelsen, 1991; Harrison and Webb, 2001) are generally used to measure ammonia emission in pasture soils. Enclosure methods are the most commonly used in NH_3 volatilisation measurements (Denmead, 1982). A variety of enclosure designs are used to measure NH_3 losses (Harrison and Webb, 2001). I used an enclosure chamber method (Bolan *et al*., 2004a; Singh, 2007) to measure ammonia emissions in this study. However with little information so far available on the effect of air flow through the chamber on measured ammonia emissions, there is a need to first establish the most appropriate rate of air flow for undertaking the chamber methods.

3.2 Materials and methods

Two glasshouse experiments were conducted to determine the optimum air flow rate to measure ammonia emissions from urine (experiment 1) and from urea applied to soil (experiment 2) using a chamber method (Figure 3.1).

Figure 3.1 Chambers used to measure ammonia emissions from urea applied to soil (Figure from Bolan *et al*., 2004a)

3.2.1 Experimental lay out

3.2.1.1 Materials preparation

The test materials used in the experiments were urine, soil, and urea. Before setting up the experiments, fresh urine was collected in air-tight sealed plastic containers from Ruakura dairy farm and stored below 4^0C to avoid hydrolysis (Dr Jiafa Luo, Personal communication, 2007). The intact soil cores used in the experiment were collected from the AgResearch farm with 100 mm diameter and depth. Commercial grade urea was collected from the AgResearch laboratory.

3.2.1.2 Treatments used in the air flow rate experiments

a. ***Experiment 1: Ammonia volatilisation from urine***

Experiment 1 was carried out in a glasshouse with 3 replicates of 9 treatments (Table 3.1). The sub-samples of urine were collected and analysed for NH_3-N. Plastic pots were used to place 100 ml urine in the chambers. The chamber method was used to measure ammonia volatilisation (as described in Section 3.3). After putting the pots in the chambers, the chambers were closed throughout the sampling period and air was continuously flowed through the chambers from the compressor through a valve stand with designed flow rates (Figure 3.1). Acid samples were collected for every 2 hrs for up to 8 hrs and a final sample was collected 24 hrs, after commencement of the experiment to calculate cumulative ammonia losses. After each sample was collected from the dreschel bottles the acid in the bottle was changed. All the samples were analysed for NH_3-N using a Skalar auto analyser (Section 3.3) following the ammonia emissions measurement method (Franson, 1998).

Table 3.1 Treatment descriptions (Varying air flow rates through chambers to measure NH_3 volatilisation from urine).

Treatment	Flow rate (L min^{-1})
T1	2
T2	4
T3	6
T4	8
T5	10
T6	12
T7	14
T8	16
T9	18

b.Experiment 2: Ammonia volatilisation from urea applied to soil

Experiment 2 was carried out in a glasshouse with 3 replicates of 8 flow rate treatments (Table 3.2). Intact soil cores of 71mm diameter and 120mm depth with grass on top were collected from the AgResearch farm was placed in plastic pots. Urea granules were broadcast on the soil at a rate of 250 kg per ha. Initially soil cores were watered with 10 ml of water and soil cores were watered daily, based on moisture loss. The soil cores were weighed every day to calculate the moisture loss and water was added to the soil cores to maintain the original moisture content. The soil cores were placed in the centre of the chambers (Figure 3.2). Trapped ammonia acid samples were collected for 5 days, using the different treatment flow rates (Table 3.2) following the application of urea to soil. Ammonia volatilisation measurements were carried out for 1 hr at a time 24, 36, 48, 60, 72, 96 and 120 hours after application of urea to soil. The sampling schedule was planned due to logistics and involvement of cost for sampling and analysis. This study was repeated twice with the same flow rates. The ammonia trapped acid samples were analysed for NH_4^+-N using a Skalar auto analyser (Section 3.3).

Table 3.2 Treatment descriptions of glasshouse experiment (Varying air flow rates through chambers to measure NH_3 volatilisation from urea applied to soil)

Treatment	Flow rate (L min^{-1})
T1	1
T2	2
T3	3
T4	4
T5	5
T6	7
T7	9
T8	11

3.3 Description of the chamber method for measurement of ammonia volatilisation

3.3.1 Chambers set up

The NH_3 volatilisation measurement system comprised a volatilisation chamber, an acid trap to capture ammonia, valves stand, and a compressor to maintain constant air flow through the chamber (Figure 3.2).

The volatilisation chamber consisted of a 16 cm long PVC pipe with 23.7 cm inner diameter. The chamber was sealed by a plastic plate welded to the base of the PVC pipe (Figure 3.2). At the top of the chamber there was a lid known as a “sewer-hatch” which had an internal half-turn locking system and a greased rubber O-ring, which formed a gas-tight seal. The lid was removable and had an intake port and an exhaust port installed in it (Figure 3.2).

The volatilisation chambers were connected to a valve stand, which consisted of 12 valves. Each valve was connected to the inlet port of the volatilisation chamber. The volatilisation stand was connected to the compressor with 48 mm diameter PVC tubes (Figure 3.1) and a valve was used to regulate the air flow through the chamber. The exhaust port was connected (Figure 3.2) through a 500 ml dreschel bottle containing 250 ml of 0.06 M sulphuric acid to trap ammonia present in the air. By integrating the rates of loss over time the total ammonia loss was calculated.

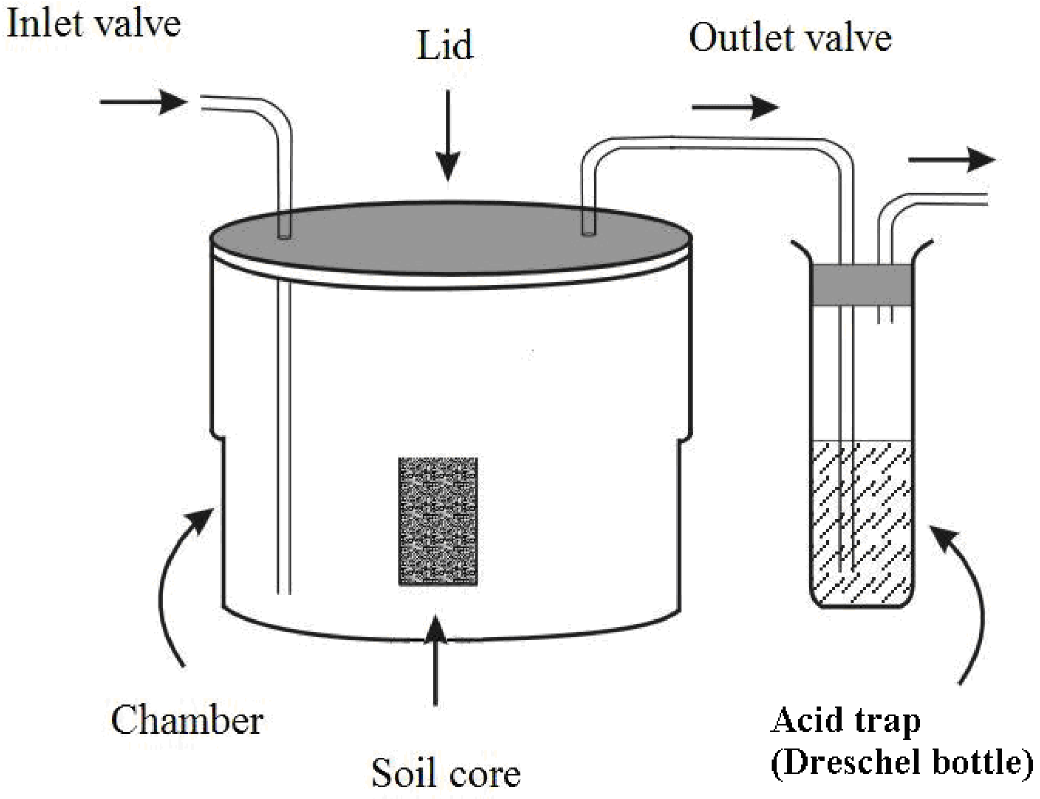

Figure 3.2 Schematic diagram of the chambers used to measure ammonia emissions.

At the end of the sampling period, the compressor was turned off, and the lids opened. The lid was closed only during ammonia volatilisation measurement for short periods. Between measurements, the lids were open and the samples were removed from the chamber and placed in the normal environmental conditions of the glasshouse.

After each sampling, acid in the dreschel bottle was replaced. The ammonia loss for each day was obtained by dividing the measured ammonia volatilisation by the proportion of the day in which sampling was undertaken.

3.3.2 Analytical method

The acid samples were analysed for ammonia on a Skalar SAN Plus segmented flow analyser (Skalar Analytical B.V., Breda, Netherlands) (Figure 3.3). The ammonia method is based on the modified Berthalot reaction. Ammonia is chlorinated to monochloramine which reacts with salicylate and is then oxidised to form a green coloured complex which was measured colorimetrically at 660 nm.

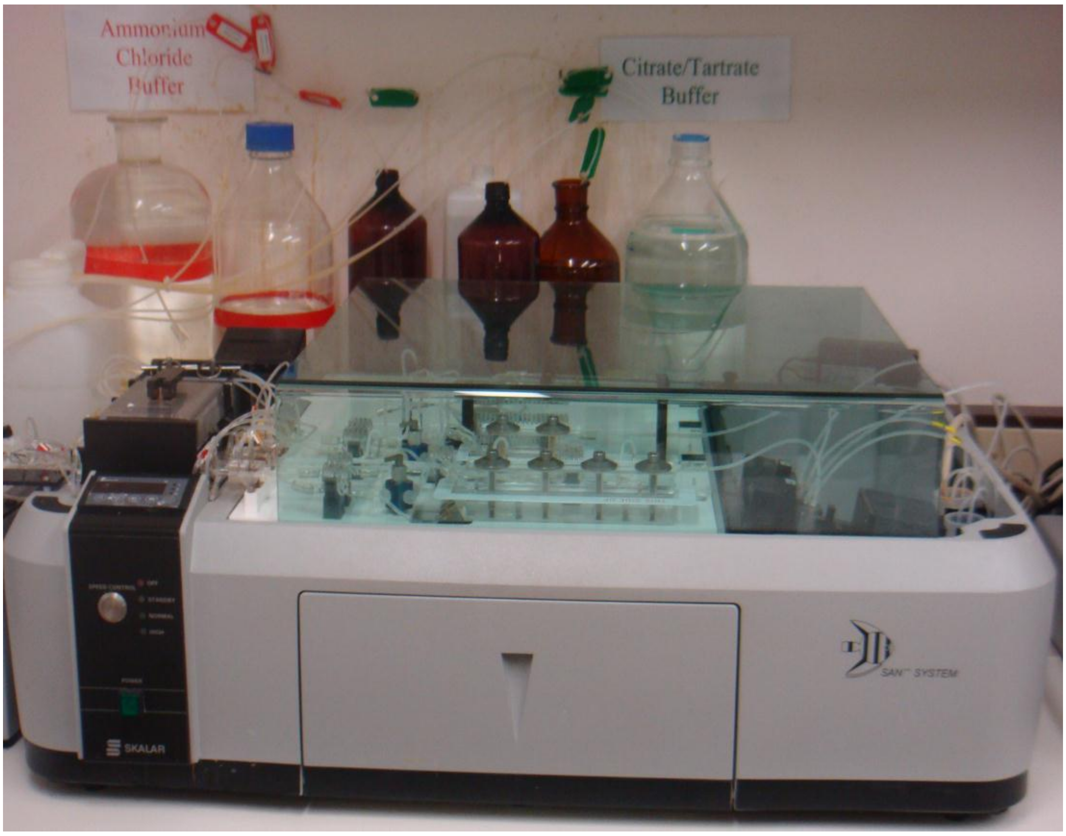

Figure 3.3 Skalar SAN Plus segmented flow analyser to measure ammonia volatilisation.

The ammonia flux (mg NH_3-N m^{-2} hr^{-1}) was calculated using the following equation (from AgResearch undated):

$$\mathbf{N_{(NH3\ flux)} = C\ x\ V / a\ x\ D}$$

Where, C = ammonia concentration in the acid trap (mg dm^{-3});

V = Volume of the acid (dm^3);

a = total cross section area (m^2) of soil cores in the chamber;

D = duration (hrs) of each sampling.

3.4 Results and Discussion

3.4.1 Experiment 1: Ammonia volatilisation from urine

Results from experiment 1 showed that maximum ammonia emissions were observed with high flow rates (10 L min^{-1} to 18 L min^{-1}). The NH_3-N content in the urine used in the experiment was 0.312 g ml^{-1} urine. Full data-sets are included in Appendix1. In the urine samples used in the three replications ammonia emissions increased with increasing flow rates up to 12 L min^{-1} and showed not much difference from 12 L min^{-1} to 18 L min^{-1}. The percentage of ammonia emissions varied from 22 to 86% of NH_3-N in the urine (Figure 3.4). There was no urine remaining in the plastic pots treated with high flow rates at the end of the measurement period (>8 L min^{-1}). The entire urine sample was evaporated from the plastic pots and trapped by the acid.

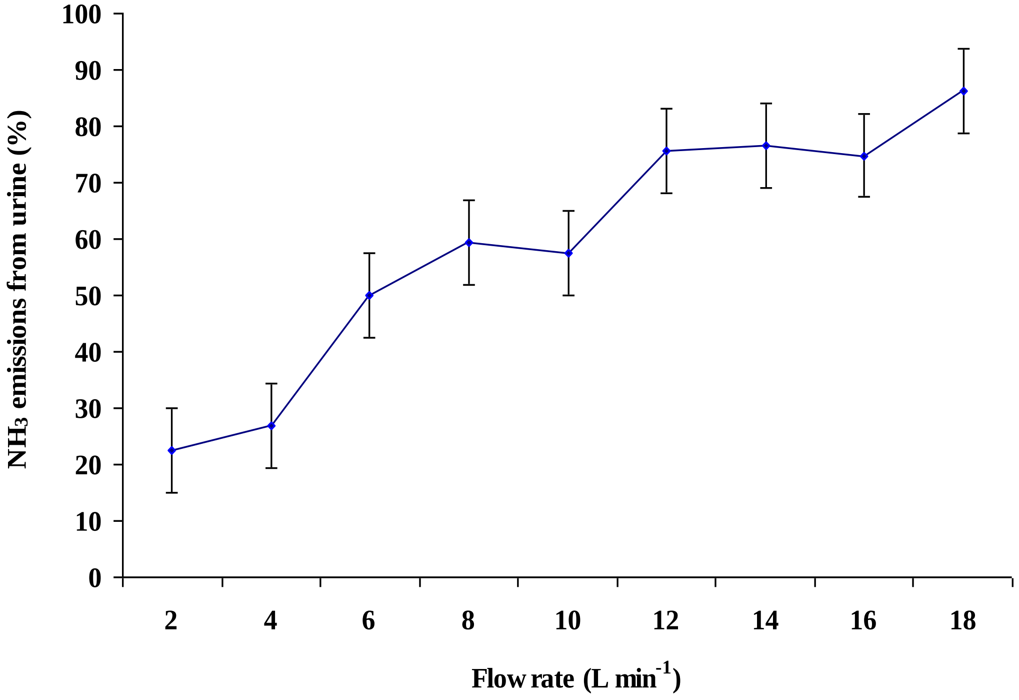

Figure 3.4 Percentage of ammonia emissions from urine (measured over 24 hrs) versus measurement chamber flow rates (2 to 18 L min^{-1}) (Error bars = 1 standard error of the mean)

Initially, before set up of the experiment we thought that with the use of urine, it would reduce the complexity of using different materials. The concentration of urea in urine is 97% (McCrory and Hobbs, 2001), and urea will be rapidly hydrolysed by urease enzymes to ammonium carbonate. Ammonium carbonate disassociates to produce NH_4^+ (Bolan *et al.*, 2004a), which may give accurate measurement in measuring ammonia emissions with different air flow rates through chambers. But, unfortunately with high flow rates (>8 L min^{-1}) all the urine sample got evaporated in the pots after 24 hrs and pave the way to design another experiment to find the optimum flow rate from soil applied with urea.

3.4.2 Experiment 2: Ammonia volatilisation from urea applied to soil

An air flow of 5 L min^{-1} or 1 exchange volume $minute^{-1}$ was found to be the optimum rate to measure ammonia emissions from urea applied to soil (Figure 3.5). The measured ammonia volatilisation loss at 120 hours after application of urea to soil increased rapidly as the air flow rate increased up to 5 L min^{-1}. Whereas, the ammonia emissions increased only 1% as the flow rate increased from 5 to 11 L min^{-1}. The ammonia volatilisation loss measured for 5 days following urea application to soil was 0.042 g m^{-2} hr^{-1}.

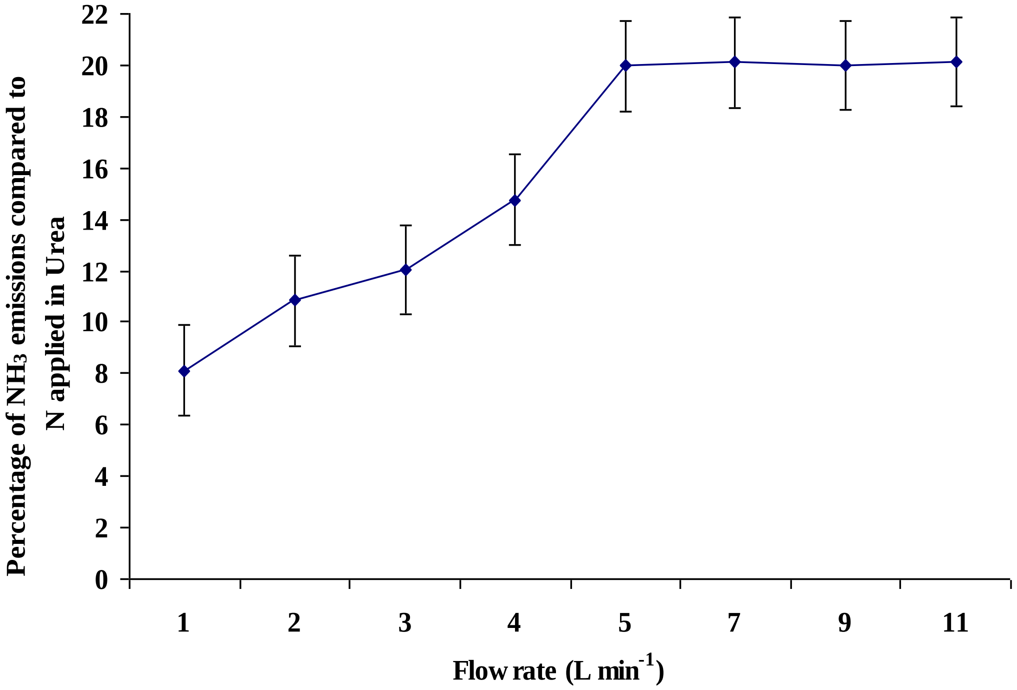

Figure 3.5 Cumulative NH_3-N volatilisation (%) over 5 days after urea application to soil with varying chamber air flow rates (1 and 11 L min^{-1}) (Error bars = 1 standard error of the mean)

The ammonia emissions obtained from urea applied to soil (0.042 g m^{-2} hr^{-1}) in this study are similar to 0.04 g m^{-2} hr^{-1} of Black *et al.*, (1985b), 0.05-0.10 g m^{-2} hr^{-1} (Wilson *et al.*, 1983), and 0.03 g m^{-2} hr^{-1} reported by Harper *et al.*, (1983). The cumulative loss of ammonia by volatilisation after 5 days was equivalent to 23 kg applied N per ha. The total ammonia emissions measured from varying flow rates reached a maximum of 20% of N applied to soil (Figure 3.5).

Several studies have previously reported that wind speed had little effect on ammonia volatilisation from a soil surface (Denmead *et al.*, 1974; Beauchamp *et al.*, 1982; Black *et al.*, 1985b; Balsari *et al.*, 2006). Contrarily, other studies (Thompson *et al.,* 1990; Sommer *et al.,* 1991; Misselbrook *et al.,* 2005) have shown that wind is the important factor influencing NH_3 emission rates. Interestingly, the results of our study found that air flow through the chambers had an effect on ammonia emissions up to 5 L min^{-1} and had no further effect with increasing wind speed from there on.

The total cumulative losses estimated in this experiment were similar to that of Black *et al.,* (1985). The results of this flow rate experiment are strong circumstantial evidence that the total NH_3 emissions are unaffected with increasing wind speed after 1 exchange volume $minute^{-1}$ (equivalent to 5 L min^{-1}). The data of my study was consistent with that of Kissel *et al.*, (1977) and Black *et al.*, (1985b).

3.5 Conclusion

The main conclusion was that 1 exchange volume $minute^{-1}$(equivalent to 5 L min^{-1} of our experimental set up) flow rate was the optimum to measure ammonia volatilisation. Increasing air flow rate above 5 L min^{-1}, or 1 exchange volume min^{-1}, had no effect on ammonia volatilisation. The optimum flow rate (5 L min^{-1}, or 1 exchange volume min^{-1}) using the chambers method can effectively be used to measure NH_3 emissions from urea applied to soil. A chamber flow rate of 5 L min^{-1} was used to quantify the effect of soil and sawdust added to manure prior to land application to measure ammonia (NH_3) emissions (Chapter 4).

Chapter 4

Gaseous emissions (NH_3, N_2O and CH_4) following manure or urea application to soil as influenced by addition of soil or sawdust

4.1 Introduction

An experiment was carried out to examine gaseous losses (NH_3, N_2O and CH_4) from manure application to soil under controlled conditions to determine the effect of soil or sawdust addition to manure, prior to application to land, on gaseous emissions. The main objectives of the experiment were to:

1. Quantify gaseous (NH_3, N_2O and CH_4) emissions from manure after application to soil.
2. Determine the effects of addition of soil or sawdust to manure prior to land application of the manure on subsequent gaseous emissions.
3. Determine the effect of surface and incorporated application of manure on gaseous emissions.

4.2 Materials and methods

4.2.1 Experimental design

An experiment comprising 27 pots was set up in a glasshouse at AgResearch, Ruakura, on the 22nd May 2007. Nine treatments were applied (Table 4.1). The volume of each pot was 2160 cm^3. The pots were classic flower pots with 14 cm height. Each pot was filled with 1200 g air dried silt loam soil which was collected from a topsoil storage site. The soil was primarily top soil derived from the Te Kowhai silt loam (a Gley Soil). The soil was passed through a 4 mm screen to remove stones and break up aggregates. The pots were filled with the sieved soil and shaken gently by hand for a minute to compact the soil. Untreated *Pinus radiata* timber sawdust was obtained from the AgResearch workshop and, to remove bigger size particles, it was passed through a 2 mm screen. The physical and chemical characteristics of soil, urine, dung and sawdust were presented in Table 4.3

Table 4. 1 Treatment descriptions.

Treatment	Manure	Application to soil
T1	Urine + dung	Surface application
T2	Urine + dung	Incorporated application
T3	Urine + dung + soil	Surface application
T4	Urine + dung + soil	Incorporated application
T5	Urine + dung + sawdust	Surface application
T6	Urine + dung + sawdust	Incorporated application
T7	Urea	Surface application
T8	Urea	Incorporated application
T9	Soil only	

Fresh dung and urine were collected from No.1 Dairy Farm at AgResearch, Ruakura near Hamilton. Urine and dung were mixed in a container in equal proportions (1:1 on wet weight basis) for the T1 and T2 treatments. Similarly, For the T3 and T4 treatments urine, dung and soil were mixed in equal proportions (1:1:1 on wet weight basis) and for treatments T5 and T6. The urine, dung, and sawdust were mixed in equal proportions (1:1:1 on wet weight basis) before applying to pots. For the surface treatments the manure mixture was applied to the surface of each pot. For incorporated application the manure mixture was mixed with the soil from the pot and packed back into the pot. Treatment mixtures were applied to each pot at the rate of 353 g/pot on wet weight basis. Urea fertiliser was applied to the treatments (T7&T8) at a rate equivalent to 100 kg N/ha. Each treatment was replicated 3 times (R1, R2 and R3). The pots were placed randomly in the glasshouse following a randomised experimental layout (Table 4.2).

Sub-samples of soil, urine, dung and sawdust were collected before application to soil and analysed for pH, total Kjeldahl nitrogen, nitrate nitrogen, total P, K, total sulphur, Ca, Na and organic carbon.

Table 4. 2 Randomised experimental layout of pots on glasshouse tables

(Treatments T1 - T9 are defined in Table 4.1)

T1	T2	T3
T4	T5	T6
T7	T8	T9
T3	T1	T2
T6	T9	T7
T5	T4	T8
T9	T6	T7
T5	T3	T1
T8	T4	T2

4.2.2 Experimental duration and analyses

The experiment was continued for 21 days after which sampling was disconnected due to consistently low gaseous emissions was observed from all treatments. Sub samples, collected immediately before application to soil, of urine, dung, soil and sawdust were sent to NZ Labs, Hamilton for analysis of pH, total N, NO_3^--N, organic C, total P, total K, total S, Ca, Na and moisture before application of manure to soil. After the last sampling all the soil in the pots was mixed thoroughly and sub samples were collected for NH_3-N and NO_3-N determination.

4.2.2.1 Total Nitrogen

Total nitrogen in all samples was analysed by Kjeldahl digestion, distillation and titration. To determine the concentration of ammonia released by the digestion and the total nitrogen content of the sample was calculated.

4.2.2.2 Organic Carbon

Sample solid materials were dried at 105°C and ground in a mortar and pestle. The residue material was analysed by infra-red spectroscopy on a TOC-5000A carbon analyser with a SSM-5000A solid sample module (Shimadzu Corporation, Kyoto, Japan) (Bremner and Tatabai, 1971).

4.2.2.3 NH_3-N and NO_3^--N

Two grams of air dried soil sample was weighed and transferred to a centrifuge tube and 30 ml of 2M KCl added. Centrifuge tubes were stoppered and shaken on an end-over-end shaker for 1hr at 20^0C. The KCl extracts suspensions were then centrifuged at 20000 rpm for 10 minutes, and the supernatant filtered through Whatman no.42 filter paper. The extracts were analysed for NH_3-N and NO_3^--N colourimetrically using a Skalar auto analyser (Section 3.3.2).

4.2.2.4 pH

The pH of the soil, sawdust and dung were measured at a 1:2.5 soil, dung or sawdust: water ratio on weight basis using a combined electrode pH meter (Blakemore *et al.*, 1987). Dung and sawdust were sampled of their field moisture contents (Table 4.3). The samples were left for 2 hours and stirred occasionally with a glass rod. The pH of the urine samples was measured in the original samples (i.e. urine sample without addition of distilled water).

4.3 Gaseous emissions measurement

4.3.1 Ammonia volatilisation

Ammonia emissions were measured using the chamber method as described in section 3.3. The airflow through the chambers was maintained at a constant 5 L min^{-1} throughout sampling. Ammonia samples were collected for 1hr every two days, and the acid was changed after each sampling. More frequent or longer sampling periods were not logistically possible. The acid samples were analysed for NH_4^+-N on a Skalar SAN Plus segmented flow analyser (Skalar Analytical B.V., Breda, Netherlands).

4.3.2 Measuring nitrous oxide and methane

The closed chamber technique was also used to measure N_2O and methane emissions (Hedley *et al.*, 2006; Singh, 2007) and the methodology was based on that from the study of Saggar *et al.*, (2004a).

The same chambers used for measuring ammonia volatilisation were used, with different lids having exhaust port only, to measure nitrous oxide and methane emissions. The plastic pots with soil after manure application were placed in the middle of the chambers during measurement time. Chamber heights were measured and the volume of each chamber was calculated. After sealing, two gas samples were taken at times 0 (T_0) and 60 minutes (T_{60}) from each chamber with 60 ml polypropylene syringes fitted with 3-way stopcocks (Figure 4.1 & 4.2). The gas samples were transferred immediately to evacuated 12 ml exetainers. The gas samples were sent to Landcare Research, Palmerston North for analysis (N_2O and CH_4) using a Shimadzu GC-17A gas chromatograph equipped with a 63 Ni-electron capture detector (Hedley *et al.*, 2006), and N_2O fluxes were then calculated as outlined in Saggar *et al.*, (2004b). The initial sample of ambient air collected 0 (T_0) after closing the chamber, was used as a reference to calculate gas fluxes. The analytical procedure and calculation of the method followed that of Dr Jiafa Luo (Personal communication, 2007).

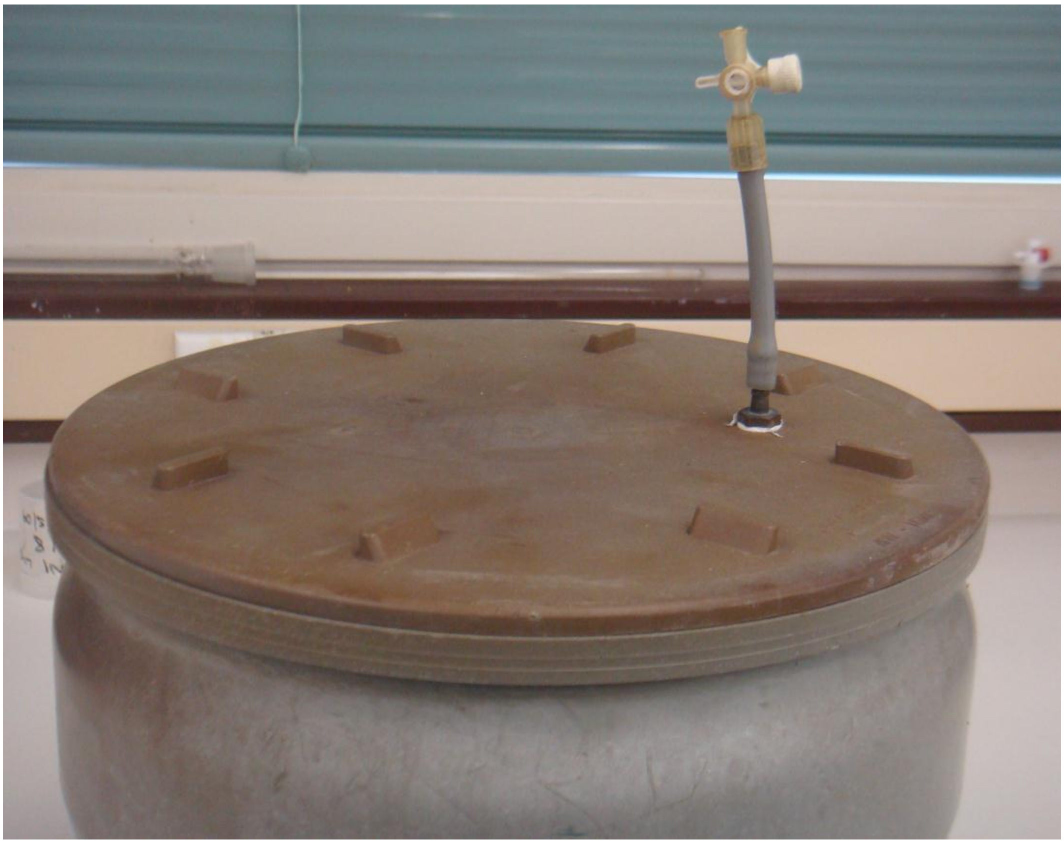

Figure 4.1 Chamber used to measure nitrous oxide and methane emissions.

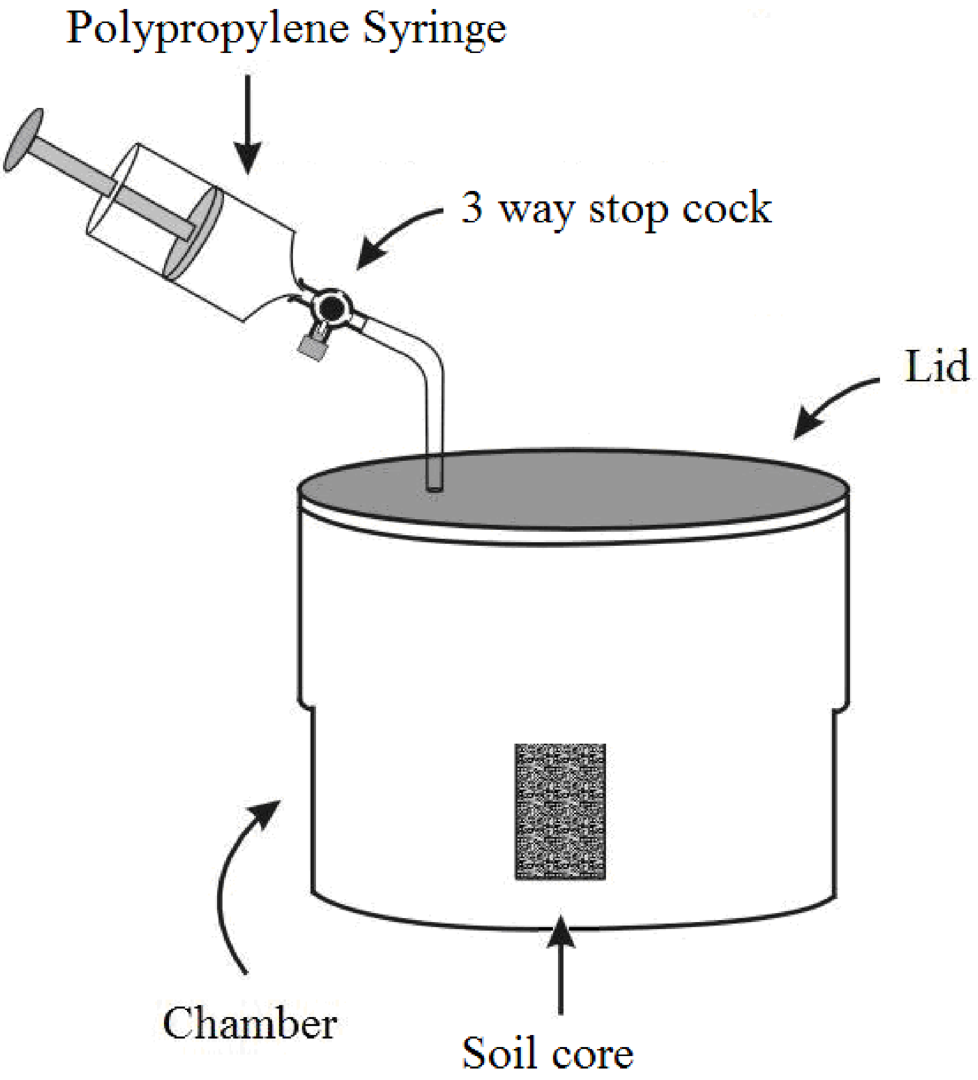

Figure 4.2 Schematic diagram of the chamber used to measure nitrous oxide and methane emissions.

The column and detector temperatures were maintained at 70 and 300^{0}C respectively. N_2O was separated on a 6mm packed column at an Ar-CH_4 (10% v v^{-1} methane) carrier gas flow rate of 30 ml min^{-1}. Sample analysis was completed within 4 minutes. A standard concentration of N_2O in N_2 gas was used to calibrate the chromatograph for N_2O concentrations (μ l^{-1}). Given a gas density for N_2O at 20^{0}C of $1.83x10^{-6}$ g N_2O μ l^{-1}, the mass concentration of N_2O (g l^{-1}) in the headspace of a chamber could be calculated. Knowing the headspace volume and allowing for N_2O dissolved in solution by using a Bunsen coefficient of 0.632 at

20^0C (Tiedje, 1982), the mass of N_2O was calculated from the following equation (Luo *et al*., 2007):

N_2O-N (g) = 1.83 x 0.636 x 10^{-6} x N_2O (μ l^{-1}) x [Volume of headspace (l) + volume of soil (l) x 0.632]

The gas samples were collected for one hour after experimental set up on days 2, 6, 10 and 14. The sampling procedure, analysis of samples and calculation of hourly N_2O emission fluxes as detailed by Luo *et al*., (2007) was followed. The hourly fluxes were integrated over time, to estimate the total emission over the measurement period.

4.3.3 Statistical analysis

The data was analysed using Proc GLM statistical analysis system (SAS) programme and treatment differences were tested using bonferroni test.

4.4 Results

4.4.1 Characteristics of materials used

The physical and chemical characteristics of soil, sawdust, urine and dung used in this study are summarised in Table 4.3. The total nitrogen was more in the urine than in dung, soil, or sawdust. The percentages of total P were greater in the dung than in the soil, urine, or sawdust. The C:N ratio of sawdust was high compared to soil and dung. The soil and sawdust were acidic and the urine and dung were both initially alkaline. The total nitrogen, nitrate N, total potassium, and total sulphur were higher in the urine than in the dung.

Table 4.3 Chemical characteristics of urine, dung, soil and sawdust before application to soil (Wet weight basis).

Chemical properties	Urine	Dung	Soil	Sawdust
pH	8.82	8.16	5.20	4.21
Total kjeldahl nitrogen (%)	0.668	0.366	0.260	0.044
Nitrate-N (%)	0.009	<0.001	0.008	<0.001
Total phosphorus (%)	0.007	0.137	0.092	<0.001
Potassium (%)	0.810	0.187	0.068	0.018
Total sulphur (%)	0.046	0.039	0.044	0.004
Calcium (%)	0.013	0.237	0.154	0.059
Sodium (%)	0.037	0.019	0.020	<0.001
Organic carbon (%)	-	5.74	2.99	20.27
Dry matter (%)	3.30	13.40	76.50	39.10
C:N ratio	-	16:1	12:1	460:1

4.4.2 Ammonia emissions

4.4.2.1 Introduction

The ammonia volatilisation rates were calculated for each treatment to estimate the total emissions during the measurement period (i.e., from day 2 to day 21). Surface application of urine and dung to soil gave the highest ammonia volatilisation with 55% of total N lost through volatilisation between days 2 and 21 (Figure 4.2). In contrast, under incorporated application of urea to soil only 2% of total N was lost as NH_3 volatilisation between days 2 and 21. Incorporated application of urine + dung + sawdust had a lower ammonia volatilisation compared with urine + dung + soil and urine + dung treatment. There was a reduction in ammonia emissions in incorporated application of urine + dung + soil compared to surface application, where incorporated application reduced ammonia volatilisation by 98%.

Addition of sawdust urine and dung led to a decrease (73%) in ammonia volatilisation following surface application of urine and dung between days 2 and

21, while only a 7% reduction was achieved by amending with soil (Figure 4.3). The total amount of NH_3 emitted was significantly ($P<0.05$) higher in all surface application treatments (T1, T3, T5 and T7) compared to the incorporated application treatments (T2, T4, T6 and T8) (Table 4.4). The addition of soil and sawdust to urine and dung prior to soil application (T3, T4, T5 and T6) resulted in a significant decrease in NH_3 emissions compared to the urine and dung applied to soil (T1 and T2).

The amount of N emitted as NH_3 decreased from 2.8 mg NH_3-N g soil^{-1} from surface application of urine and dung to soil to 0.52 mg NH_3-N g soil^{-1} in the incorporated application of urine and dung to soil, resulting in an 82% decrease in NH_3-N emissions. The total amount of NH_3-N emitted was reduced from 2.41 to 0.10 mg NH_3-N g soil^{-1} with the incorporated application of urine and dung with soil, resulting in a 96% decrease in NH_3-N emissions (Figure 4.3).

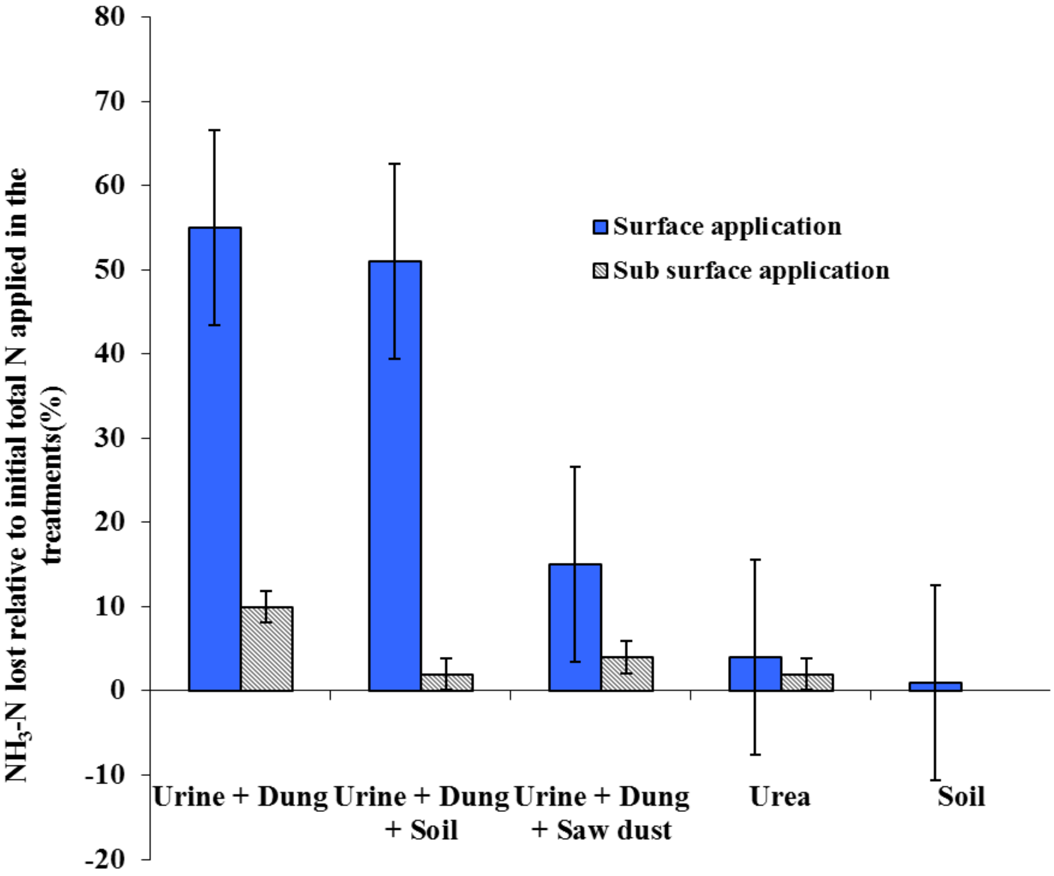

Figure 4.3 Percentage of Total N volatilised as NH_3-N between days 2 and 21 from soil with addition of soil or sawdust to manure prior to surface or incorporated application to soil cores (Error bars = 1 standard error of the mean).

The emission of NH_3-N with the incorporated application of sawdust added to urine and dung followed a similar trend with decrease in emissions from 0.66 to 0.19 mg NH_3-N g soil^{-1}. The surface application of sawdust addition treatment resulted in a 73% decrease in NH_3-N emissions compared to the surface application of urine and dung treatment.

Table 4.4 Cumulative total ammonia emissions from different treatments between days 2 and 21.

Treatments	Method of application	Initial total N (mg)*	NH_3-N (mg NH_3-N g soil^{-1})	% of NH_3 emissions to total N
Urine + dung	Surface	5.0544	2.799	55
Urine + dung	Incorporated	5.0544	0.517	10
Urine + dung + soil	Surface	4.7554	2.410	51
Urine + dung + soil	Incorporated	4.7554	0.102	2
Urine + dung + sawdust	Surface	4.4920	0.656	15
Urine + dung+ sawdust	Incorporated	4.4920	0.192	4
Urea	Surface	3.3926	0.136	4
Urea	Incorporated	3.3926	0.079	2
Soil only		3.216	0.041	1

(*Initial total N of the treatments were calculated by adding total N of all the materials used in the particular treatments)

4.4.2.2 Surface application versus incorporated application of "urine + dung"

The highest ammonia volatilisation rate measured was on day two for surface application of "urine + dung" (Figure 4.4). The initial NH_3 volatilisation from the surface application was higher than that from incorporated application. The surface application of the "urine and dung" treatment recorded a maximum of

0.68 mg NH_3-N g soil^{-1} day^{-1}, compared to 0.07 mg NH_3-N g soil^{-1} day^{-1} for the incorporated application. The ammonia volatilisation values declined to 0.01 mg NH_3-N g soil^{-1} day^{-1} for the surface application, compared to 0.001 mg NH_3-N g soil^{-1} day^{-1} for the incorporated application after 21 days (Figure 4.4). More than 50% of the emissions were observed in the first two days after surface application of "urine and dung" to the soil. Ammonia volatilisation loss from surface application of urine + dung was 55% of initial total N compared with 10% of incorporated application between days 2 and 21. Incorporated application of urine and dung (T2) significantly ($P<0.05$) reduced ammonia volatilisation by 82% compared to surface application (T1).

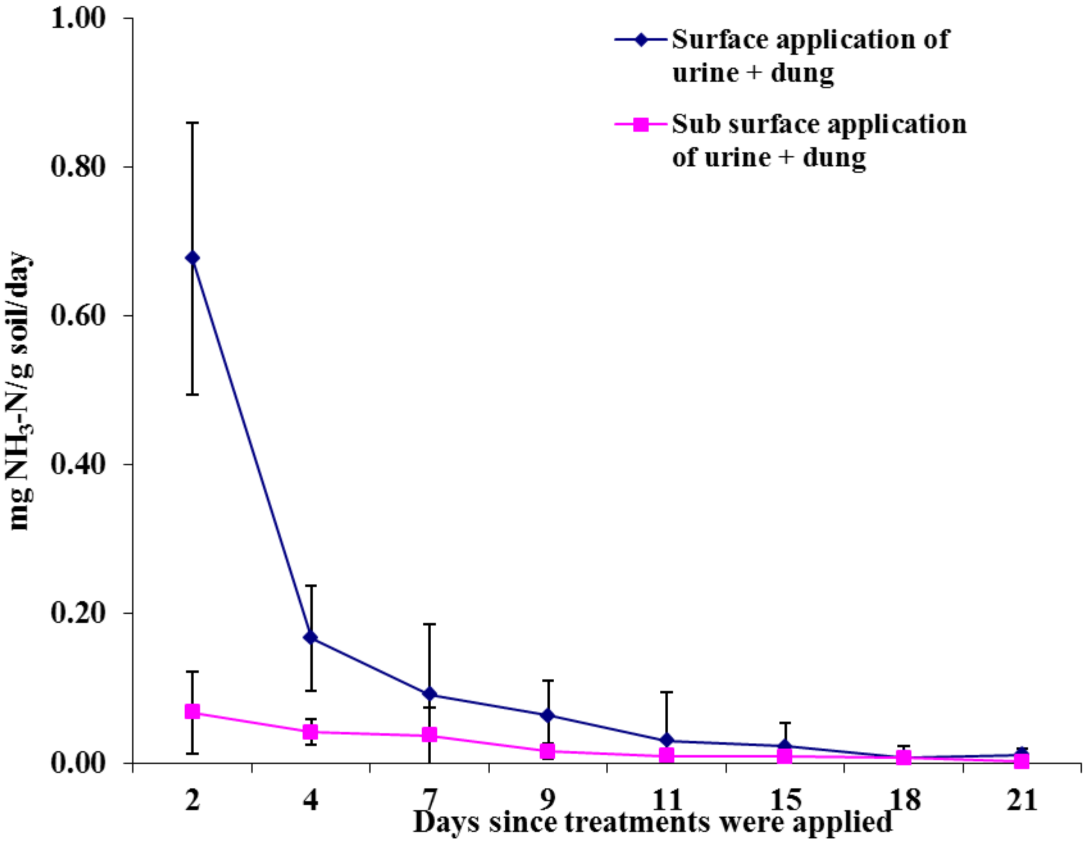

Figure 4.4 Rate of ammonia volatilisation from surface and incorporated application of "urine and dung" (Error bars = 1 standard error of the mean).

4.4.2.3 Surface application versus incorporated application of “urine + dung + soil”

Maximum ammonia volatilisation was observed in the first two days after the application of “urine + dung + soil” with a value of 0.470 mg NH_3-N g soil^{-1} day^{-1} compared with 0.005 mg NH_3-N g soil^{-1} day^{-1} emitted from the incorporated application on the second day after application (Figure 4.5). The total ammonia volatilisation from surface application of urine + dung + soil was 2.410 mg NH_3-N g soil^{-1} (51% of initial total N) and from incorporated application of urine + dung + soil was 0.102 mg NH_3-N g soil^{-1} (2% of initial total N). The incorporated application of urine + dung + soil treatment records almost negligible emissions compared with surface application. There was a significant ($P<0.05$) decrease in ammonia emissions from incorporated application of soil addition to urine and dung prior to soil application compared to the surface application. The cumulative ammonia volatilisation following incorporated application between days 2 and 21 was only 2% of the ammonia volatilisation following surface application (figure 4.5).

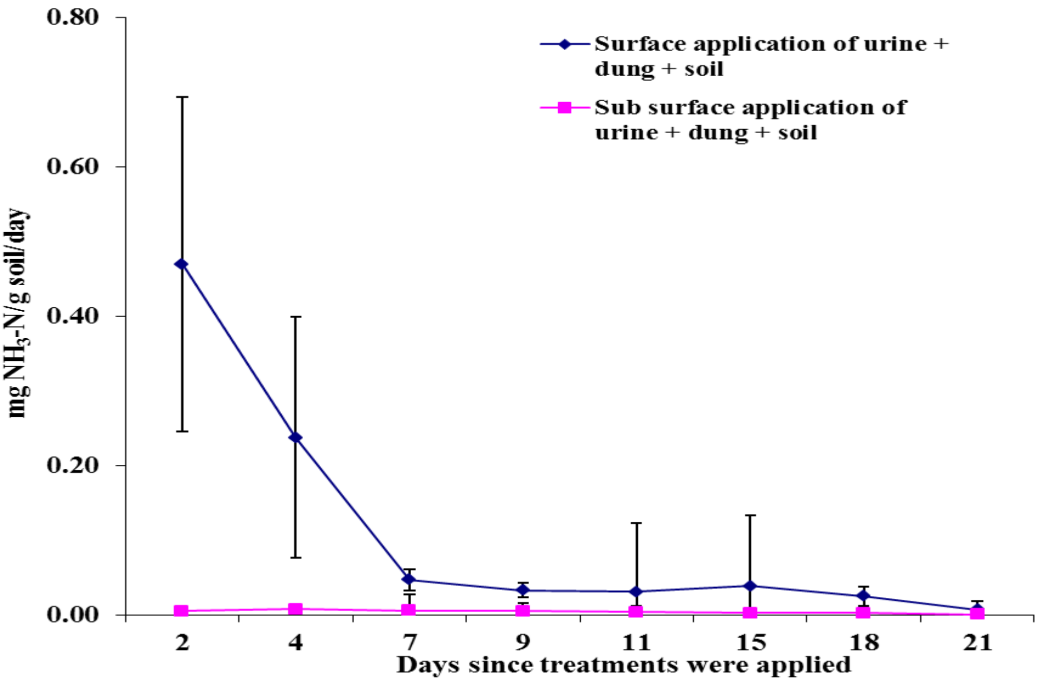

Figure 4.5 Rate of ammonia volatilisation from surface and incorporated application of “urine, dung, and soil” (Error bars = 1 standard error of the mean).

4.4.2.4 Surface application versus incorporated application of "urine + dung + sawdust"

The measured ammonia volatilisation losses from surface application of urine, dung, and sawdust were highest at the first time of measurement, i.e., two days after the surface application of "urine, dung and sawdust" (0.120 mg NH_3-N g soil^{-1} day^{-1}) and declined rapidly over the first week. This compared with 0.010 mg NH_3-N g soil^{-1} day^{-1} from incorporated application of urine, dung and sawdust (Figure 4.6). The cumulative ammonia emissions measured from surface and incorporated application of urine + dung + sawdust between days 2 and 21 was 0.656(15% of initial total N) and 0.192 mg NH_3-N g soil^{-1} (4% of initial total N). Surface application of urine + dung + sawdust showed greater reduction of ammonia emissions than urine + dung or the urine + dung + sawdust treatments. Cumulative ammonia emissions were 73% lower from incorporated application of urine + dung + sawdust than from surface application.

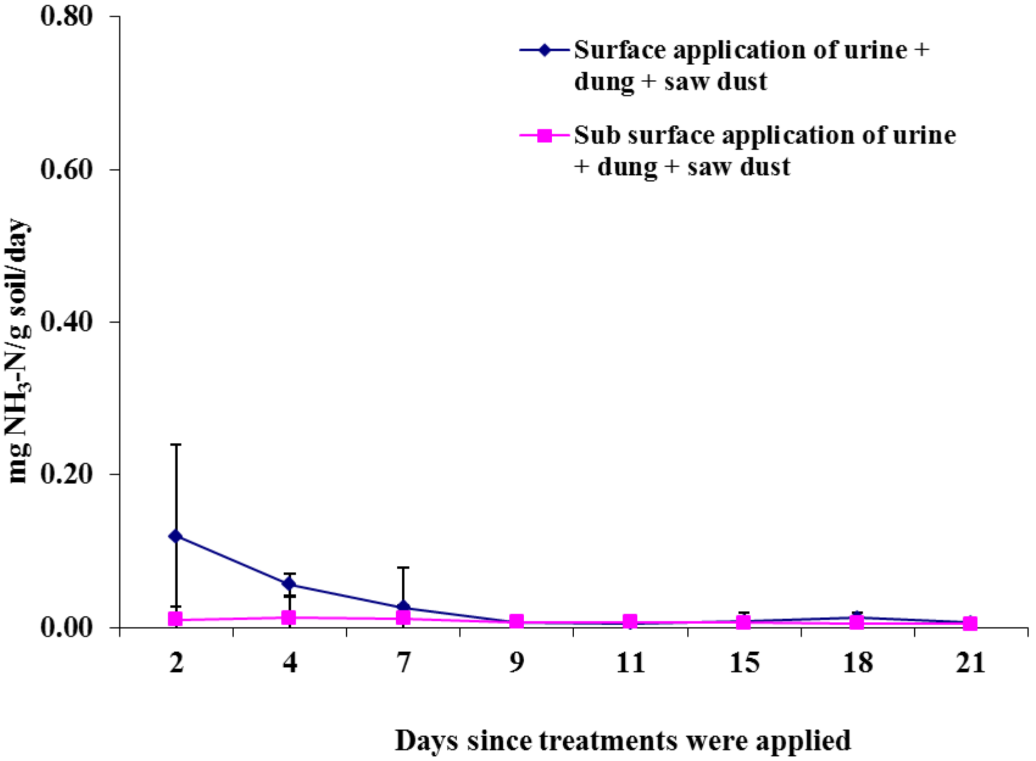

Figure 4.6 Rate of ammonia volatilisation from surface and incorporated application of "urine, dung, and sawdust" (Error bars = 1 standard error of the mean).

However, surface application of sawdust added to urine and dung before soil application gave no significant reduction in NH_3 emissions compared to incorporated application of sawdust + urine + dung.

4.4.2.5 Surface application versus incorporated application of "urea"

Following application of urea to soil, ammonia volatilisation was generally low (Fig 4.7). The highest measured ammonia volatilisation occurred on day four for the surface application (0.024 mg NH_3-N g soil^{-1} day^{-1}), and on day 7 (0.011 mg NH_3-N g soil^{-1} day^{-1}) for the incorporated application of urea. The total ammonia volatilisation losses from surface (0.136 mg NH_3-N g soil^{-1}) and incorporated applications (0.079 mg NH_3-N g soil^{-1}), were equal to 4% and 2% of the initial total N (figure 4.7). Throughout the experimental days (2 to 21) surface application of urea did not give a significantly lower ammonia volatilisation than incorporated application of urea.

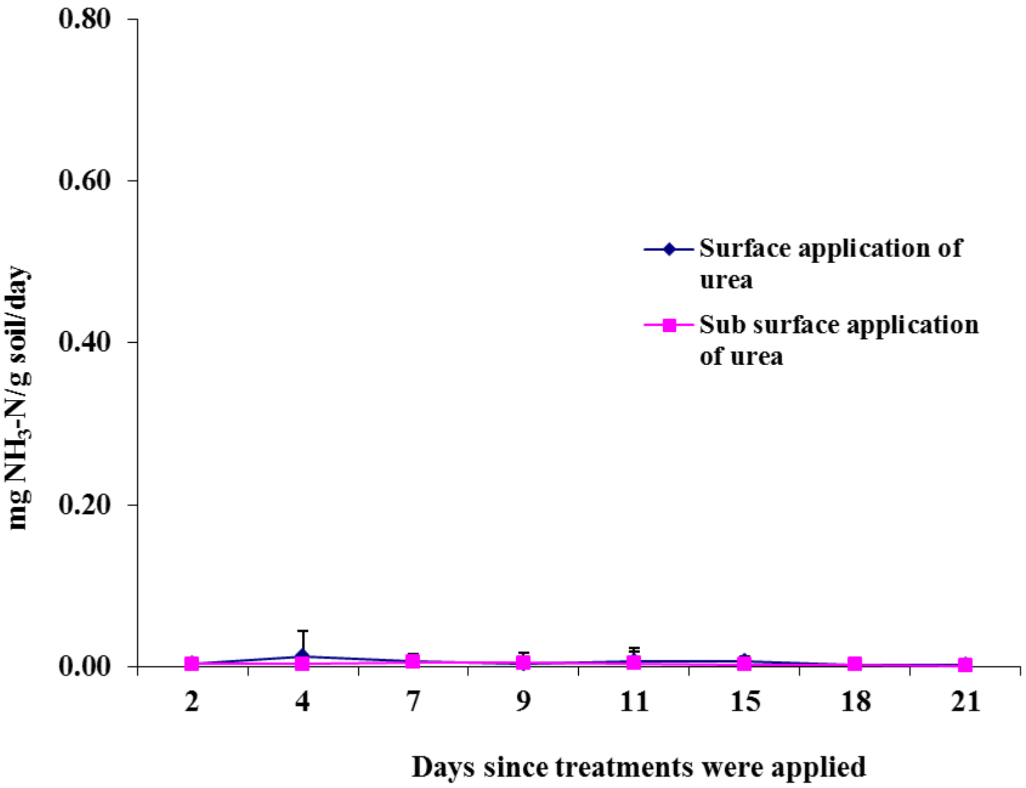

Figure 4.7 Rate of ammonia volatilisation from surface and incorporated application of "urea" (Error bars = 1 standard error of the mean).

4.4.3 Nitrous oxide emissions

Nitrous oxide fluxes from all treatments were generally low for the first 10 days after manure application to soil. The maximum fluxes were observed 14 days after the treatments were applied and N_2O fluxes declined subsequently. Cumulative nitrous oxide emissions from different treatments ranged from 0.073 (incorporated application of urea) to 0.619 mg N_2O-N g soil^{-1} (incorporated application of urine + dung + sawdust)) (Table 4.5).

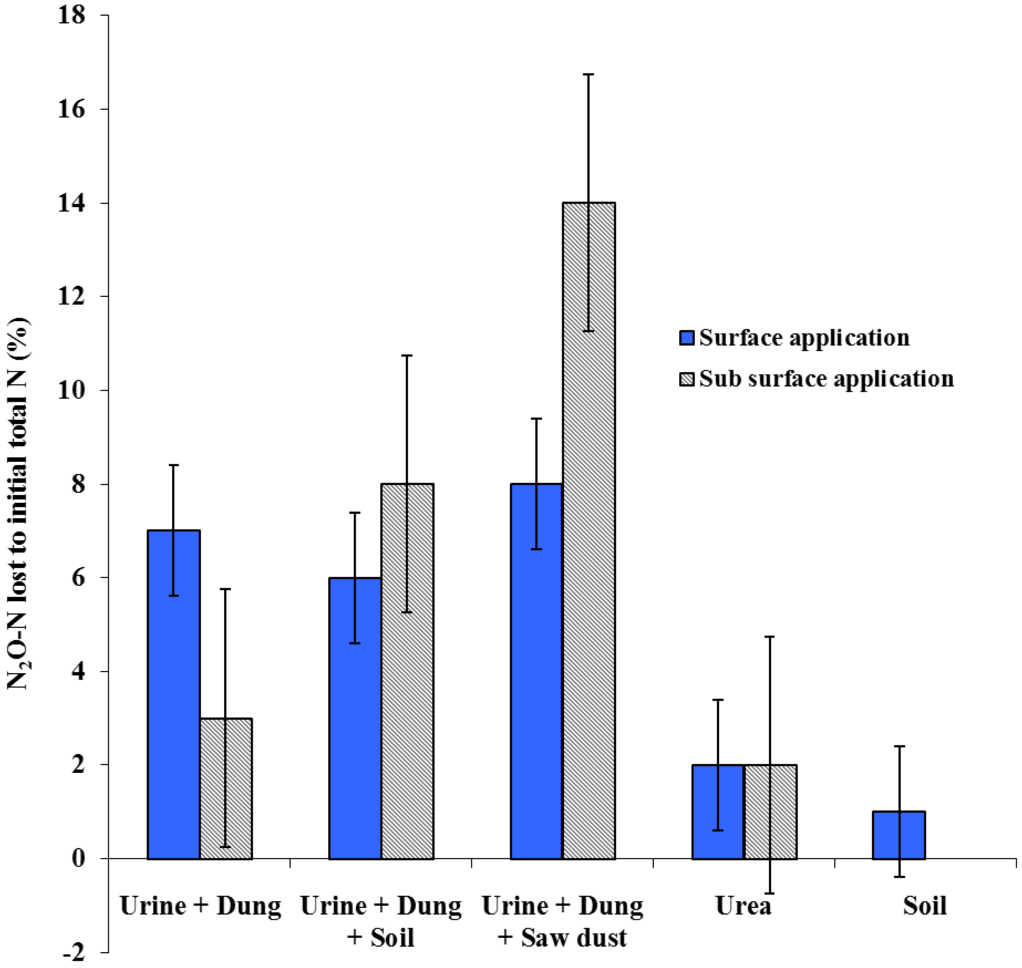

Figure 4.8 Percentage of N_2O-N emissions from different treatments between days 1 and 16 (Error bars = 1 standard error of the mean).

The highest emissions of N_2O (14% of the applied N) were observed from the soil with incorporated application of “urine, dung, and sawdust” followed by incorporated application of urine + dung + soil (8%) and surface application of urine + dung + sawdust treatments applied to soil (Figure 4.8). Surface and incorporated application of urea to soil resulted in 2% emission of the total N applied in the treatments as N_2O, which was low compared with most other treatments.

Table 4.5 Cumulative total N_2O emissions from different treatments between days 1 and 16.

Treatments	Method of application	Initial total N (mg)*	N_2O-N (mg N_2O-N g soil^{-1})	% of N_2O emissions
Urine + dung	Surface	5.0544	0.368	7
Urine + dung	Incorporated	5.0544	0.167	3
Urine + dung + soil	Surface	4.7554	0.265	6
Urine + dung + soil	Incorporated	4.7554	0.392	8
Urine + dung + sawdust	Surface	4.4920	0.359	8
Urine + dung+ sawdust	Incorporated	4.4920	0.619	14
Urea	Surface	3.3926	0.083	2
Urea	Incorporated	3.3926	0.073	2
Soil only		3.216	0.041	1

(*Initial total N of the treatments were calculated by adding total N of all the materials used in the particular treatments)

4.4.3.1 Surface application versus incorporated application of “urine and dung”

The maximum N_2O emissions were observed in between 8-12 days after urine and dung were applied to soil in both surface and incorporated applications (Figure 4.9). Nitrous oxide emissions from the surface application “urine and dung” was higher than that from incorporated application. The maximum N_2O emission recorded from the surface application of the “urine and dung” treatment was a maximum of 0.368 mg N_2O-N g soil^{-1}, where it was 0.167 mg N_2O-N g soil^{-1} for the incorporated application. Nitrous oxide emissions from the surface application of urine + dung were 7% of initial total N compared with 3% of incorporated application. The higher total N_2O emissions in the surface application of urine and dung to soil (0.368 mg N_2O-N g soil^{-1}) did not significantly differ from those in the incorporated application (0.167 mg N_2O-N g soil^{-1}). Incorporated application of urine and dung reduced ammonia volatilisation by 57% compared to surface application.

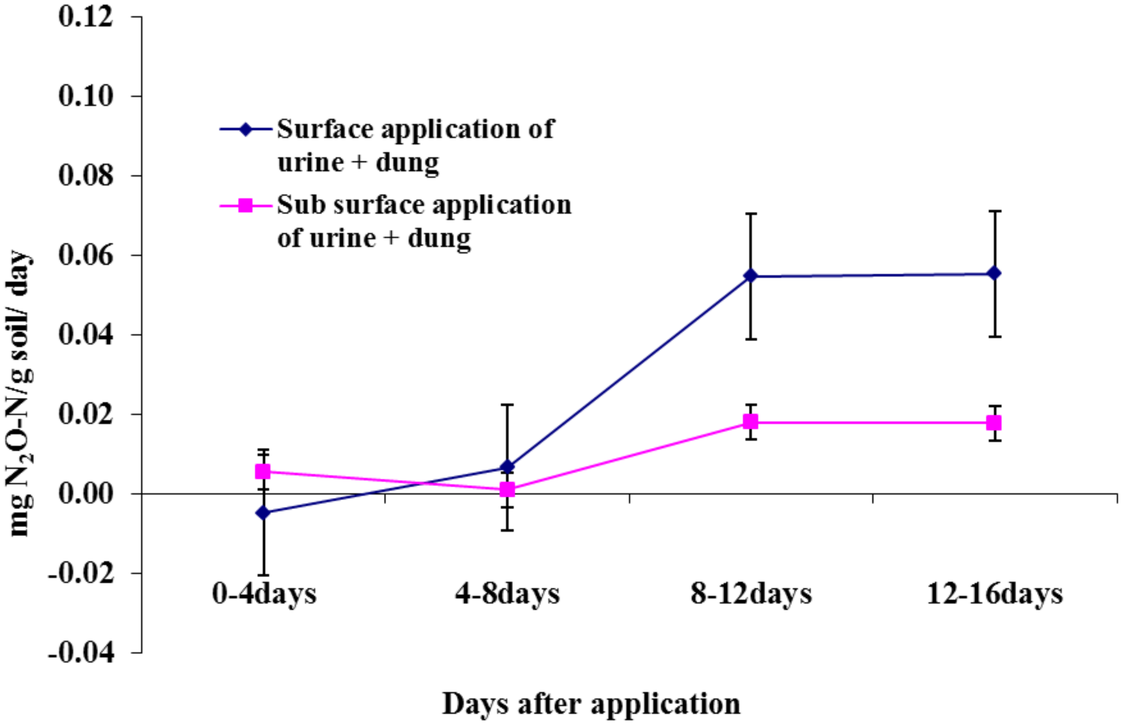

Figure 4.9 Nitrous oxide emissions from surface and incorporated application of “urine and dung” from 1 to 16 days after application to soil (Error bars = 1 standard error of the mean).

4.4.3.2 Surface application versus incorporated application of “urine + dung + soil”

Maximum N_2O emission was observed 8-12 days after the application of “urine + dung + soil” from both the surface and incorporated (Figure 4.10) methods. Addition of soil to urine and dung resulted in an increase in total N_2O emissions in both surface and incorporated applications, although the increase was not significant.

The total N_2O emission from surface and incorporated application of urine, dung and soil treatments were 0.265 and 0.392 mg N_2O-N g soil^{-1}, which are equal to 6% and 8% of initial total N in the applied manure. The incorporated application of urine + dung + soil enhances the nitrous oxide emissions by 25% compared to surface application.

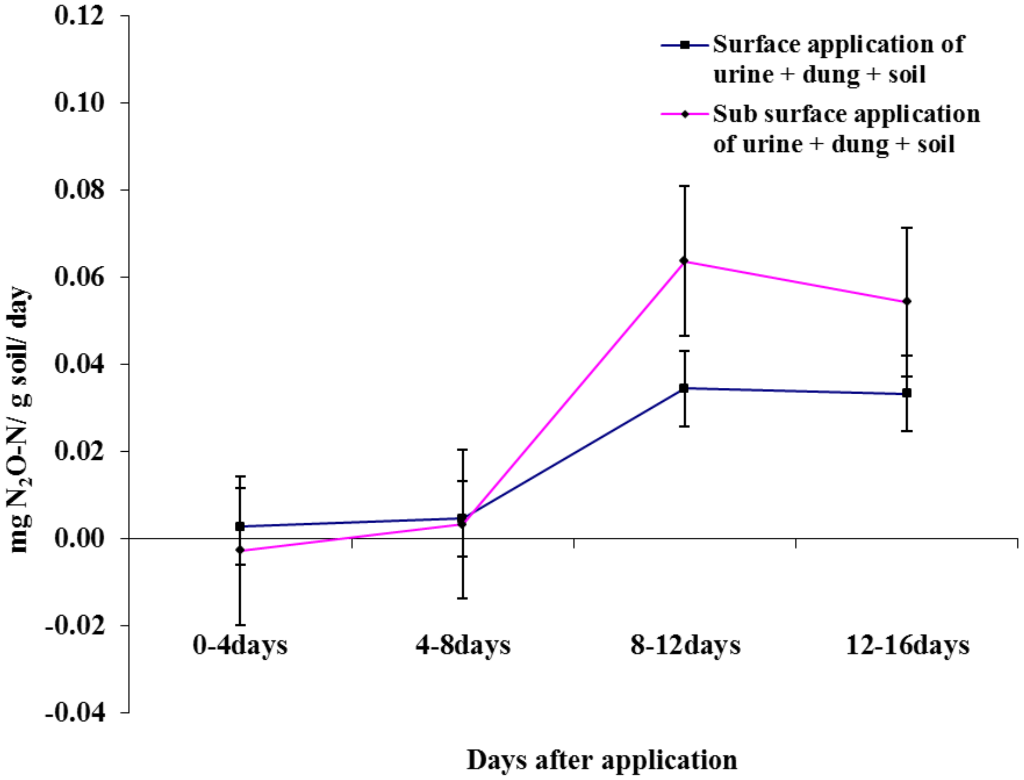

Figure 4.10 Nitrous oxide emissions from surface and incorporated application of “urine, dung and soil” from 1 to 16 days after application to soil (Error bars = 1 standard error of the mean).

4.4.3.3 Surface application versus incorporated application of “urine + dung + sawdust”

The cumulative N_2O emissions measured from surface and incorporated application of urine + dung + sawdust was 0.359 and 0.619 mg N_2O -N g soil^{-1} (Figure 4.11). N_2O emission from surface and incorporated application of urine, dung and sawdust are equal to 8% and 14% of initial total N. Surface application of urine + dung + sawdust showed greater reduction of N_2O emissions than urine and dung and urine + dung + soil treatments (Figure 4.8). The total increase in

N_2O emissions with the addition of sawdust to urine and dung prior to soil application from 0.359 mg N_2O-N g soil^{-1} (surface application) to 0.619 mg N_2O-N g soil^{-1} (incorporated application) was, however, not significant. Incorporated application increased cumulative N_2O emissions by 75% compared to surface application of urine, dung and sawdust.

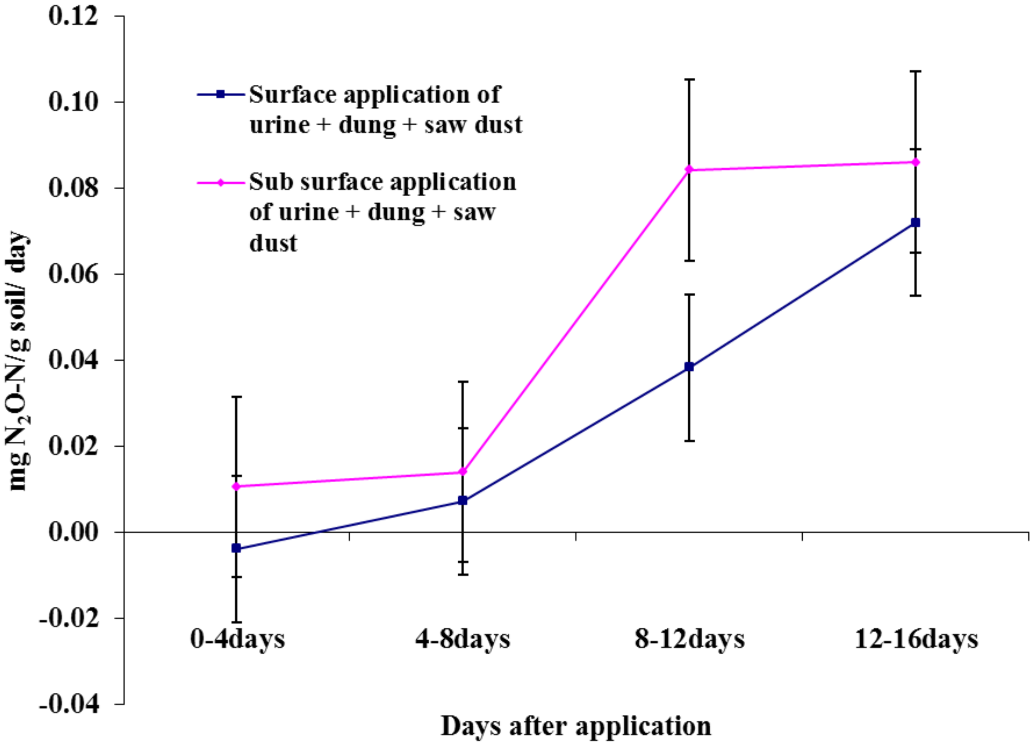

Figure 4.11 Nitrous oxide emissions from surface and incorporated application of “urine, dung and sawdust” from 1 to 16 days after application to soil (Error bars = 1 standard error of the mean).

4.4.3.4 Surface application versus incorporated application of “urea”

The maximum N_2O emission following surface application of urea occurred during the first 4 days with surface application (0.009 mg N2O-N g soil^{-1} day^{-1}), and 12-16 days (0.019 mg N_2O -N g soil^{-1} day^{-1}) with incorporated application. The total nitrous oxide emissions from surface and incorporated applications were 0.083 and 0.073 mg N_2O-N g soil^{-1}, which are equal to 2% of the initial total N (Figure 4.12), however, the treatment differences were not significant.

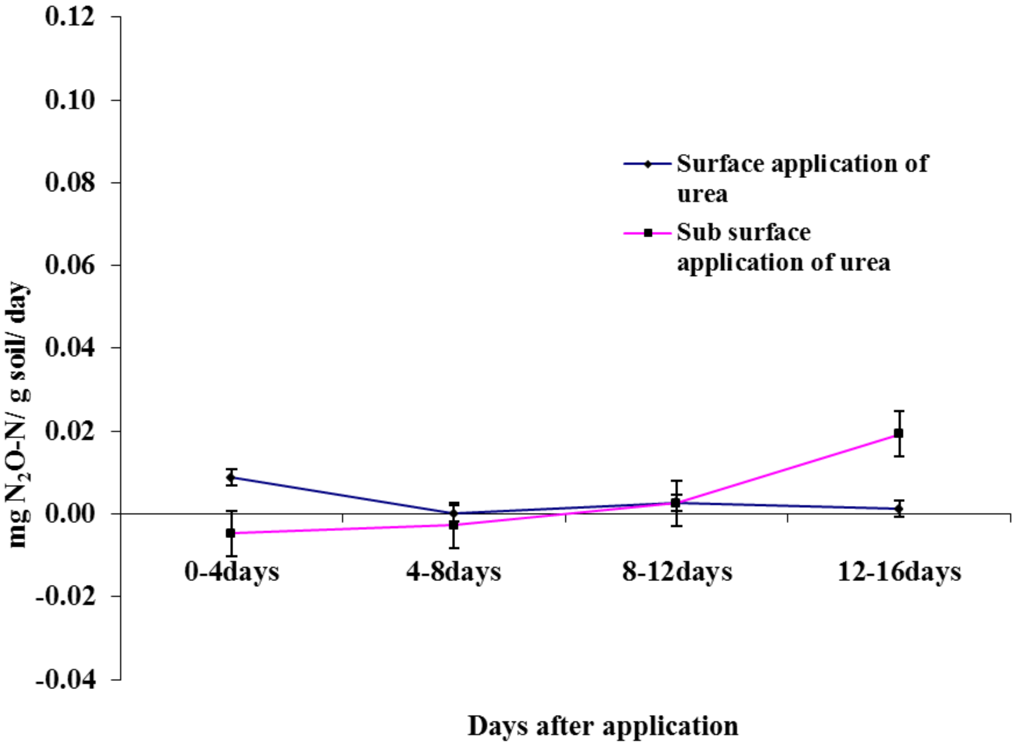

Figure 4.12 Nitrous oxide emissions from surface and incorporated application of "urea" from 1 to 16 days after application to soil (Error bars = 1 standard error of the mean).

4.4.4 Methane (CH_4) emissions

The soil and manure mixtures in all treatments acted as a methane sink except for the soil receiving surface application of urea (Table 4.6). Cumulative methane emissions ranged from -0.8361 to +0.096 mg CH_4-C g soil^{-1} across the treatments. Small emissions of methane were measured on the second day after the treatments were applied. On day 2 higher methane emissions were generally measured from the surface application than from the incorporated application.

Table 4.6 Cumulative total CH_4 emissions from different treatments between days 1 and 16.

Treatments	Method of application	Initial total N (mg)	CH_4-C (mg CH_4-C g soil^{-1})
Urine + dung	Surface	5.0544	-0.211
Urine + dung	Incorporated	5.0544	-0.661
Urine + dung + soil	Surface	4.7554	-0.022
Urine + dung + soil	Incorporated	4.7554	-0.541
Urine + dung + sawdust	Surface	4.4920	-0.651
Urine + dung + sawdust	Incorporated	4.4920	-0.816
Urea	Surface	3.3926	0.096
Urea	Incorporated	3.3926	-0.831
Soil only		3.216	-0.690

4.5 Discussion

4.5.1 Ammonia emissions

The ammonia emissions followed a similar trend of rapid emissions on day 2 after the application of the urine and dung, urine + dung + soil, and urine + dung + sawdust to soil and a progressive decrease over time for both the surface and incorporated application for all the treatments applied. The highest measured ammonia volatilisation was recorded on the 2nd day for all treatments except for surface application of urea which was highest on day 4 and for incorporated application of urea which was highest on day 7. The volatilisation rate gradually decreased after day 2 for all treatments except the urea applications.

The surface and incorporated application of urine and dung to soil showed maximum ammonium concentration on day 2 and decreased rapidly by day 4 in surface application. Urine + dung + soil and urine + dung + sawdust treatments showed the same pattern, where maximum recorded emissions occurred at day 2 and then declined rapidly by day 7. The initial high rates of ammonia emissions most likely occurred from urine + dung, urine + dung + soil and urine + dung +

sawdust treatments are due to the rapid hydrolysis of urine and ammonification to produce NH_4^+ (Bolan *et al.*, 2004a and Zaman *et al.*, 2009) and activity of microorganisms present in the dung as per equation 4.1.

$$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightarrow 2NH_4^+ + OH^- + CO_2 \qquad \textbf{(4.1)}$$

Hydrolysis of urea releases OH^- ions, which would be expected to increase the pH of the manure. Under alkaline conditions conversion of NH_4^+ ions to NH_3 will take place (Equation 4.2), which was probably the major process regulating the volatilisation loss of NH_3 from manure (Bolan *et al.*, 2004a).

$$NH_4^+ + OH^- \rightarrow NH_3 \uparrow + H_2O \qquad \textbf{(4.2)}$$

4.5.1.1 Surface and incorporated application of urine and dung

Surface application of urine + dung had 73% higher ammonia losses than the urine + dung + sawdust treatment and 7% higher than the urine + dung + soil treatment. When urine and dung were mixed together, production of amines and amino acids by hydrolysing macro molecules takes place giving a “priming effect’’ (Jenkinson *et al.*, 1985). The amines and amino acids undertake ammonification reaction and convert them into NH_4^+ ions. In the urine + dung treatment, it is likely that urea was hydrolysed by microorganisms, and carbohydrate materials contained in the dung supply energy to support the activity of microorganisms. The majority of the nitrogen in the fresh dung is in organic form and only a small percentage is available as urea or NH_4^+. A large quantity of the carbon content is from undigested fibrous material, such as cellulose, hemi cellulose and lignin (Bolan *et al.*, 2004; Qiu, 2007).

4.5.1.2 Surface and incorporated application of urine, dung and soil

When urine and dung were mixed with soil prior to application, of the mixture to the soil core, the initial ammonia emissions was reduced compared to surface applied urine and dung to soil (Figures 4.3 to 4.6). The huge quantity of proteolytic and deaminative bacteria present in dung and soil hydrolyze proteins to peptides and amino acids and finally converted them in to NH_4^+ ions. The reduction in ammonia volatilisation could be possible in urine, dung and soil treatment is due to the soil's exchange capacity for NH_4^+ ions and ability to fix NH_4^+ (Qiu, 2007). Likewise, Selvarajah *et al*., (1989) reported that decline in ammonia volatilisation was due to an inverse relationship between ammonia volatilisation and cation exchange capacity of many soils.

4.5.1.3 Surface and incorporated application of urine, dung and sawdust

Addition of sawdust to urine and dung reduces the pH and alkaline conditions and thereby decreases the production of NH_4^+. Similarly, Pain *et al*., (1990) also observed that the acidic conditions of soil and sawdust would reduce ammonia emissions.

Ammonia volatilisation from the surface application of urine and dung amended with sawdust was 73% lower than surface application of urine and dung, while only a 7% reduction was achieved by amending with soil. Similarly, Luo *et al*., (2004) found pine bark was the most efficient in reducing NH_3 loss, achieving a reduction of 58% compared with unamended manure, followed by soil (30%), wood shavings (25%) and sawdust (24%).

C-rich materials like sawdust or soil reduce ammonia emissions due to microbial immobilisation or absorption of manure nitrogen, which reduces ammonium concentrations, which subsequently leads to ammonia losses as suggested by Bolan *et al*., (2004) and Luo and Lindsey, (2006). Similarly, Mahimairaja *et al.***,** (1994) found ammonia volatilisation was reduced with addition of amendments, such as woodchips, elemental sulphur (S) and zeolite.

Addition of sawdust increases the C/N ratio of the manure, and at the same time it enhances the immobilisation potential of nitrogen, and increases the NH_4^+ absorption capacity due to more surface area. The effect of natural amendment additions in reducing ammonia volatilisation depends on their ability to fix NH_4^+ ions and their exchange capacity for NH_4. Chadwick *et al*., (2000) stated that fibrous carbon material removes the manure NH_4^+ from the manure by disturbing the potential mineralisation of manure organic nitrogen.

Among the results discussed above, it can be concluded that the surface application of manure always lost more ammonia by volatilisation than the incorporated application of manure. Ammonia volatilisation was reduced in manure incorporated treatments because manure nitrogen was incorporated into soil, reducing surface nitrogen concentrations as suggested by Cameron, (1996). The surface application of urine and dung lost 55% of the applied nitrogen through ammonia volatilisation compared with 10% from incorporated application of urine and dung. Similarly, 92% (Huijsman *et al*., 2001), 90% (Malgeryd, 1998; Webb *et al*., 2010), 86% (Mkhabela, 2008), 75% (Hansen *et al*., 2003) and 73% (Misselbrook *et al*., 2002) ammonia volatilisation reduction was reported with injection and incorporation compared to spreading of manure.

4.5.2 Nitrous oxide emissions

Nitrous oxide emissions were higher with incorporated applications than surface applications except for the urine and dung application treatment. Nitrous oxide emissions from soil are affected by a number of soil factors, including soil temperature, pH, mineral nitrogen, available carbon and moisture content, and weather conditions (Luo *et al*., 1999 and Saggar *et al*., 2007a, b). The highest N_2O emissions (14% of the applied N) were observed from the soil with incorporated application of “urine, dung and sawdust” followed by 8% from incorporated application of urine + dung + soil and surface application of urine + dung + sawdust treatments applied to soil. Nitrous oxide emission was higher from urine and dung treatments than urea treatments. The hydrolysis of the urine urea is more rapid in urine and dung treatments than that of pure urea under similar conditions due to the presence of hippuric acid (Bhandral *et al*., 2007; Haynes and Williams, 1993). The addition of natural materials to urine and dung during storage enhanced the N_2O emissions after application to soil. There is considerable interaction among these processes, which makes it difficult to predict the precise fate of manure nitrogen in soil. Nitrification and denitrification processes in the soil cause nitrogen emissions in various forms, with the primary forms being N_2O and N_2.

4.5.3 Methane emissions

Emissions of methane from all treatments were short lived, with most measured on the second day following application. Negative fluxes of methane were measured for all other sampling times. Similarly, Rodhe *et al*., (2006) also found that CH_4 emissions were short-lived and most of the total emissions occurred within the first two days after manure application with a total negative flux of up to -362 g C ha^{-1}. When manure was incorporated into the soil, the methanogens in the slurry were probably inhibited by oxygen.

4.6 Summary and Conclusion

4.6.1 Summary

An experiment was conducted in a glasshouse to determine the gaseous losses of ammonia (NH_3), methane (CH_4) and nitrous oxide (N_2O) after application of cow manure to soil. Treatments included surface and incorporated application of urine + dung, urine + dung + soil, urine + dung + sawdust and urea. Ammonia samples were collected once every two days for 21 days after application of manure to soil. Nitrous oxide and methane samples were collected and analysed one hour after experimental set up and on days 2, 6, 10 and 14. Major findings include:

- The incorporated application of all the manure treatments gave lower ammonia volatilisation compared to surface application.

- Sawdust reduced ammonia volatilisation when added to urine and dung before surface and incorporated application to soil.

- Cumulative ammonia losses measured between days 2 and 21 were 2.80 mg NH_3-N g $soil^{-1}$ from surface and 0.52 mg NH_3-N g $soil^{-1}$ from the incorporated application of “urine and dung” (equivalent to 55% and 10% of the applied N).

- Cumulative ammonia losses measured between days 2 and 21 were 2.41 mg NH_3-N g $soil^{-1}$ from surface and 0.12 mg NH_3-N g $soil^{-1}$ from the incorporated application of “urine, dung and soil” (equivalent to 51% and 2% of the applied N).

- Cumulative ammonia losses measured between days 2 and 21 were 0.66 mg NH_3-N g soil^{-1} from surface and 0.19 mg NH_3-N g soil^{-1} from the incorporated application of “urine, dung and sawdust” (equivalent to 15% and 4% of the applied N).
- Cumulative ammonia losses measured between days 2 and 21 were 0.14 mg NH_3-N g soil^{-1} from surface and 0.08 mg NH_3-N g soil^{-1} from the incorporated application of urea (equivalent to 4% and 2% of the applied N).
- Nitrous oxide emissions were higher when soil or sawdust was added to urine and dung prior to application to the soil cores than when un-amended urine and dung was applied to the soil cores.
- Maximum N_2O emissions were recorded in incorporated application of “urine and dung with sawdust”.
- Nitrous oxide emissions measured between days 1 and 16 ranged from 0.07 mg N_2O-N g soil^{-1} (Incorporated application of urea to soil) to 0.62 mg N_2O-N g soil^{-1} (Incorporated application of manure added with sawdust to soil) (equivalent to 2% and 14% of the applied N).
- For all the treatments, except surface application of urea, there were no net methane emissions.

4.6.2 Conclusion

Addition of soil or sawdust to urine and dung (manure) prior to soil application reduced ammonia volatilisation and enhanced the nitrous oxide emissions. Sawdust was more effective in reducing ammonia volatilisation than soil. The incorporated application of all treatments reduced ammonia volatilisation compared to surface application of manure to soil. As these experiments were conducted in the glasshouses, the effect of climatic factors, like temperature, rain fall and wind speed need to be verified in the field.

4.7 Practical implications of study

Field studies are required to study the effect of soil or sawdust on gaseous emissions. For example, in the present study there was clear evidence that sawdust addition to manure prior to land application decreases NH_3 volatilisation, whereas the N_2O emissions show the contrary effect.

4.8 Limitations of the study

The ammonia emissions measured on day 2 were the highest emissions observed, which raises the question of ammonia emissions might have occurred on day 1. As the experiment was conducted in the glass house there is a need to evaluate the potential effects of gaseous emissions from grass and clover.

4.9 Recommendations for further study

This study highlighted many questions, for example, is the use of sawdust economically viable and do the benefits outweigh potential adverse environmental effects? There is a need to carry out further field experiments to measure gaseous emissions and N transformations from the urine and dung deposition to land application along with amendments.

References

Aarons, S.R., O'Connor, C.R., Gourley, C.J.P., 2004a. Dung decomposition in temperate dairy pastures I. Changes in soil chemical properties. *Australian journal of Soil Research* 42, 107-114.

Aarons, S.R., Hosseini, H.M., Dorling, L., Gourley, C.J.P., 2004b. Dung decomposition in temperature dairy pastures II. Contribution to plant-available soil phosphorus. *Australian Journal of Soil Research* 42, 115-123.

Addiscott, T.M., 2005. Nitrate, Agriculture and the Environment, CABI Publishing, London.

AgResearch undated. AgResearch technical manual. Ammonia volatilization (enclosure method). 12B, 1-3.

Amon, B., Boxberger, J., Amon, T., Zaussinger, H., Pollinger, A., 1997. Emission data of NH_3, CH_4 and N_2O from fattening bulls, milking cows and during different ways of storing solid manure. In: Voermans, J.A.M., Monteney, G.J. (Eds.), Ammonia and Odour Control from Animal Production Facilities. pp. 397-404.

Amon, B., Boxberger, J., Amon T., Zaussinger A., Pollinger., 1997a. Ammonia and odour emissions from animal production facilities, proceedings. Vols 1 and 2, 397-404.

Amon, B., Amon, T., Boxberger, J., Alt, C., 2001. Emissions of NH_3, N_2O and CH_4 from dairy cows housed in a farmyard manure tying stall (housing, manure storage, manure spreading). *Nutrient Cycling in Agroecosystems* 60, 103-113.

Amon, B., Kryvoruchko, V., Moitzi, G., Amon, T., Zechmeister-Boltenstern, S., 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. *Agriculture, Ecosystems and Environment* 112, 153-162.

Atallah, T., Andreux, F., Chone, T., Gras, F., 1995. Effect of storage and composting on the properties and degradability of cattle manure. *Agriculture, Ecosystems and Environment* 54, 203-213.

Balsari, P., Gioelli, F., Dinuccio, E., 2006. Ammonia nitrogen emission from land spread farmyard manure. *International Congress Series* 1293, 327- 330.

Barkle, G.F., Stenger, R., Singleton, P.L., Painter, D.J., 2000. Effect of regular irrigation with dairy farm effluent on soil organic matter and soil microbial biomass. *Australian Journal of Soil Research* 38, 1087-1097.

Barkle, G.F., Stenger, R., Sparling, G.P., Painter, D.J., 2001. Immobilisation and mineralisation of carbon and nitrogen from dairy farm effluent during laboratory soil incubations. *Australian Journal of Soil Research* 39, 1407-1417.

Barton, L., Schipper, L.A., 2001. Regulation of nitrous oxide emissions from soils irrigated with dairy farm effluent. *Journal of Environmental Quality 30*, 1881-1887.

Beauchamp, E.G., Kidd, G.E., Thurtell, G., 1982. Ammonia volatilisation from liquid dairy cattle manure in the field. *Canadian Journal of Soil Science* 62, 11-19.

Black, A.S., Sherlock, R.R., Smith, N.P., Cameron, K.C., Goh, K.M., 1985a. Effects of form of nitrogen, season, and urea application rate on ammonia volatilisation from pastures. *New Zealand Journal of Agricultural Research* 28, 469-474.

Blakemore, L.C., Searle, P.L., Daly, B.K., 1987. Methods for chemical analysis of soils. In: *New Zealand Soil Bureau Science Report No. 80* Lower Hutt.

Berg, W., Brunsch, R., Pazsiczki, I., 2006. Greenhouse gas emissions from covered slurry compared with uncovered during storage. *Agriculture, ecosystems and environment* 112, 129-134.

Bertram, H., Flesh, T., McGinn, S., Coates, S., Dzikowski, T., Llewellyn, P., Cheng., L., 2000. ‘‘Measurement of Ammonia Emissions from Intensive Livestock Facilities by Open Path Tunable Diode Laser.’’ Alberta Environment, Lethbridge, Canada.

Bhandral, R., Saggar, S., Bolan, N.S., Hedley, M.J., 2003a. Nitrous oxide fluxes in soil as influenced by compaction. *Proceedings of the New Zealand Grassland Association 65*, 265-271.

Bhandral, R., Saggar, S., Bolan, N.S., Hedley, M.J., 2003b. Nitrous oxide emission from effluent irrigation. Proceedings of the 2nd Joint Australia/ New Zealand Forum on Non-CO_2 Emissions, 20-22 October 2003, Melbourne, Australia. Abstract E10.

Bhandral, R., Saggar, S., Bolan, N.S., Hedley, M.J., 2004. Factors controlling nitrous oxide emissions from effluent application. Proceedings of the Trace Gas Workshop, 18-19 March 2004, Wellington, New Zealand. Pp. 70-73.

Bhandral, R., Saggar, S., Bolan N.S., Hedley, M.J., 2007. Transformation of nitrogen and nitrous oxide emission from grassland soils as affected by compaction. *Soil and Tillage Research*, 94, 482-492.

Bierman, S., Erickson, G.E., Klopfenstein, T.J., Stock, R.A. Shain, D.H., 1999. Evaluation of nitrogen and organic matter balance in the feedlot as affected by level and source of dietary fiber. *Journal of Animal Science* 77, 1645-1653.

Black, A.S., Sherlock, R.R., Cameron, K.C., Smith, N.P., Goh, K.M., 1985b. Comparison of three field methods for measuring ammonia volatilisation from urea granules broadcast on to pasture. *Journal of Soil Science* 36, 271-278.

Bolan, N.S., 1998. Nutrient removal from farm effluents. In “New Zealand Water and Wastes Association, 40th Annual conference and Expo”. *New Zealand Water and Wastes*, Wellington, New Zealand.

Bolan, N.S., 2001. Nutrient recycling from farm effluents. *Water & Waste in New Zealand*, 117, 32-35.

Bolan, N.S., Horne, D.J., Currie, L.D., 2004. Growth and chemical composition of a legume based pasture irrigated with dairy farm effluent. *New Zealand Journal of Agricultural Research* 47, 85-93.

Bolan, N.S., Saggar, S., Luo, J., Bhandral, R., Singh, J., 2004a. Gaseous emissions of nitrogen from grazed pastures: processes, measurements and modelling, environmental implications, and mitigation. *Advances in Agronomy* 84, 37-120.

Bolan, N.S., Wang, L., Adriano, D.C., 2004b. Nutrient removal from farm effluents. *Bioresource technology* 94, 251-260.

Bouwman, A.F., Lee, D.S., Asman, W.A.H., Dentener, F.J., Van Der Hoek, K.W., Olivier, J.G.J., 1997. A global high-resolution emission inventory for ammonia. *Global Biogeochemical Cycles* 11, 561-587.

Braam, C.R., Ketelaars, J.J.M.H., Smits, M.C.J., 1997. Effects of floor design and floor cleaning on ammonia emission from cubicle houses for dairy cows. *Netherlands Journal of Agricultural Science* 45, 49-64.

Braam, C.R., Swierstra, D., 1999. Volatilisation of ammonia from dairy housing floors with different surface characteristics. *Journal of Agricultural Engineering Research* 72, 59-69.

Bremner, J.M., Tabatabai, M.A., 1971. Use of automated combustion techniques for total carbon, total nitrogen, and total sulphur analysis of soils. In: *Instrumental methods for analysis of soils and plant tissue* (ed. Walsh LM). Soil Science Society of America, Madison.

Brown, L., Syed, B., Jarvis, S.C., Sneath, R.W., Phillips, V.R., Goulding, K.W.T., Li, C., 2002. Development and application of a mechanistic model to estimate emission of nitrous oxide from UK agriculture. *Atmospheric Environment* 36, 917-928.

Burton, C.H., Turner, C., 2003. Manure Management: Treatment Strategies for Sustainable Agriculture, 2nd ed. Silsoe Research Institute, UK.

Bussink, D.W., 1992. Ammonia volatilisation from grassland receiving nitrogen fertiliser and rotationally grazed by dairy cattle. *Fertiliser Research* 33, 257-265.

Bussink, D.W., Oenema, O., 1998. Ammonia volatilisation from dairy farming systems in temperate areas: a review. *Nutrient Cycling in Agroecosystems* 51, 19-33.

Cameron, K.C., Rate, A.W., Noonan, M.J., Moore, S., Smith, P., Kerr, L.E., 1996. Lysimeter study of the fate of nutrients following subsurface injection and surface application of dairy pond sludge to pasture. *Agriculture, Ecosystems and Environment* 58, 187-197.

Cameron, K.C., Di, H.J., Reijnen, B.P.A., Li, Z., Russell, J.M., Barnett, J.W., 2002. Fate of nitrogen in dairy factory effluent irrigated onto land. *New Zealand Journal of Agricultural Research* 45, 207-216.

Cameron, K.C., Di, H.J., 2004. Nitrogen leaching losses from different forms and rates of farm effluent applied to a Templeton soil in Canterbury, New Zealand. *New Zealand Journal of Agricultural Research* 475, 429-437.

Chadwick, D.R., 1997. Nitrous oxide and ammonia emissions from grassland following applications of slurry. Potential abatement practices. *In*: Jarvis, S. C., Pain, B. F. *ed*. Gaseous nitrogen emissions from grasslands. Wallingford, CAB International. Pp. 257-264.

Chadwick, D. R., 2005. Emissions of ammonia, nitrous oxide and methane from cattle manure heaps: Effect of compaction and covering. *Atmospheric Environment* 39, 787-799.

Chadwick, D.R., Ledgard, S.F., Brown, L., 2002. Nitrogen flows and losses in dairy farms in New Zealand and the UK: effects of grazing management. In: Currie, L.D., Loganathan, P. (Eds.), Dairy Farm Soil Management. Occasional Report. Fertiliser and Lime Research Centre, Massey University, Palmerston North, pp. 319-332.

Chadwick, D.R., Pain, B.F., Brookmann, S.K.E., 2000. Nitrous oxide and methane emissions following application of animal manures to grassland. *Journal of Environmental Quality* 29, 277-287.

Chadwick, D.R., Sneath, R.W., Phillips, V.R., Pain, B.F., 1999. A UK inventory of nitrous oxide emissions from farmed livestock. *Atmospheric Environment* 33, 3345-3354.

Chadwick, D.R., Webb, J., 2001. Will storing farmyard manure in compact heaps reduce emissions of ammonia and nitrous oxide during storage and spreading? Final report, project WA0707, DEFRA, UK.

Chambers, B.J., Smith, K.A., van der Weerden, T.J., 1997. Ammonia emissions following the land spreading of solid manures. In: Gaseous Nitrogen Emissions from Grasslands (Jarvis S C; Pain B F, eds), pp 275-280. CAB International, Wallingford, UK

Chambers, B.J., Williams, J.R., Cooke, S.D., Kay, R.M., Chadwick, D.R., Balsdon, S.L., 2003. Ammonia losses from contrasting cattle and pig manure management systems. In ‘‘Agriculture, Waste and the Environment’’ (I. McTaggart and L. Gairns, Eds.), pp. 19-25. SAC/SEPA Biennial conference III, Edinburgh, Scotland.

Chang, C., Cho, C.M., Janzen, H.H., 1998. Nitrous oxide emissions from long-term manured soils. *Soil Science Society of America Journal* 62, 677-682.

Chardon, W., Oenema, O., del Castilho, P., Vriesema, R., Japenga, J., Blaauw, D., 1997. Organic phosphorus in solutions and leachates from soils treated with animal slurries. *Journal of Environmental Quality* 26, 372-378.

Christensen, S., 1983. Nitrous oxide emissions from a soil under permanent grass: seasonal and diurnal fluctuations as influenced by manuring and fertilization. *Soil Biology and Biochemistry* 15, 531-536.

Christie, P., 1987. Some long-term effects of slurry on grassland. *Journal of Agricultural Science* 108, 529-541.

Clemens, J., Bergmann, S., and Vandre, R., 2002. Reduced ammonia emissions from slurry after self-acidification with organic supplements. *Environmental Technology* 23, 429-435.

Comfort, S.D., Kelling, K.A., Keeney D.R., Converse J.C., 1990. Nitrous-oxide production from injected liquid dairy manure. *Soil Science Society of America Journal* 54, 421-427.

Cooke, J.G., Tillman, R.W., Macgregor, A.N., Syers, J.K., 1979. Studies on the chemical and microbiological characteristics of soil-filtered dairy-shed effluent. *Progress in Water Technology* 11. 19-30.

Craggs, R.J., Sukias, J.P., Tanner, C.T., Davies-colley, R.J., 2004. Advanced pond system for dairy-farm effluent treatment. *New Zealand Journal of Agricultural Research* 47, 449-460.

Crawford, J.H., 1985. Composting of agricultural waste. In: Biotechnology, Applications and Research (Cheremisno! PN; Quelietee R P, eds), pp. 68-77. Technomic, Lancaster, PA.

Crutzen, P., 1976. The influence of nitrogen oxide on the atmospheric ozone content. *Quarterly Journal of the Royal Meteorological Society* 96, 320-325.

Degens, B.P., Schipper, L.A., Claydon, J.J., Russell, J.M., Yeates, G.W., 2000. Irrigation of an allophanic soil with dairy factory effluent for 22 years: responses of nutrient storage and soil biota. *Australian Journal of Soil Research* 38, 25-35.

de Klein, C.A.M., van Logtestijn, R.S.P., 1994. Denitrification and N_2O emission from urine-affected grassland soil. *Plant and Soil* 163, 235-242.

de Klein, C.A.M., Ledgard, S.F., 2001. An analysis of environmental and economic implications of nil- and restricted-grazing systems designed to reduce nitrate leaching from New Zealand dairy farms. I. Nitrogen losses. *New Zealand Journal of Agricultural Research* 44, 201-215.

de Klein, C.A.M., Clark, H., 2002. Potential mitigation options for reducing methane and nitrous oxide emissions from dairy farms. In: Currie, L.D., Loganathan, P. (Eds.), Dairy Farm Soil Management. Occasional Report Fertiliser and Lime Research Centre, Massey University, Palmerston North, pp. 233-246.

de Klein, C.A.M., Barton, L., Sherlock, R.R., Li, Z., Littlejohn, R.P., 2003. Estimating a nitrous oxide emission factor for animal urine from some New Zealand pastoral soils. *Australian Journal of Soil Research* 41, 381-399.

de Klein, C.A.M., Li, Z., Sherlock, R.R., 2004. Determination of the N_2O emission factor from animal excreta or urea fertiliser, following a winter application in two regions of New Zealand. Report to the Ministry of Agriculture & Forestry, Wellington, New Zealand, p. 31.

de Klein, C.A.M., Smith, L.C., Monaghan, R.M., 2006. Restricted autumn grazing to reduce nitrous oxide emissions from dairy pastures in Southland, New Zealand. *Agriculture, Ecosystems and Environment* 112,192-199.

de Klein, C.A.M., van Logtestijn, R.S.P., van de Meer, H.G., Geurink, J.H., 1996. Nitrogen loss due to denitrification from cattle slurry injected into grassland soil with and without nitrification inhibitor. *Plant and Soil* 183, 161-170.

Demmers, T.G.M., Burgess, L.R., Short, J.L., Phillips, V.R., Clark, J.A., Wathes, C.M., 1998. First experiences with methods to measure ammonia emissions from naturally ventilated buildings in the UK. *Atmospheric Environment* 32, 285-293.

Denmead, O.T., Simpson, J.R., Freney, J.R., 1974. Ammonia flux into the atmosphere from a grazed pasture. *Science* 185, 609-610.

Denmead, O.T., 1982. Micrometeorological methods for measuring gaseous losses of nitrogen in the field. In "Gaseous Loss of Nitrogen from Plant Soil Systems" (J. R. Freney and J. R. Simpson, Eds.), pp. 134-157.

Denmead, T., Chen, D., Turner, D., Li, Y., Edis, R.B., 2004. Micrometeorological measurements of ammonia emissions during phases of the grazing rotation of irrigated dairy pastures. Super Soil 2004: 3rd Australian New Zealand Soils Conference, 5 - 9 December 2004, University of Sydney, Australia.

Dewes, T., 1996. Effect of pH, temperature, amount of litter and storage density on ammonia emissions from stable manure. *Journal of Agricultural Science* 127, 501-509.

Di, H.J., Cameron, K.C., Moore, S., Smith, N.P., 1998. Nitrate leaching from dairy shed effluent and ammonium fertiliser applied to a free-draining pasture soil under spray or flood irrigation. *New Zealand Journal of Agricultural Research* 41, 263-270.

Di, H.J., Cameron, K.C., Silva, R.G., Russell, J.M., Barnett, J.W., 2002. A lysimeter study of the fate 15N-labelled nitrogen in cow urine with and without farm dairy effluent in a grazed dairy pasture soil under flood irrigation. *New Zealand Journal of Agricultural Research* 45, 235-244.

Eckard, R.J., Chen, D., White, R.E., Chapman, D.F., 2003. Gaseous nitrogen loss from perennial grass and clover dairy pastures in south-eastern Australia. *Australian Journal of Agricultural Research* 54, 561- 570.

Eghball, B., Power, J.F., Gilley, J.E., Doran, J.W., 1997. Nutrient, carbon and mass loss during composting of beef cattle feed lot manure. *Journal of Environmental Quality* 26, 189-193.

Ellis, S., Yamulki, S., Dixon, E., Harrison, R., Jarvis, S.C., 1998. Denitrification and N_2O emissions from a UK pasture soil following the early spring application of cattle slurry and mineral fertiliser. *Plant and Soil* 202, 15-25.

Falkiner, R.A., Smith, C.J., 1997. Changes in soil chemistry in effluent-irrigated *Pinus radiata* and *Eucalyptus grandis* plantations. *Australian Journal of Soil Research* 35, 131-147.

Fox, R.H., Piekielek, W.P., and Macneal, K.E., 1996. Estimating ammonia volatilisation losses from urea fertilisers using a simplified micrometeorological sampler. *Soil Science society of America Journal* 60, 596-601.

Franson, M.A.H., editor. 1998. Standard methods for the examination of water and waste water. 20th edition. American Public Health association, 1015 Fifteenth street NW, Washington, DC 20005. pp 417-418.

Fraser, P.M., Cameron, K.C., Sherlock, R.R., 1994. Lysimeter study of the fate of nitrogen in animal urine returns to irrigated pasture. *European Journal of Soil Science* 45, 439-447.

Freibauer, A., Kaltschmitt, M., 2001. Biogenic Greenhouse Gas Emissions from Agriculture in Europe. Forschungsbericht 78, University of Stuttgart, IER, 220 pp.

Gibson, C., 1995. Farm dairy effluent management. *New Zealand Dairy Exporter* 72, 22-24.

Goold, G.J., 1980. Rates of farm dairy effluent applied to pastures on clay soils in Northland. *New Zealand Journal of Experimental Agriculture* 8, 93-99.

Gordon, R., Patterson, G., Harz, T., Rodd, V., MacLeod, J., 2000. Soil aeration for dairy manure spreading on forage: effects on ammonia volatilisation and yield. *Canadian Journal of Soil Science* 80, 319-326.

Groenestein, C.M., van Faassen, H.G., 1996. Volatilisation of ammonia, nitrous oxide and nitric oxide in deep litter systems for fattening pigs. *Journal of Agricultural Engineering Research* 65, 269-274

Gronauer, A., Schon, H., Claassen, N., Boxberger, J., 1994. Ammonia volatilisation during slurry application. *Landtech*. 2, 70-71.

Groot Koerkamp, P.W.G., Metz, J.H.M., Uenk, G.H., Phillips, V.R., Holden, M.R., Sneath, R.W., Short, J.L., White, R.P., Hartung, J., Seedorf, J., Schro¨der, M., Linkert, K.H., 1998. Concentrations and emissions of ammonia in livestock buildings in Northern Europe. *Journal of Agricultural Engineering Research* 70, 79-95.

Hansen, M.N., Sommer, S.G., Madsen, N.P., 2003. Reduction of ammonia emission by shallow slurry injection: injection efficiency and additional energy demand, *Journal of Environmental Quality* 32, 1099-1104.

Harper, L.A., Catchpoole, V.R., Davis, R., Weir, K.L., 1983. Ammonia volatilisation: soil, plant and microclimate effects on diurnal and seasonal variations. *Agronomy Journal* 75, 212-218.

Harper, L.A., Sharpe, R.R., Parkin, T.B., Visscher, A.D., van Cleemput, O., Byers, F.M., 2004. Nitrogen cycling through swine production systems: ammonia, dinitrogen, and nitrous oxide emissions. *Journal of Environmental Quality* 33, 1189-1201.

Harrison, R., and Webb, J., 2001. A review of the effect of N fertiliser type on gaseous emissions. *Advances in Agronomy* 73, 65-108.

Hawke, R.M., Summers, S.A., 2003. Land application of farm dairy effluent: results from a case study, Wairarapa, New Zealand. *New Zealand Journal of Agricultural Research* 46, 339-346.

Haynes R.J., Williams P.H., 1993. Nutrient cycling and soil fertility in the grazed pasture ecosystem. *Advances in Agronomy* 49, 119-199.

Heatley, P., 1996. Dairying and the environment - managing farm dairy effluent. Operational design manual. Dairying and the environment committee of the New Zealand Dairy Board.

Hedley C.B., Saggar S., Tate K.R., 2006. Procedure for fast simultaneous analysis of the greenhouse gases: Methane, carbon dioxide, and nitrous oxide in air samples. *Communications in Soil Science and Plant Analysis*, 37, 1501-1510.

Hellmann, B., Zelles, L., PalojaK rvi, A., Bai, Q., 1997. Emission of climate-relevant trace gases and succession of microbial communities during open-windrow composting. *Applied Environmental Microbiology* 63, 1011-1018.

Henry, C., Sullivan, D., Rynk, R., Dorsey, K., Cogger, C., 1999. “Managing Nitrogen from Biosolids”.

Hensen, A., Groot, T.T., van den Bulk, W.C.M., Vermeulen, A.T., Olesen, J.E., Schelde, K., 2006. Dairy farm CH_4 and N_2O emissions from one square metre to the full farm scale. *Agriculture Ecosystems and Environment* 112, 146-152.

Hoff, J. D., Nelson, D. W., Sutton, A. L., 1981. Ammonia volatilisation from liquid swine manure applied to cropland. *Journal of Environmental Quality* 10, 90-94.

Holter, P., 1997. Methane emissions from Danish cattle dung pats in the field. *Soil Biology and Biochemistry* 29, 31-37.

Hornig, G., Turk, M., Wanka, U., 1999. Slurry covers to reduce ammonia emission and odour nuisance. *Journal of Agricultural Engineering Research* 73, 151-157.

Huijsmans, J.F.M., 1999. Slurry application. In: Steenvoorden, J.H.A.M. (Ed.), Monitoring of National Ammonia Emissions from Agriculture. Towards an improved Calculation Methodology. Chapter 4. Reeks Milieuplanbureau, vol. 6. DLO-Staring Centrum, Wageningen. In Dutch, 139 pp.

Huijsmans, J.F.M., Hol, J.M.G., Hendriks, M.M.W.B., 2001. Effect of application technique, manure characteristics, weather and field conditions on ammonia volatilisation from manure applied to grassland, *Netherlands Journal of Agricultural Science* 49, 323-342.

Huisintveld, J.W.H., Monteney, G.J., 2003. Methane emission from cubicle housing systems for dairy cows. Report 2003-01. IMAG, The Netherlands. Jungbluth, T., Hartung, E., Brose, G., 2001. Greenhouse gas emissions from animal houses and manure stores. *Nutrient Cycling in Agroecosystems* 60, 133-145.

Husted, S., Jensen, L.S., Jørgensen, S., 1991. Reducing NH_3 loss from cattle slurry by the use of acidifying additives: the role of the buffer system. *Journal of the Science of Food and Agriculture*57, 335-349.

Husted S., 1994. Seasonal variation in methane emission from stored slurry and solid manure. *Journal of Environmental Quality* 23, 585-592.

Jarvis, S.C., Hatch, D.J., Pain, B.F., Klarenbeek, J.V., 1994. Denitrification and the evolution of nitrous oxide after the application of cattle slurry to a peat soil. *Plant and Soil* 166, 231-241.

Jarvis, S.C., Hatch, D.J., Roberts, D.H., 1989. The effects of grassland management on nitrification losses from grazed swards through ammonia volatilisation: the relationship to excretal N returns from cattle. *Journal of Agricultural Sciences* 112, 205-216.

Jarvis, S.C., Pain, B.F., 1990. Ammonia volatilisation from agricultural land. *Proceedings of Fertilisers Society* 298, 3-33.

Jarvis, S.C., Pain, B.F., 1994. Greenhouse gas emissions from intensive livestock systems: their estimation and technologies for reduction. *Climate Change* 27, 27-38.

Jayaweera, G.R., Mikkelsen, D. S., 1991. Assesment of ammonia volatilisation from flooded soil systems. *Advances in Agronomy* 45, 303-357.

Jenkinson, D.S., Fox, R.H., Rayner, J.H., 1985. Interactions between fertiliser nitrogen and soil nitrogen-the-so-called ’priming’ effect. *Journal of soil Science* 36, 425-444.

Jeppson, K.G., 1999. Volatilisation of ammonia in deep litter systems with different bedding materials for young cattle. *Journal of Agricultural Engineering Research* 73, 49-57.

Jungbluth, T., Hartung, E., Brose, G., 2001. Greenhouse gas emissions from animal houses and manure stores. *Nutrient Cycling in Agroecosystems* 60, 133-145.

Kaparaju, P.L.N., Rintala, J.A., 2008. Effects of solid-liquid separation on recovering residual methane and nitrogen from digested dairy cow manure. *Bioresource Technology* 99, 120-127.

Karlsson, S., Jeppson, K. H., 1995. Deep Litter in Livestock Buildings and Field Storage. JTI Report 204, Swedish Institute of Agricultural Engineering, Ultuna Uppsala, Sweden.

Keck, M., 1997. Ammonia emission and odour thresholds of cattle houses with exercise yards. In ‘‘Ammonia and Odour Emissions from Animal

Production Facilities'' (J. Voermans and G. J. Monteny, Eds.), pp. 349-354. NVTL, Rosmalen, Vinkeloord, The Netherlands.

Khan, R.Z., 1999. Influence of soil water potentials, soil temperature and soil gas composition on the generation, absorption and transportation of soil gases. Unpublished PhD thesis, Lincoln University, Lincoln, New Zealand.

Kirchmann, H., 1985. Losses, plant uptake and utilisation of manure nitrogen during a production cycle. *Acta Agriculture Scandinavia*, 24 (Suppl.), 77 pp

Kirchmann, H., Witter, E., 1989. Ammonia volatilisation during aerobic and anaerobic manure decomposition. *Plant and Soil* 115, 35-41.

Kissel, D.E., Brewer, H.L., Arkin, G.F., 1977. Design and test of a field sampler for ammonia volatilisation. *Soil Science Society of America Journal* 41, 1133-1138.

Knight, R.L., Payne Jr, V.W.E., Borer, R.E., Clarke Jr, R.E., Pries, J.H., 2000. Constructed wetlands for livestock wastewater management. *Ecological Engineering* 15, 41-55.

Kroodsma, W., Huisintveld, J.W.H., Scholtens, R., 1993. Ammonia emission and its reduction from cubicle houses by flushing. *Livestock Production Science* 35, 293-302.

Kulling, D.R., Menzi, H., Sutter, F., Lisher, P., and Kreuzer, M., 2003. Ammonia, nitrous oxide and methane emissions from differently stored dairy manure derived from grass- and hay-based rations. *Nutrient Cycling in Agroecosystems* 65, 13-22.

Lammers, P.S., Romer, G., and Boeker, P., 1997. Amount and limitation of ammonia volatilisation from stored solid manure. In ``Ammonia and Odour Volatilisation From Animal Production Facilities'' (J.A.M. Voermans and G.J. Monteny, Eds.), pp. 43-48. NVTL, Rosmalen, The Netherlands.

Ledgard, S.F., Clark, D.A., Sprosen, M.S., Brier, G.J., Nemaia, E.K.K., 1996. Nitrogen losses from grazed dairy pasture, as affected by nitrogen fertiliser, *Proceedings of the New Zealand Grassland Association* 57, 21-25.

Ledgard, S.F., Penno, J.W., Sprosen, M.S., 1999. Nitrogen inputs and losses from clover/grass pastures grazed by dairy cows, as affected by nitrogen fertiliser application. *Journal of Agricultural Science* 132, 215-225.

Ledgard, S.F., Sprosen, M.S., Judge, A., Lindsey, S., Jensen, R., Clark, D., Luo, J., 2006. Nitrogen leaching as affected by dairy intensification and mitigation practices in the resource efficient dairying (RED) trial. In: Currie, L.D., Hanly, J.A. (Eds.), Implementing sustainable nutrient management strategies in agriculture. Occasional Report No. 19. Fertiliser and Lime Research Centre, Massey University, Palmerston North, New Zealand, pp. 263-268.

Lightner, J.W., Mengal, D.B., Rhykerd, C.L., 1990. Ammonia volatilisation from nitrogen fertiliser surface applied to orchard grass sod. *Soil Science Society of America Journal* 54, 1478-1482.

Lockyer, D.R., 1984. A system for the measurement in the field of losses of ammonium through volatilisation. *Journal of Science, Food and Agriculture* 35, 837-848.

Loehr, R., 1984. Pollution Control for Agriculture, pp 450-454. Academic Press, Orlando, FL, USA.

Longhurst, R.D., Lambourne, A., 2006. What options are there for wintering cows off pasture? *Proceedings of the 4th Dairy 3 Conference* 4, 3-9.

Longhurst, R.D., Luo, J., O’Connor, M.B., 2006. Herdhomes:Nutrient management and farmer perceptions of performance. *Proceedings of the New Zealand Grassland Association* 68, 309-313.

Longhurst, R.D., O’Connor, M.B., Roberts, A.H.C., Waller, J.E., 1999. Farm dairy effluent: findings of recent research studies in the Waikato. *In*: Currie, L.D., Loganathan P., Hedley, M.J., Horne, D.J. *ed*. Best soil management practices for production. Massey University, Palmerston North, Fertiliser and Lime Research Centre. *Occasional Report No. 12*, 273-282.

Longhurst, R.D., Roberts, A.H.C., O’Connor, M.B., 2000. Farm dairy effluent: Review of published data on physical and chemical characteristics. *New Zealand Journal of Agricultural Research* 43, 7-14.

Lovell, R.D., Jarvis, S.C., 1996. Effects of urine on soil microbial biomass, methanogenesis, nitrification and denitrification in grassland soils. *Plant and Soil* 186, 265-273.

Luo, J., Kulasegarampillai, M., Bolan, N., Donnison, A., 2004. Control of gaseous emissions of ammonia and hydrogen sulphide from cow manure by use of natural materials. *New Zealand Journal of Agricultural Research* 47, 545-556.

Luo, J., Ledgard, S.F., Lindsey, S.B., 2007a. Nitrous oxide emissions from application of urea on New Zealand pasture. *New Zealand Journal of Agricultural Research* 50, 1-11.

Luo, J, Lindsey, S., 2006. The use of pine bark and natural zeolite as biofilter media to remove animal process odours. *Bioresource technology* 97, 1461-1469.

Luo, J., Qiu, W., Longhurst, R.D., Ledgard, S.F., Bolan, N., Kear, M., 2007a. Use of stand-off pads and herd-homes for wintering cows. In: *Proceeding of the work shop" designing sustainable farms, critical aspects of soil and water management"* (in press).

Luo, J., Saggar, S., Bhandral, R., Bolan, N., Ledgard, S., Lindsey, S., Sun, W., 2008a. Effects of irrigation dairy-grazed grassland with farm dairy effluent on nitrous oxide emissions. *Plant Soil*, 309, 119-130.

Luo, j., Saggar, S., Bhandral, R., Lindsey, S., Bolan, N., Qiu, W., Kear, M., Sun, W., 2007b. Nitrous oxide emissions from a livestock stand-off pad and farm dairy effluent applied to pastoral soils. In: *Proceedings of the workshop" New Zealand land treatment collective"* (in press).

Luo, J., Tillman, R.W., Ball, P.R., 2000. Nitrogen loss through denitrification in a soil under pasture in New Zealand. *Soil Biology and Biochemistry* 32, 497-509.

Luo, J., Van Oostrom., 1999. Application of bio filter for odour control. In: manual of wastewater odour management, edited by NZWWA.pp.B1-B13.

Luostarinen, S.A., Rintala, J.A., 2005. Anaerobic on-site treatment of black water and dairy parlour wastewater in UASB-septic tanks at low temperatures. *Water Research* 39, 436-448.

Macgregor, A. N., Stout, J. D., Jackson, R. J., 1979. Quality of drainage water from pasture treated with dairy shed effluent. *Progress in Water Technology* 11, 11-17.

Magesan, G.N., Williamson, J.C., Sparling, G.P., Schipper, L.A., Lloyd-Jones, A.Rh., 1999. Hydraulic conductivity in soil irrigated with wastewaters of differing strengths: field and laboratory studies. *Australian Journal of Soil Research* 37, 391-402.

Mahimairaja, S., Bolan, N.S., Hedley, M.J., Mcgregor, A.N., 1994. Losses and transformation of nitrogen during composting of poultry manure with different amendments; an incubation experiment. *Bioresource technology* 47, 265-273.

Malgeryd, J., 1998. Technical measures to reduce ammonia losses after spreading of animal manure. *Nutrient Cycling in Agroecosystems* 51, 51-57.

Martins, O., Dewes, T., 1992. Loss of nitrogenous compounds during composting of animal wastes. *Bioresource Technology* 42, 103-111.

Mattila, P., Joki-Tokola, E., 2003. Effect of treatment and application technique of cattle slurry on its utilization by ley-I: slurry properties and ammonia volatilisation, *Nutrient Cycling in Agroecosystems* 65, 221-230.

McCrory, D. F., Hobbs, P.J., 2001. Additives to reduce ammonia and odor emissions from livestock wastes. *Journal of Environmental Quality* 30, 345-355.

Menzi, H., 2002. Manure management in Europe: Results of a recent survey. In ‘‘Proceedings of the 10th Conference of the FAO/ESCORENA Network on Recycling Agricultural, Municipal and Industrial Residues in Agriculture (RAMIRAN),’’ May 14-18, pp. 93-102.

Menzi, H., Katz, P., Frick, R., Fahrni, M., Keller, M., 1997. Ammonia emissions following the application of solid manure to grassland. In: Jarvis, S.C., Pain, B.F. (Eds.), Gaseous Nitrogen Emissions from Grasslands. CAB International, Wallingford, pp. 265-275.

Menzies, N.W., Skilton, J.A., Guppy, C.N., 1999. Phosphorus storage on effluent irrigated land. *Journal of Environmental Quality* 28, 750-754.

Michel Jr, F.C., Pecchia, J.A., Rigot, J., Keener, H.M., 2004. Mass and Nutrient Losses During the Composting Of Dairy Manure Amended with Sawdust or Straw. *Compost Science & Utilization* 12, 323-334

Ministry for the Environment, 2006. New Zealand's Greenhouse Gas Inventory 1990-2004. The National Inventory Report and Common Reporting Format, April 2006. Wellington, New Zealand. New Zealand Climate Change Office. Available online at:http;//www.climatechange.govt.nz

Ministry for the Environment, 2008. New Zealand's Greenhouse Gas Inventory 1990-2006. The National Inventory Report, Wellington, New Zealand. Also online:http://www.mfe.govt.nz/publications/climate/nz-greenhouse-gas inventory-apr08/.

Misselbrook, T.H., Brookman, S.K.E., Smith, K.A., Cumby, T., Williams, A.G., McCrory, D.F., 2005. Crusting of stored dairy slurry to abate ammonia emissions: Pilot-scale studies. *Journal of Environmental Quality* 34, 411-419.

Misselbrook, T.H., Pain, B.F., Headon, D.M., 1998. Estimates of ammonia emission from dairy cow collecting yards. *Journal of Agricultural Engineering Research* 71, 127-135.

Misselbrook, T.H., Powell, J.M., 2005a. Influence of bedding material on ammonia emissions from cattle excreta. *Journal of Dairy Science* 88, 4304-4312.

Misselbrook, T.H., Smith, K.A., Johnson, R.A., B.F. Pain, B.F., 2002. Slurry application techniques to reduce ammonia emissions: results of some UK field-scale experiments. *Biosystems Engineering* 81, 313-321.

Misselbrook, T.H., Van Der Weerden, T.J., Pain, B.F., Jarvis, S.C., Chambers, B.J., Smith, K.A., Phillips, V.R., Demmers, T.G.M., 2000. Ammonia emission factors for UK agriculture. *Atmospheric Environment* 34, 871-880.

Misselbrook, T.H., Webb, J., Chadwick, D.R., Ellis, S., Pain, B.F., 2001. Gaseous emissions from outdoor concrete yards used by livestock. *Atmospheric Environment* 35, 5331-5338.

Mkhabela, M.S., Madani, A., Gordon, R., Burton, D., Cudmore, A., Elmi, A., Hart, W., 2008. Gaseous and leaching nitrogen losses from no-tillage and conventional tillage systems following surface application of cattle manure. *Soil & Tillage Research*, 98, 187-199.

Mogge, B., Kaiser, E.A., Munch, J.C., 1999. Nitrous oxide emissions and denitrification N-losses from agricultural soils in the Bornhoved Lake region: influence of organic fertilisers and land-use. *Soil Biology and Biochemistry* 31, 1245-1252.

Moller, D., Schieferdecker, H., 1985. A relationship between agricultural ammonia emissions and atmospheric sulphur dioxide content over industrial areas. *Atmospheric Environment* 19, 695-700.

Monaghan, R., Paton, R., Smith, L., Drewry, J., Littlejohn, R., 2005. The impacts of nitrogen fertilisation and increased stocking rate on pasture yield, soil physical condition and nutrient losses in drainage from a cattle-grazed pasture. *New Zealand Journal of Agricultural Research* 48, 227-240.

Monteny, G.J., and Erisman, J.W., 1998. Ammonia emission from dairy cow buildings: A review of measurement techniques, influencing factors and possibilities for reduction. *Netherlands Journal of Agricultural Science* 46, 225-227.

Morken, J., 1992. Ammonia losses after application of slurry to grassland. The effect of application techniques and type of slurry. Norsk Landbruksforskning 6, 315-329 (Summary and legends are in English).

Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., van Cleemput, O., 1998. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient Cycling in Agroecosystems* 52, 225-248.

Mosquera, J., Hol, J.M.G., Monteny, G.J., 2006. Gaseous emissions from a deep litter farming system for dairy cattle. *International Congress Series* 1293, 291- 294.

Muirhead, R.W., Collins, R.P., Bremer, P.J., 2005. Erosion and subsequent transport state of *Escherichia coli* from cow pats. *Applied and Environmental Microbiology* 71, 2870-2875.

Newman, J.M., Clausen, J.C., Neafsey, J.A., 2000. Seasonal performance of a wetland constructed to process dairy milk house wastewater in Connecticut. *Ecological Engineering* 14, 181-198

Nihlgard, B., 1985. The ammonium hypothesis-an additional explanation to forest dieback in Europe. *Ambio* 14, 2-8.

Oenema, O., Bannink, A., Sommer, S.G., Velthof, G., 2001. Gaseous nitrogen emission from livestock farming system. In ‘‘Nitrogen in the Environment: Sources, Problems, and Management’’ (R. F. Follet and B. V. Hatfield, Eds.), pp. 255-289. Elsevier Science, Amsterdam.

Ogink, N.W.M., and Kroodsma, W., 1996. Reduction of ammonia emission from a cow cubicle house by flushing with water or a formalin solution. *Journal of Agricultural Engineering Research* 63, 197-204.

Oosthoek, J., Kroodsma, W., and Hoeksma, P., 1991. Ammonia emission from dairy and pig housing systems. In ‘‘Odour and Ammonia Emissions from Livestock Farming’’ (V. C. Nielsen, J. H. Voorburg, and P. L’Hermite´, Eds.), pp. 31-41. Elsevier Applied Science, London.

Osada, T., Sommer, S.G., Dahl, P., Rom, H.B., 2001. Gaseous emission and changes in nutrient composition during deep litter composting. *Soil and Plant Science* 51, 137-142.

O'Toole, S.E., 1996. Assessing farm dairy effluent application on a number of Waikato dairy farms. Unpublished BSc (Technology) Industry report, The University of Waikato, Hamilton, New Zealand.

Pain, B.F., Phillips, V.R., Clarkson, C.R., Karenbeck, J.V., 1989. Loss of nitrogen through ammonia volatilisation during and following the application of pig or cattle slurry to grassland. *Journal of Science Food and Agriculture* 47, 1-12.

Pain, B.F., Phillips, V.R., Clarkson, C.R., Misselbrook, T.H., Ress, Y.J., Farrent, J.W., 1990. Odour and ammonia emissions following the spreading of aerobically-treated pig slurry on grassland. *Biological wastes*34:149-160.

Pain, B.F., Weerden van der, T.J., Chambers, B.J., Phillips, V.R., Jarvis, S.C., 1998. A new inventory for ammonia emissions from UK agriculture. *Atmospheric Environment* 32, 309-313

Paul, J.W., Beauchamp, E.G., Zhang, X., 1993. Nitrous and nitric-oxide emissions during nitrification and denitrification from manure-amended soil in the laboratory. *Canadian Journal of Soil Science* 73, 539-553.

Paul, J.W., Zebarth, B.J., 1997. Denitrification during the growing season following dairy cattle slurry and fertiliser application for silage corn. *Canadian Journal of Soil Science* 77, 231-240.

Peacock, A.D., M.D. Mullen, D.B. Ringelberg, D.D. Tyler, D.B. Hedrick, P.M. Gale, D.C.W., 2001. Soil microbial responses to dairy manure or ammonium nitrate applications. *Soil Biology and Biochemistry* 33, 1011-1019.

Petersen, S., 1999. Nitrous oxide emissions from manure and inorganic fertilisers applied to spring barley. *Journal of Environmental Quality* 28, 1610-1618.

Petersen, S.O., Lind, A.M., Sommer, S.G., 1998. Nitrogen and organic matter losses during storage of cattle and pig manure. *Journal of Agricultural Science* 130, 69-79.

Phillips, V.R., Bishop, S.J., Price, J.S., and You, S., 1998. Summer emissions of ammonia from a slurry-based, UK, dairy cow house. *Bioresource Technology* 65, 213-219.

Pidwirny, M., 2006. "The Nitrogen Cycle". *Fundamentals of Physical Geography, 2nd Edition*. Date Viewed. http://www.physicalgeography.net/fundamentals/9s.html

Poincelot, R.P., 1974. A scientific examination of the principles and practice of composting. *Compost Science* 3, 24-31.

Portejoie, S., Martinez, J., Guiziou, F., and Coste, C.M., 2003. Effect of covering pig slurry stores on the ammonia emission processes. *Bioresource Technology* 87, 199-207.

Poth, M., Focht, D.D., 1985. 15N kinetic analysis of N_2O production by *Nitrosomonas europeae*: an examination of nitrifier denitrification. *Applied Environmental Microbiology* 49, 1134-1141.

Poulsen, H.D., Børsting, C.F., Rom, H.B., and Sommer, S.G., 2001. Nitrogen, Phosphorus and Potassium in Animal Manure: Norm Values 2000. DIAS Report: Animal Manure No. 36. Ministry of Food, Agriculture and Fisheries, Danish Institute of Agricultural Sciences, Tjele, Denmark [in Danish].

Prasertsak, P., Freney, J.R., Denmead, O.T., Saffigna, P.G., and Prove, B.G., 2001. Significance of gaseous nitrogen loss from a tropical dairy pasture fertilised with urea. *Australian Journal of Experimental Agriculture* 41, 625-632.

Qiu, W., 2007. Transformation and loss of excretal nitrogen under winter management systems. M.Sc. Thesis. Massey University, New Zealand.

Qiu, W., Luo, J., Longhurst, B., Bolan, N., Sun, W., 2007. Control of nitrogen losses from a dairy wintering system. New Zealand Land Treatment Collective: Proceedings for the 2007 annual conference.

Redding, M.R., 2001. Pig effluent-P application can increase the risk of P transport: two case studies. *Australian Journal of Soil Research* 39, 161-174.

Rico, J.L., Garcia, H., Rico, C., 2007. Characterisation of solid and liquid fractions of dairy manure with regard to their component distribution and methane production. *Bioresource Technology* 98, 971-979.

Roach, C.G., Longhurst, R.D., O'Connor, M.B., 2001. Land application of farm dairy effluent for sustainable dairy farming. *Proceedings of the New Zealand Grassland Association* 63, 53-57.

Robertson, G.P., Tiedje, J.M., 1987. Nitrous oxide sources in aerobic soils; nitrifi cation, denitrification and other biological processes. *Soil Biology and Biochemistry 19,* 187-193.

Rodhe, L., Johansson, S., 1996. Ammonia emission and nutrient utilization from urine using different techniques for application. JTI-rapport, Landbruk & Industri Nr. 217. Jordbrukstekniska institutet, S-Uppsala, pp.107.

Rodhe, L., Pell, M., Yamulki, S., 2006. Nitrous oxide, methane and ammonia emissions following slurry spreading on grassland. *Soil Use and Management* 22, 229-237.

Rodhe, L., Rammer, C., 2002. A comparison of methods for applying cattle slurry to ley. *Biosystems Engineering* 83, 107-118.

Roelofs, J.G.M., 1986. The effect of air-borne sulphur and nitrogen deposition on aquatic and terrestrial heathland vegetation. *Experimentia* 42, 372-377.

Rom, H. B., and Henriksen, K., 2000. Nitrogen loss from cattle housed on deep litter. In ‘‘Husdyrgødning og kompost [Animal Manure and Compost]’’ (S. G. Sommer and J. Eriksen, Eds.), pp. 5-13.

Rotz, C.A., 2004. Management to reduce nitrogen losses in animal production. *Journal of Animal Science* 82(E. Suppl.), E119-E137.

Rotz, C.A., Oenema, J., 2006. Predicting management effects on ammonia emissions from dairy and beef farms. *Transactions of the ASABE* 49, 1139-1149.

Rumburg, B., Mount, G.H., Yonge, D., Lamb, B., Westberg, H., Filipy, J., Bays, J., Kincaid, R., Johnson, K., 2006. Atmospheric flux of ammonia from sprinkler application of dairy waste. *Atmospheric Environment* 40, 7246-7258

Ryden, J.C., Whitehead, D.C., Lockyer, D.R., Thompson, R.B., Skinner, J.H., Garwood, E.A., 1987. Ammonia emission from grassland and livestock production systems in the UK. *Environmental Pollution* 48, 173-184.

Saggar, S., Andrew, R.M., Tate, K.R., Hedley, C.B., Rodda, N.J., 2004a. Modelling nitrous oxide emissions from New Zealand dairy grazed pastures. *Nutrient Cycling in Agroecosystems* 68, 243-255.

Saggar, S., Bhandral, R., Bolan, N.S., Hedley, C.B., Luo, J., 2004b. A review of emissions of methane, ammonia and nitrous oxide from animal excreta deposition and farm effluent application in grazed pastures. *New Zealand Journal of Agricultural research* 47:513-544.

Saggar, S., Bhandral, R., Bolan, N.S., Luo, J., 2004c. Nitrous oxide emissions from farm effluents. Abstract accepted for oral presentation at the 3rd International Nitrogen Conference, Nanjing, China, 12-16 October 2004.

Saggar, S., Giltrap, D.L., Li, C., Tate, K.R., 2007a. Modelling nitrous oxide emissions from grazed grasslands in New Zealand. *Agriculture, Ecosystems and Environment* 119, 205-216.

Saggar, S., Hedley, C.B., Giltrap, D.L., Lambie, S.J., 2007b. Measured and modeled estimates of nitrous oxide emission and methane consumption from sheep-grazed pasture. *Agriculture, Ecosystems and Environment* 122, 357-365.

Saggar, S., Hedley, C.B., Tate, K., 2003. Methane sources and sinks in New Zealand grazed pastures. *New Zealand Soil News* 51, 6-7.

Schaffman, S.S., Walker, J.M., Dalton, P., Lorig, T.S., Raymer, J.H., Shusterman, D., Williams, C.M., 2000. Potential health effects of odor from animal operations, wastewater treatment, and recycling of byproducts. *Journal of Agromedicine* 7, 7-81.

Schipper, L.A., Williamson, J.C., Kettles, H.A., Speir, T.W., 1996. Impact of land-applied tertiary-treated effluent on soil biochemical properties. *Journal of Environmental Quality* 25, 1073-1077.

Schjoerring, J.K., Sommer, S.G., and Ferm, M., 1992. A simple passive sampler for measuring ammonia emmision in the field. *Water Air Soil Pollution* 62, 13-42.

Selvarajah, N., Sherlock, R.R., Smith, N.P., Cameron, K.C., 1989. In "*Proceedings of the work shop on nitrogen in New Zealand Agriculture and Horticulture*" (L.D.Currie and P.Loganathan, Eds.), Pp. 145-156. Massey University, Palmerston North.

Selvarajah, N., 1995. Current research related to dairy farm effluent management in New Zealand. *New Zealand Soil News* 43, 110-118.

Selvarajah, N., 1996. Dairy farm effluent treatment pond performance in the Waikato region: a preliminary review of the regional survey. *In:* Mason, I. G. *ed.* Tertiary treatment options for dairy shed and piggery wastewaters. *Proceedings of a Seminar, Massey University*, 28 June. Pp. 18-25.

Sharpe, R.R., Harper, L.A., 1997. Ammonia and nitrous oxide emissions from sprinkler irrigation applications of swine effluent. *Journal of Environmental Quality* 26, 1703-1706.

Sharpley, A.N., 1995. Identifying sites vulnerable to phosphorus loss in agricultural runoff. *Journal of Environmental Quality* 24, 947-951.

Sherlock, R.R., de Klein, C.A.M., Li, Z., 2003. Determination of N_2O and CH_4 emission factors from animal excreta, following a summer application in 3 regions of New Zealand. A final report of an N_2O net study prepared for Ministry of Agriculture and Forestry. 27 p.

Sherlock, R.R., Freney, J.R., Bacon, P.E., van der Weer, T.J., 1995. Estimating ammonia volatilisation from unsaturated urea fertilised and urine affected soils by an indirect method. *Fertiliser Research* 40, 197-205.

Sherlock, R.R., Freney, J.R., Smith, N.P., Cameron, K.C., 1989. Evaluation of a sampler for assessing ammonia losses from fertilised fields. *Fertiliser Research* 21, 61-66.

Sherlock, R.R., Goh, K.M., 1984. Dynamics of ammonia volatilisation from simulated urine patches and aqueous urea applied to pasture I. Field experiments. *Fertiliser Research* 5, 181-197.

Silva, R.G., Cameron, K.C., Di, H.J., Hendry, T., 1999. A lysimeter study of the impact of cow urine, dairy shed effluent, and nitrogen fertiliser on nitrate leaching. *Australian Journal of Soil Research* 37, 357-369.

Singh, J., 2007. The role of inhibitors in mitigating nitrogen losses from cattle urine and nitrogen fertiliser inputs in pastures. Ph.D. Thesis. Massey University, New Zealand.

Singleton, P.L., McLay, C.D.A., Garkle, G.F., 2001. Nitrogen leaching from soil lysimeters irrigated with dairy shed effluent and having managed drainage. *Australian Journal of Soil Research* 39, 385-396.

Singleton, P.L., Boyes, M., Addison, B., 2000. Effect of treading by dairy cattle on topsoil physical conditions for six contrasting soil types in Waikato and Northland, New Zealnd, with implications of monitoring. *New Zealand journal of Agricultural research* 43, 559-567.

Skiba, U., DiMarco, C., Hargreaves, K., Sneath, R., McCartney, L., 2006. Nitrous oxide emissions from a dung heap measured by chambers and plume methods. *Agriculture, Ecosystems and Environment* 112, 135-139.

Smith, K.A., Brewer, A.J., Crabb, J., Dauven, A., 2001. A survey of the production and use of animal manures in England and Wales. II. Poultry manure. *Soil Use Manage* 17, 48-56.

Smith, K.A., Jackson, D.R., Misselbrook, T.H., Pain, B.F., Johnson, R.A., 2000. Reduction of ammonia emission by slurry application techniques. *Journal of Agricultural Engineering Research* 77, 277-287.

Sneath, R.W., Beline, F., Hilhorst, M.A., 2006. Monitoring GHG from manure stores on organic and conventional dairy farms. *Agriculture, Ecosystems and Environment* 112, 122-128.

Sommer, S.G., 1997. Ammonia volatilisation from farm tanks containing anaerobically digested animal slurry. *Atmospheric Environment* 31, 863-868.

Sommer, S.G., 2001. Effect of composting on nutrient loss and nitrogen availability of cattle deep litter. *European Journal of Agronomy* 14, 123-133.

Sommer, S.G., Christensen, B.T., 1990. NH_3 emission from solid manure and raw, fermented and separated slurry after surface application, injection, incorporation into the soil and irrigation. Tidsskr. Planteavl. 94, 407-417 (Summary and legends are in English).

Sommer, S.G., Christensen, B.T., Nielsen, N.E., Schjørring, J.K., 1993. Ammonia volatilisation during storage of cattle and pig slurry: Effect of surface cover. *Journal of Agricultural Science* 121, 63-71.

Sommer, S.G., Dahl, P., 1999. Emission of ammonia, nitrous oxide, methane and carbon dioxide during composting of deep litter. *Journal of Agricultural Engineering Research* 74, 145-153.

Sommer, S.G., Hutchings, N.J., 2001. Ammonia emission from field applied manure and its reduction. *European Journal of Agronomy* 15, 1-15.

Sommer, S.G., Jensen, C., 1994. Ammonia volatilisation from urea and ammoniac fertilisers surface applied to winter wheat and grassland. *Fertiliser Research* 37, 85-92.

Sommer, S.G., Olesen, J.E., Christensen, B.T., 1991. Effects of temperature, wind speed and air humidity on ammonia volatilisation from surface applied cattle slurry. *Journal of Agricultural Science* 117, 91-100.

Sommer, S.G., Petersen, S.O., Moller, H.B., 2004. Algorithms for calculating methane and nitrous oxide emissions from manure management. *Nutrient Cycling in Agroecosystems* 69, 143-154

Sørensen, P., Amato, M., 2002. Remineralisation and residual effects of N after application of pig slurry to soil. *European Journal of Agronomy* 16, 81-95.

Sparling, G.P., Schipper, L.A., Russell, J.M., 2001. Changes in soil properties after application of dairy factory effluent to New Zealand volcanic ash and pumice soils. *Australian Journal of soil Research* 39, 505-518.

Statistics New Zealand, 2010. Agricultural Production Statistics: June 2009 (final). Date viewed. http://www.stats.govt.nz/browse_for_stats/industry_sectors/agriculture-horticulture-forestry/AgriculturalProduction_HOTPJun09final.aspx

Steed, J., Hashimoto, A.G., 1994. Methane emissions from typical manure management systems. *Bioresource Technology* 50, 123-130.

Sweeten, J.M., Wolfe, M.L., 1990. Runoff and wastewater management systems for open lot dairies. 1990. In: Agricultural and Food Processing Waste. Proceedings of the 6th International Symposium on Agricultural and Food Processing Wastes, pp 361-375. ASAE, St. Joseph, MIC, USA

Swierstra, D., Braam, C.R., 1999. Grooved floor system for cattle housing: Ammonia emission reduction and good slip resistance, Paper No. 994012, ASAE meeting presentation. p. 8.

Swierstra, D., Smits, M.C.J., og Kroodsma, W., 1995. Ammonia emission from cubicle houses for cattle with slatted and solid floors. *Journal of Agricultural Engineering Research* 62, 127-132.

Takashi, O., Sommer, S.G., Dahl, P., Rom, H.B., 2001. Gaseous emission and changes in nutrient composition during deep litter composting. *Acta Agriculture* Scandinavica. Section B 51, 137-143.

Tanner, C.C., Clayton, J.S., Upsdell, M.P., 1995. Effect of loading rate and planting on treatment of dairy farm wastewaters in constructed wetlands-II. Removal of nitrogen and phosphorus. *Water Research* 29, 27-34

Thompson, R. B., 1989. Denitrification in slurry-treated soil: occurrence at low-temperatures, relationship with soil nitrate and reduction by nitrification inhibitors. *Soil Biology and Biochemistry 21*, 875-882.

Thompson, R.B., Pain, B.F., Rees, Y.J., 1990. Ammonia volatilisation from cattle slurry following surface application to grassland. *Plant and Soil* 125, 119-128.

Thompson, R.B., Pain, B.F., 1991. Denitrification from cattle slurry applied to grassland. *In*: Hansen, J. A.; Henriksen, K. *ed*. Nitrogen in organic wastes applied to soils. London, Academic Press. Pp. 247-260.

Thompson, R.B., Ryden, J.C., Lockyer, D.R., 1987. Fate of nitrogen in cattle slurry following surface application or injection to grassland. *Journal of Soil Science* 38, 689-700.

Tiedje, J.M., 1982. Denitrification. *In Methods of Soil Analysis, part 2. Second edition*, pp. 1011-1026. American Society of Agronomy, Madison, Wisconsin.

Tiedje, J.M., Sexstone, A.J., Parkin, T.B., Revsbech, N.P., Shelton, D.R., 1984. Anaerobic processes in soil. *Plant and Soil* 76, 197-212.

Toor, G., Condron, L., Di, H., Cameron, K., Sims, J., 2004. Impact of farm-dairy effluent application on the amounts and forms of phosphorus by leaching from irrigated agriculture. *New Zealand Journal of Agricultural Research* 47, 479-490.

Trolove, M., 1997. Dairy effluent application to pastoral soils. Unpublished BSc (Technology) report. The University of Waikato, Hamilton, New Zealand.

Vallis, I., Peake, D.C.I., Jones, R.K., McCown, R.L., 1985. Fate of urea-nitrogen from cattle urine in a pasture crop sequence in a seasonally dry tropical environment. *Australian Journal of Agricultural Research* 36, 809-817.

van Amstel, A., Kroeze, C., van Eerdt, M., Dumont, M., Both, D., 2003. National emissions of methane and nitrous oxide from agriculture in The Netherlands: current estimates and future trends, Workshop on Inventories and projections of greenhouse gas and ammonia emissions from agriculture, 27-28 February 2003, European Environmental Agency, Copenhagen.

van der Hoek, K.W., 1993. Low emission housing systems, criteria for” green label” (Groen label,). Commissie groen label.Den Haag(in Dutch)

Van der Stelt, B., Temminghoff, E.J.M., Van Vliet, P.C.J., Van Riemsdijk, W.H., 2007. Volatilisation of ammonia from manure as affected by manure additives, temperature and mixing. *Bioresource Technology* 98, 3449-3455.

Van’t Ooster, A., 1994. Using natural ventilation theory and dynamic heat balance modelling for real time prediction of ventilation rates in naturally ventilated livestock houses. In report N.94-C-026, XII World Congress on Agricultural Engineering. Milan, Italy 1994, pp. 1-12 CIGR, Merelbeke.

Velthof, G.L., Kuikman, P.J., Oenema, O., 2003. Nitrous oxide emissions from animal manures applied to soil under controlled conditions. *Biology and Fertility of Soils* 37, 221-230.

Velthof, G.F., Oenema, O., Postma, R., van Beusichem, M.L., 1996. Effects of type and amount of applied nitrogen fertiliser on nitrous oxide fluxes from intensively managed grassland. *Nutrient Cycling in Agroecosystems 46*, 257-267.

Verboon, M.C., Mandersloot, F., Gunnink, H., 2000. Straw crusts in slurry stores. The potential for using a straw crust as a slurry cover, Translation- Silsoe research Institute. Silsoe Research Institute Silsoe UK 2000. 63 (New series) 25.11 ref.

Wang, H., Magesan, G., Bolan, N., 2004. Overview of the environmental effects of land application of farm effluents. *New Zealand Journal of Agricultural Research* 47, 389-403.

Warburton, D.J., 1977. Studies in anaerobic/aerobic treatment of dairy shed effluent. Unpublished PhD thesis, Massey University, Palmerston North, New Zealand.

Watanabe, T., Osada, T., Yoh, M., Tsuruta, H., 1997. N_2O and NO emissions from grassland soils after the application of cattle and swine excreta. *Nutrient Cycling in Agroecosystems* 49, 35-39.

Webb, J., Misselbrook, T.H., 2004. A mass-flow model ofammonia emissions from UK livestock production. *Atmospheric Environment* 38, 2163-2176.

Webb, J., Pain B., Bittman, S., Morgan, J., 2010. The impact of manure application methods on emissions of ammonia, nitrous oxide and on crop response. *Agriculture, Ecosystems & Environment* 137, 39-46.

Weerden van der, T.J., Moal, J.F., Martinez, J., Pain, B.F., and Guiziou, F., 1996. Evaluation of the wind-tunnel method for measurement of ammonia volatilisation from land. *Journal of Agricultural Engineering and Research* 64, 11-14.

Weiske, A., Vabitsch, A., Olesen, J.E., Schelde, K., Michel, J., Friedrich, R., Kaltschmitt, M., 2006. Mitigation of greenhouse gas emissions in European conventional and organic dairy farming. *Agriculture, Ecosystems & Environment* 112, 221-232.

Whitehead, D.C., Raistrick, N., 1990. Ammonia volatilisation from five nitrogen compounds used as fertilisers following surface application to soils. *Journal of Soil Science* 41, 387-394.

Whitehead, D., Walcroft, A., Saggar, S., Parker, W., 2009. A dairy farm is not greenhouse gas neutral. Landcare Research, Article prepared for DairyNZ. http://www.carbonzero.co.nz/publications/dairyNZ_mar09.pdf

Wilson, J.D., Catchpoole, V.R., Denmead, O.T., Thurtell, G.W., 1983. Verification of a simple micrometeorological method for estimating the rate of gaseous mass transfer from the ground to the atmosphere. *Agricultural meteorology* 29, 183-189.

Wood, C.W., Marshall, S.B., Cabrera, M. L., 2000. Improved method for field-scale measurement of ammonia volatilisation. *Soil Science Plant Analysis* 31, 581-590.

Wright, P.E., Graves, R.R., 1990. Guideline for milking center wastewater. Northeast Regional Agricultural Engineering Service, Cooperative Extension. Ithaca, NY, USA

Xue, S.K., Chen, S., Hermanson, R.E., 1999. Wheat straw cover for reducing ammonia and hydrogen sulfide emissions from dairy manure storage. *Transactions of ASAE* 42, 1095-1101.

Yamulki, S., Jarvis, S.C., 2002. Short-term effects of tillage and compaction on nitrous oxide, nitric oxide, nitrogen dioxide, methane and carbon dioxide fluxes from grassland. *Biology and Fertility of Soils* 36, 224-231.

Yamulki, S., Jarvis, S.C., Owen, P., 1998. Nitrous oxide emissions from excreta applied in a simulated grazing pattern. *Soil Biology and Biochemistry* 30, 491-500.

Zaman, M., Saggar, S., Blennerhassett, J.D., Singh, J., 2009. Effect of urease and nitrification inhibitors on N transformation, gaseous emissions of ammonia and nitrous oxide, pasture yield and N uptake in grazed pasture system. *Soil Biology & Biochemistry* 41, 1270-1280.

Zhang, G., Strom, J.S., Li, B., Rom, H.B., Morsing, S., Dahl, P., Wang, C., 2005. Emission of ammonia and other contaminant gases from naturally ventilated dairy cattle buildings. *Biosystems Engineering* 92, 355-364.

Zhu, T., Pattey, E., Desjardins, R.L., 2000. Relaxed eddy-accumulation technique for measuring ammonia volatilisation. *Environmental Science and Technology* 34, 199-203.

Appendices

Appendix 1

A. Ammonia emissions from urine with different flow rates (g l^{-1})

Treatments	2hr	4hr	6hr	8hr	24hr	Total
T1	0.08	0.15	0.22	0.24	0.91	1.60
T2	0.18	0.18	0.27	0.32	0.95	1.91
T3	0.29	0.38	0.59	0.49	1.80	3.55
T4	0.33	0.41	0.51	0.51	2.47	4.23
T5	0.38	0.51	0.49	0.52	2.18	4.09
T6	0.58	0.61	0.66	0.57	2.95	5.38
T7	0.55	0.61	0.74	0.54	3.01	5.45
T8	0.61	0.59	0.69	0.62	2.81	5.33
T9	0.58	0.61	0.74	0.73	3.47	6.13

B. Percentage of ammonia emissions from urine with varying flow rates

Treatments	2hr	4hr	6hr	8hr	24hr	Total
T1	1.18	2.10	3.06	3.32	12.79	22.45
T2	2.52	2.57	3.85	4.43	13.39	26.76
T3	4.14	5.29	8.24	6.93	25.29	49.90
T4	4.57	5.79	7.12	7.16	34.72	59.35
T5	5.34	7.23	6.93	7.26	30.66	57.41
T6	8.13	8.55	9.32	8.07	41.45	75.52
T7	7.75	8.61	10.33	7.54	42.34	76.57
T8	8.51	8.33	9.72	8.76	39.50	74.83
T9	8.17	8.55	10.38	10.27	48.75	86.12

Appendix 2

A. NH_3 emissions (ppm) from urea applied to soil with varying flow rates

Treatments	24 hrs	36 hrs	48 hrs	60 hrs	72 hrs	96 hrs	120 hrs
T1	0.519	0.410	1.630	5.366	14.561	1.411	0.591
T2	0.673	1.228	2.356	3.940	14.431	2.347	0.789
T3	0.941	2.542	4.364	7.743	13.390	2.633	1.145
T4	1.279	3.787	4.772	6.911	12.218	5.633	1.422
T5	1.180	4.500	9.009	9.653	17.361	4.800	1.951
T6	3.413	5.835	9.184	4.944	16.986	4.011	1.699
T7	3.314	4.671	9.097	4.535	17.311	5.904	1.468
T8	2.586	6.542	12.232	4.839	15.584	4.586	1.726
T1	2.138	3.718	5.924	3.915	5.270	1.128	0.439
T2	2.324	4.776	6.136	5.218	9.250	2.514	0.932
T3	2.028	4.169	5.881	5.215	12.028	3.151	1.169
T4	1.406	5.057	4.901	7.903	16.102	4.155	1.927
T5	1.542	9.186	10.701	12.500	21.102	4.305	2.589
T6	1.851	6.163	10.986	13.908	21.585	5.950	2.141
T7	2.393	7.838	10.023	14.250	21.353	4.262	2.085
T8	3.824	5.947	8.512	14.460	20.238	6.252	1.815
T1	0.976	4.304	4.760	5.335	5.049	2.053	1.251
T2	2.311	5.904	7.937	5.928	8.154	3.355	1.297
T3	1.631	5.755	5.889	7.419	7.232	4.451	2.269
T4	1.675	4.456	2.972	10.799	14.993	5.260	3.647
T5	1.647	4.028	3.331	15.357	20.338	8.985	4.298
T6	1.210	5.663	8.482	18.174	21.338	5.688	2.982
T7	2.913	6.682	9.222	16.071	16.117	4.783	4.227
T8	1.759	6.157	6.808	17.276	18.990	4.989	4.256

B. NH_3 emissions (%) from urea applied to soil with varying flow rates

Treatments	24 hrs	36 hrs	48 hrs	60 hrs	72 hrs	96 hrs	120 hrs	Total	Net
T1	0.041	0.163	0.537	1.456	0.141	0.059	0.354	8.103	
T2	0.123	0.236	0.394	1.443	0.235	0.079	0.473	8.872	
T3	0.254	0.436	0.774	1.339	0.263	0.114	0.687	11.243	
T4	0.379	0.477	0.691	1.222	0.563	0.142	0.853	13.307	
T5	0.450	0.901	0.965	1.736	0.480	0.195	1.171	16.916	
T6	0.584	0.918	0.494	1.699	0.401	0.170	1.019	16.559	
T7	0.467	0.910	0.453	1.731	0.590	0.147	0.881	17.095	
T8	0.654	1.223	0.484	1.558	0.459	0.173	1.035	17.098	
T1	0.372	0.592	0.391	0.527	0.113	0.044	0.264	7.871	
T2	0.478	0.614	0.522	0.925	0.251	0.093	0.559	11.076	8.125
T3	0.417	0.588	0.522	1.203	0.315	0.117	0.701	11.996	10.834
T4	0.506	0.490	0.790	1.610	0.416	0.193	1.156	14.682	12.046
T5	0.919	1.070	1.250	2.110	0.431	0.259	1.554	21.109	14.768
T6	0.616	1.099	1.391	2.158	0.595	0.214	1.285	21.758	19.966
T7	0.784	1.002	1.425	2.135	0.426	0.209	1.251	21.283	20.114
T8	0.595	0.851	1.446	2.024	0.625	0.181	1.089	21.882	19.987
T1	0.430	0.476	0.534	0.505	0.205	0.125	0.751	8.402	20.117
T2	0.590	0.794	0.593	0.815	0.336	0.130	0.778	12.555	
T3	0.575	0.589	0.742	0.723	0.445	0.227	1.362	12.899	
T4	0.446	0.297	1.080	1.499	0.526	0.365	2.188	16.315	
T5	0.403	0.333	1.536	2.034	0.898	0.430	2.579	21.874	
T6	0.566	0.848	1.817	2.134	0.569	0.298	1.789	22.025	
T7	0.668	0.922	1.607	1.612	0.478	0.423	2.536	21.582	
T8	0.616	0.681	1.728	1.899	0.499	0.426	2.554	21.372	

Appendix2: A. Ammonia emissions (ppm) from urea applied to soil with varying flow rates

B. Ammonia emissions (%) from urea applied to soil with varying flow rates

Appendix 3

A. Ammonia concentration (ppm) from different manure treatments applied to soil

Treatments	2nd day	4th day	7th day	9th day	11th day	15th day	18th day	21st day
T1	123.84	39.63	25.76	12.05	2.74	6.51	0.31	2.19
T1	125.72	29.16	17.96	8.45	4.17	2.36	1.60	2.91
T1	156.83	31.85	11.46	17.30	11.17	4.38	2.72	1.50
T2	9.40	7.47	5.37	4.03	1.63	1.56	1.94	0.29
T2	19.27	10.06	10.70	2.77	0.96	1.45	1.17	0.30
T2	11.77	7.16	5.96	2.50	2.81	1.78	1.02	0.00
T3	76.26	57.32	9.09	6.31	0.76	2.02	4.19	1.68
T3	118.54	52.16	8.21	6.25	4.94	6.87	5.95	0.62
T3	87.13	32.89	11.11	7.36	12.94	14.43	4.96	2.12
T4	0.89	1.24	2.84	1.91	0.75	0.87	0.45	0.07
T4	0.90	1.39	0.57	0.75	1.03	0.13	0.47	0.16
T4	1.36	2.09	0.23	0.46	0.79	0.53	0.65	0.38
T5	18.67	10.79	8.85	0.84	1.90	1.68	2.05	1.25
T5	37.14	10.61	5.60	2.16	0.33	1.24	2.37	1.46
T5	15.93	12.59	1.28	1.24	0.91	1.80	3.17	1.06
T6	0.62	1.49	1.58	1.08	1.14	1.33	0.85	0.82
T6	1.47	1.07	1.01	1.90	1.03	0.40	0.42	0.65
T6	4.20	5.05	4.39	1.48	1.99	1.98	1.88	1.26
T7	0.27	0.35	1.12	0.44	1.79	1.14	0.36	0.83
T7	0.97	4.93	0.63	0.37	1.80	1.66	0.26	0.18
T7	1.30	2.36	1.78	0.94	0.41	1.25	0.96	0.55
T8	1.05	0.84	1.64	2.00	0.55	0.95	0.78	0.30
T8	0.15	0.78	1.02	0.21	1.45	0.14	0.00	0.38
T8	0.81	0.34	0.78	0.51	0.26	0.52	0.63	0.00
T9	0.74	0.40	0.02	0.00	0.63	0.22	0.25	0.00
T9	0.05	0.86	0.16	0.78	0.01	0.32	0.00	0.33
T9	0.98	0.59	0.76	0.01	0.71	0.23	0.21	0.10

B. Cumulative total ammonia volatilisation(mg NH_3-N g soil^{-1}) from different treatments

Treatments	2nd day	4th day	7th day	9th day	11th day	15th day	18th day	21st day	Total
T1	1.355	0.419	0.230	0.126	0.090	0.066	0.019	0.028	2.800
T2	0.135	0.103	0.092	0.031	0.027	0.024	0.017	0.002	0.517
T3	0.940	0.593	0.118	0.066	0.093	0.117	0.063	0.018	2.411
T4	0.010	0.020	0.015	0.010	0.013	0.008	0.007	0.003	0.102
T5	0.239	0.142	0.066	0.014	0.016	0.024	0.032	0.016	0.656
T6	0.021	0.032	0.029	0.015	0.021	0.019	0.013	0.011	0.193
T7	0.008	0.032	0.015	0.006	0.020	0.020	0.007	0.006	0.137
T8	0.007	0.008	0.014	0.009	0.011	0.008	0.006	0.003	0.080
T9	0.006	0.008	0.004	0.003	0.007	0.004	0.002	0.002	0.041

C. Total ammonia volatilisation (mg NH_3-N g soil^{-1}day^{-1}) from different treatments per day

Treatments	0-2 days	2-4 days	4-7 days	7-9 days	9-11 days	11-15days	15-18 days	18-21 days
T1	0.677	0.168	0.092	0.063	0.030	0.022	0.008	0.011
T2	0.067	0.041	0.037	0.015	0.009	0.008	0.007	0.001
T3	0.470	0.237	0.047	0.033	0.031	0.039	0.025	0.007
T4	0.005	0.008	0.006	0.005	0.004	0.003	0.003	0.001
T5	0.120	0.057	0.026	0.007	0.005	0.008	0.013	0.006
T6	0.010	0.013	0.012	0.007	0.007	0.006	0.005	0.005
T7	0.004	0.013	0.006	0.003	0.007	0.007	0.003	0.003
T8	0.003	0.003	0.006	0.005	0.004	0.003	0.002	0.001
T9	0.003	0.004	0.002	0.001	0.003	0.002	0.001	0.001

D. Total N2O emissions (g) from different treatments after manure or urea application to soil

Treatments	0-4 days	4-8 days	8-12 days	12-16 days	Total
T1	0.009	0.040	0.223	0.169	0.442
T2	0.051	0.017	0.075	0.057	0.200
T3	0.040	0.032	0.142	0.103	0.317
T4	0.018	0.027	0.259	0.167	0.470
T5	0.013	0.043	0.156	0.219	0.431
T6	0.071	0.070	0.340	0.262	0.742
T7	0.064	0.014	0.014	0.007	0.099
T8	0.010	0.003	0.014	0.061	0.088
T9	0.029	0.014	0.003	0.003	0.049

E. Total methane emissions (g) from different treatments after manure or urea application to soil

Treatments	0-4 days	4-8 days	8-12 days	12-16 days	Total
T1	0.226	0.078	0.127	0.147	0.577
T2	0.208	0.025	-0.035	-0.160	0.038
T3	0.416	0.020	0.020	0.349	0.804
T4	0.005	-0.002	0.020	0.158	0.181
T5	0.008	-0.015	-0.004	0.060	0.049
T6	0.022	-0.004	-0.001	-0.165	-0.148
T7	0.144	-0.006	-0.001	0.809	0.946
T8	0.003	0.001	-0.004	-0.167	-0.167
T9	0.367	-0.006	0.000	0.471	0.831

Appendix 3: A. Ammonia concentration (ppm) from different manure treatments applied to soil

B. Cumulative total ammonia volatilisation (mg NH_3-N g soil^{-1}) from different treatments after manure or urea application to soil

C. Total ammonia volatilisation (mg NH_3-N g $soil^{-1}day^{-1}$) from different treatments after manure or urea application to soil per day

D. Total N_2O emissions (g) from different treatments after manure or urea application to soil

E. Total methane emissions (g) from different treatments after manure or urea application to soil