



Ammonia Volatilisation from Grazed Pastures

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Executive Summary

This report reviews the processes, measurement techniques, and modelling tools of N volatilisation from grazed pastures. The volatilisation process consists of the exchange of ammonia from the soil to the air above and then its transport and dissipation in the atmosphere. It can be a major component of the N balance, being especially important in areas where mineral N is concentrated, such as urine patches, where volatilisation and denitrification are competing losses of nearly equal magnitude. The purpose of the review is to assist with the identification of research and development priorities within Dairy Australia's "Dairy Nitrogen Use Efficiency and Loss Pathways" and to assist with improvement of confidence in the modelling of N₂O losses for the New Zealand Agricultural Greenhouse Gas Research Centre integrated systems theme.

The review starts with a brief description of the current understanding of the volatilisation process and its major drivers. Next, we present a review of the methodologies for measuring volatilisation losses, focussing on agricultural fields, and then we describe a selection of modelling approaches in use for estimating volatilisation losses. Next, a brief description of possible useful datasets for model validation is given. We conclude with a series of recommendations for future research.

In the soil–atmosphere system, total ammoniacal N (TAN) can exist in several pools: within the clay interlayers, on the soil exchanger, in the soil liquid phase, in the soil gas phase, or in the air near (boundary layer) or above the soil (atmosphere). Exchange between each of these pools is possible, but with varying strengths. In the soil–atmosphere system, TAN can exist in the forms of either ammonium (NH₄⁺, solid) or ammonia (NH₃, gas). Exchange among these pools happens at varying rates and is influenced by environmental factors and management practices, which ultimately also affect N volatilisation. The factors with the largest influence that are not controllable are: hot, dry, windy weather; rainfall; soil clay content and mineralogy; and soil pH and buffering. Those that are somewhat controllable are: fertiliser type, urease and nitrification inhibitors, and grazing management.

Methods for measuring volatilisation can be described into two basic categories: those based on enclosed chambers and those that measure NH₃ fluxes in the open air. Each has strengths and limitations, and both rely on determining NH₃ concentrations in the air. Of the techniques for measuring NH₃ in the air, denuder systems are the most reliable at present, although optical techniques seem to be a promising approach for future work. Measurements by open techniques are the most reliable measures of NH₃ losses, especially at the field scale, but there is a place for well-designed chamber techniques where high spatial resolution or targeted manipulation of processes is desired.

There is a wide range of modelling tools available to simulate NH₃ volatilisation. The tools differ in the level of detail (scale and number of processes) accounted for and whether their description is mechanistic or empirical. Many of the models have been applied only locally by the developers and require more testing before they can be more generally applied.

Several experimental efforts studying the volatilisation process and its implications for the N balance were reviewed. With respect to the farm systems of Australia and New Zealand, the datasets generated by the experimental work of Richard Eckard¹, and Debra Turner², as well as the series published by Sherlock and collaborators are worth pursuing further as potential data sources for model validation.

Our recommendations for future experimental work include:

1. Greater quantitative understanding of the changes in pH following fertiliser and urine addition – this is major control on volatilisation is poorly understood;
2. Greater quantitative understanding of the transport of NH₃ through the soil, the exchange with the atmosphere, and the factors affecting this transfer;
3. Quantitative understanding of the re-deposition of NH₃ to the soil after volatilisation is also needed and has large implications for net losses and in indirect N₂O emissions;
4. A compilation of existing data for model testing, particularly the experimental results discussed above;
5. Targeted experimentation that measures the fate of the total N in the soil so that we can ensure that the models are not achieving good simulation of volatilisation at the expense of another important process. This experimental work should be well integrated with model development and testing so that the models can be rigorously tested and then used to extrapolate the measurements that can be undertaken with only limited scales of time and space;
6. Models at two levels of detail will probably best serve the industry's needs with regards to NH₃ losses. A more detailed process-based model would assist researchers, while a simpler model would assist with farm-level decision making.
7. Open methods are favoured for determining NH₃ volatilisation, especially Integrated Horizontal Flux and Backward Lagrangian Stochastic methods. Chambers still have a role to play in more detailed studies. Optical methods to measure NH₃ concentration have qualities that make them promising if further developed.

¹ Eckard RJ, Chen D, White RE, Chapman DF (2003) Gaseous nitrogen loss from temperate perennial grass and clover dairy pastures in south-eastern Australia. *Australian Journal of Agricultural Research* **54**, 561-570.

² Turner DA (2010) Quantification and mitigation of gaseous nitrogen emissions from pasture and cropping systems. PhD Thesis, University of Melbourne, Melbourne, Australia

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1. Introduction and Background

Nitrogen (N) is one of the most important nutrients to plants and its management is paramount for sustaining high agricultural yields. The use of N fertilisers is one of the pillars of the green revolution which brought increases in food production per area of agricultural land throughout the last century (Hazell 2009). However, the continuous intensification of land use has resulted in increasing losses of nutrients to the environment (Tilman *et al.* 2002). Losses of nutrients via leaching and runoff are responsible for increasing concentrations of N in the ground water or surface water bodies where high N concentrations can be harmful to aquatic life as well as for human use. Losses in gaseous forms can also be a water pollutant, but the biggest concern is related to their contribution to climate change due to the greenhouse effect. For farmers these losses also mean an economic cost, as the N lost from the soil needs to be replenished by using fertilisers.

The present review focuses on N volatilisation, one of the major forms of gaseous N losses from soils. The volatilisation process consists of the exchange of ammonia from the soil to the air immediately above the soil and then its transport and dissipation in the atmosphere. This review starts with a brief description of the current understanding of the volatilisation process and its major drivers. The next section presents the methodology for measuring volatilisation losses, especially in agricultural fields. The review then focuses on a selection of models or modelling approaches that are available for estimating volatilisation losses. This is followed by a brief description of a selection of datasets which have the potential to be part of a database that could be used to test models and expand our knowledge of the drivers for volatilisation. Finally, as a conclusion, a series of recommendations for areas that require further attention are listed.

2. Current Understanding of Processes and Drivers

2.1 Forms of Ammoniacal N in the Soil and their Inter-Relationships

Total ammoniacal N (TAN or sometimes Am-N or $\text{NH}_x\text{-N}$) is a general term that collectively refers to all the forms of molecular ammonia (NH_3) and ionic ammonium (NH_4^+). In the soil–atmosphere system, TAN can exist in several pools (Figure 1): within the clay interlayers, on the soil exchanger, in the soil liquid phase, in the soil gas phase, or in the air near (boundary layer) or above the soil (atmosphere). Exchange to and from each of these pools is possible, but with varying strengths. The diagram in Figure 1 presents a substantially simplified diagram of the TAN cycle which ignores the processes that occur within each pool. For example, the chemistry of TAN in the

atmosphere is quite complex (see the literature reviewed by Fangmeier *et al.* 1994): ammonia gases interact with other air components, ammonia can be absorbed or emitted by plant leaves (Sharpe and Harper 1995), and significant quantities can be deposited back to the terrestrial environment within relatively short distances from the location of emission.

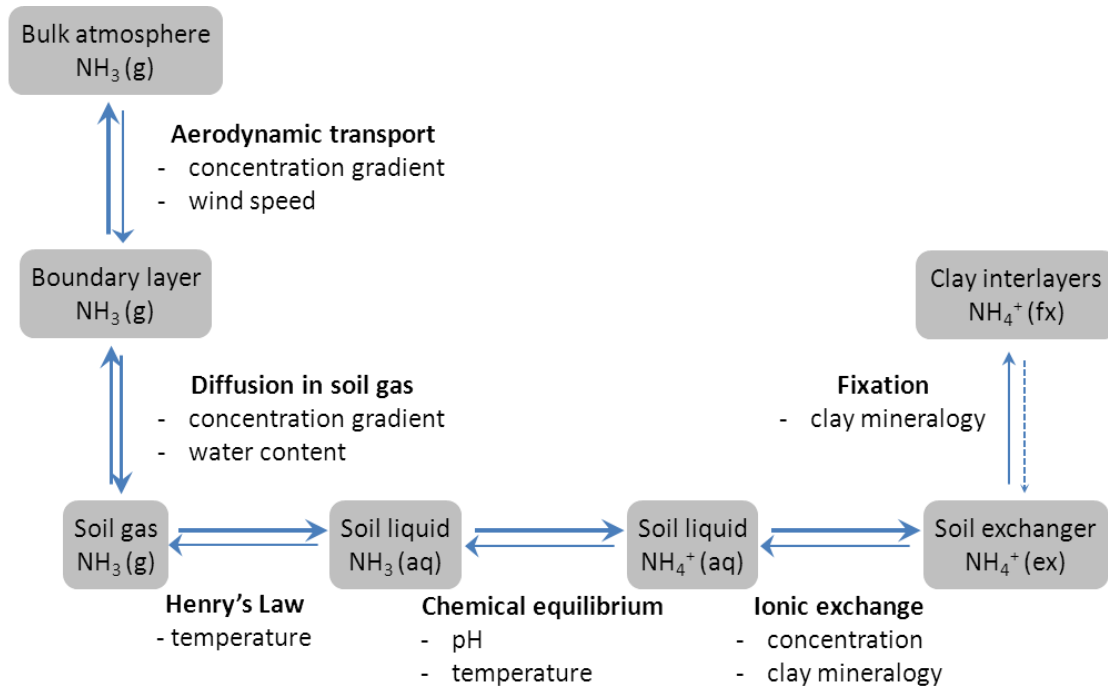


Figure 1. Simplified diagram of the forms of TAN in the soil and atmosphere, with an indication of the major drivers of the exchange between the different forms. The thickness of the arrows gives a relative indication of the strength of the exchanges. Also identified is the form of the TAN in each pool; (g) - in the gas phase, (aq) – dissolved in aqueous solution, (ex) – attached to the soil exchanger, (fx) – fixed within the soil interlayers.

Ammoniacal N is regarded as a major pollutant in Europe and the USA, where it has been reported as causing damage to vegetation and waterways (Buijsman *et al.* 1987; Fangmeier *et al.* 1994). In these regions, emissions from agriculture are mainly from feedlots and animal housing (Hristov *et al.* 2011). TAN emissions are significantly lower from the less intensive animal agricultural systems typically used in Australia and New Zealand. Here, the major concerns arise from the economic loss to farmers (Bacon and Freney 1989; Ball *et al.* 1979a) and the indirect greenhouse gas emissions (Cullen and Eckard 2011).

2.2 Pools of Ammoniacal N

One very common perception is that nitrate is the dominant form of mineral N in agricultural soils, and Young and Aldag (1982) suggest that this has led to an under-

appreciation of the quantities of fixed ammonium in soils. Fixed ammonium is variably exchanged with the soil solution (Nommik and Vahtras 1982) and substantial quantities might be effectively unavailable. Young and Aldag (1982) suggest that substantial proportions of the total N in subsoils might be fixed (it is often assumed to be in a stable organic form). Crush and Evans (1988) found that fixed ammonium was 6–12% of the total N in the topsoil of New Zealand silt loams and sandy loams in the Manawatu region, and that 5–8% of urinary N was at least temporarily immobilised by fixation. Ammonium fixation is affected by potassium status (Kilic *et al.* 1999) and may be substantially higher in the subsoil than the topsoil (Nielsen 1972).

There is a strong dynamic relationship between the TAN held on the soil exchanger, and the molecular and ionic forms in the soil solution. The surfaces of the soil mineral particles hold negative charge, and a diffuse double layer of cations and neutralising anions forms between the particles' surface and the bulk soil solution (Bohn *et al.* 1979). The ions in this pool are readily exchanged with the bulk solution but still can reduce the availability of these ions for transport by leaching, loss by volatilisation and uptake by plants. The bond between NH_4^+ and the soil exchanger can be strong and has probably led to a perception that it will not leach. This is perhaps true when concentrations are low but experimental studies have shown that substantial movement of NH_4^+ can occur under urine patches (Menneer *et al.* 2008; Wachendorf *et al.* 2005a). The relationship between the concentration of TAN adsorbed onto the soil exchanger and the concentration in solution can be measured using standard analytical techniques, while a range of mathematical functions can be used to describe this relationship (Hinze 2001; Sparks 1996). Relatively recent publications provide relatively simple (Li *et al.* 2006) and more complex (Vogeler *et al.* 2011) pedotransfer functions to estimate that relationship from more commonly known soil properties.

In the soil solution, the chemical equilibrium between ammonia and ammonium, which is mainly dependent on temperature and the pH of the soil solution, can be written as:

[1]

The equilibrium equation can be re-written for the ratio between ammonium and ammonia as:

—

[2]

where pK_A is the equilibrium constant, dependent on temperature (T, in Celsius), which can be estimated by (Sherlock and Goh 1985a):

[3]

At typical agricultural soil pH values (<7.0), most of the TAN in solution will be in the ionised form but when pH is high (e.g. soon after a substantial amount of urea hydrolysis has occurred), the balance will tip considerably towards large amounts of NH_3 . The factors increasing the amount of NH_3 are thus: high pH, high temperature, high TAN concentrations, and low cation exchange capacity.

The ammonia in the soil is present as aqueous ammonia ($\text{NH}_{3,\text{aq}}$) dissolved in the soil solution, and in gas form ($\text{NH}_{3,\text{g}}$) dissolved in the soil gas phase. These two forms co-exist in thermodynamic equilibrium, which is described with Henry's constant as (Hales and Drewes 1979):

[4]

where pK_G is the equilibrium constant, which is also dependent on the temperature and given by (Sherlock and Goh 1985a):

[5]

Ammonia volatilisation is defined as the exchange of NH_3 gas from the soil to the bulk atmosphere. This process is powered by the concentration gradient from the soil to the bulk atmosphere, at some reference height, and the transport is controlled by soil and atmospheric conditions. Using analogy with an electrical circuit (Figure 2), volatilisation is affected by a boundary layer resistance, which accounts for the atmospheric turbulence and is dependent on surface roughness, temperature, and wind speed, and by a diffusive resistance in the soil. The resistance to transport through the soil is dependent on soil type, moisture, and temperature, and its importance to volatilisation varies markedly with time. Maximum loss rates happen when large quantities of NH_3 are present at the surface, but they decrease quickly as NH_3 is depleted. The transport through the tortuous soil porous media is very slow and any NH_3 deep in the soil is likely to be consumed before it reaches the surface. The presence of pasture or surface organic matter can add another resistance term to the volatilisation process.

A single exchange coefficient, k_v , is typically used to represent the transport resistance. It is considered to be dependent on soil structure and moisture, as well as on air temperature and wind speed. The volatilisation rate (V_{NH_3}) can then be expressed as (Denmead *et al.* 1982):

[6]

where $NH_{3,Soil}$ is the concentration of ammonia in the soil and $NH_{3,ATM}$ is the concentration in the bulk atmosphere. Assuming that the transport is relevant only when the NH_3 concentration in the soil is much higher than in the atmosphere, Equation 6 can be simplified to:

[7]

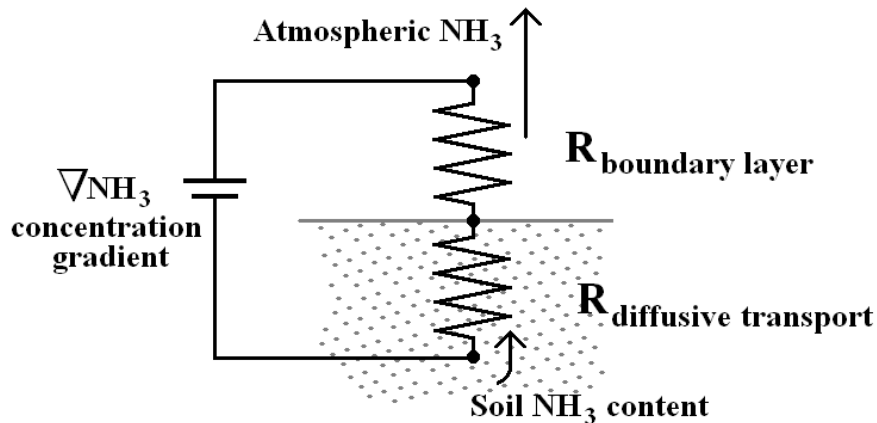


Figure 2. Simplified schematic of the volatilisation process using an analogy with an electrical circuit.

2.3 Sources and Sinks of Ammoniacal N

The major sources (additions to the pool) of TAN in the soil are mineralisation of the soil organic matter or dung from the soil surface and the addition of fertiliser, effluent, or urine. In areas close to a large NH_3 -emitting source, such as around animal housing facilities, atmospheric depositions can be relevant; this may also happen, to a limited extent, in areas surrounding effluent or urine depositions. Note that for some fertilisers and urine, urea is the form of N applied to the soil, which thus needs to be converted to TAN by hydrolysis.

Sinks of TAN from the soil are nitrification (oxidation of TAN to NO_3), uptake by plants, uptake or immobilisation by the soil microbes, volatilisation, and leaching. Only volatilisation and leaching cause immediate removal of N from the system, while plant uptake depends on the management of plant residues. These residues, as well as the microbial biomass, only lock up the N temporarily.

2.4 Properties and Practices Likely to Affect Volatilisation Losses

Factors likely to affect the amount of volatilisation include:

- Hot, dry, windy weather – volatilisation is strongly dependent on the transport of TAN near to the soil surface and then on rapid transport through the boundary layer to near-zero concentrations in the bulk atmosphere. Highly evaporative conditions will assist with transport of TAN to the soil surface and enhance transport through the boundary layer. All the equilibria affecting the form of TAN in the soil are affected by temperature in a way that high temperatures will force the equilibrium towards the molecular and gaseous forms and thus also enhance volatilisation.
- Rainfall – rainfall will act to reduce volatilisation in several ways. NH_3 is highly soluble and will dissolve in rainfall to be deposited back to the soil surface. Rainy conditions also act to depress transport through the boundary layer and will push TAN below the soil surface. Finally, the equilibrium between $\text{NH}_3(\text{g})$ in the soil solution and $\text{NH}_3(\text{g})$ in the soil gas phase is partially dependent on the volume of air in close contact with the soil solution. If the soil is nearly saturated, as it might be under rainy conditions, the volume of soil gas is reduced, which will also slow the volatilisation process.
- Soil pH and buffering – if the soil is acid then the equilibrium between NH_3 and NH_4^+ strongly favours the ionic form and there will be no volatilisation. Thus at typical agricultural pH values (<7.0), there will be little volatilisation. When pH is high, as in calcareous soils or following the hydrolysis of urea, volatilisation can occur at a high rate if other conditions are favourable. Soils that are poorly buffered (i.e. those with low clay and organic matter content) will show greater increases in pH for the same addition of H^+ ions and so are likely to have higher volatilisation rates after application of urea application. These soils will also suffer a quicker drop in pH after the hydrolysis is complete, so the high volatilisation rates are likely to be short-lived.
- Soil clay content and mineralogy – if the soil mineralogy is such that much of the TAN is held on the soil exchanger or fixed into the clay interlayers then the N will not be available for volatilisation. This is more important for volatilisation from fertiliser sources, as the concentration of TAN in urine will usually overwhelm the ability of the soil to exchange or fix TAN.
- Fertiliser type – urea-based fertilisers result in transiently high soil pH when the urea hydrolyses. Fertilisers that are based on TAN, NO_3 or organic N will not have the same effect on pH and so will result in less volatilisation. When the pH of organic fertilisers, such as farm effluent, is kept low, volatilisation losses will also be very small.
- Urine depth penetration – urine that is transported more than a few centimetres below the soil surface upon deposition is unlikely to contribute substantially to

volatilisation losses because any $\text{NH}_3(\text{g})$ emitted at depth would be reabsorbed before it could be emitted from the soil surface.

- Urine N concentration – high urine N concentrations are likely to enhance volatilisation because the pH will increase sharply when the urea hydrolyses, which will favour equilibrium towards NH_3 and consequently more volatilisation.
- Urease inhibitors – inhibitors that slow the rate of urea hydrolysis will reduce volatilisation in two ways. First, the source concentration of TAN will be lowered because there will probably be a closer match between the rate of production (hydrolysis by the urease enzyme) and the rate of consumption (nitrification to NO_3). Secondly, there will not be the same spike in alkalinity because the hydrolysis rate is lower and so the equilibrium will not be as favourable towards NH_3 .
- Nitrification inhibitors – nitrification inhibitors slow the nitrification of ammonium and thus act to increase the duration of high TAN concentrations in the soil. They are likely to have the effect of increasing volatilisation but the magnitude of that effect is unclear because of their interaction with soil pH and rainfall. The interaction with rainfall happens because inhibitors can be leached, thus decreasing the efficacy of the inhibitor. The interaction with pH is unclear. If nitrification is inhibited, there will not be a release of acidity to neutralise the alkalinity produced by the hydrolysis of urea. However, the soil will buffer that alkalinity through other processes, and thus the magnitude of the effect will depend on soil type.

Of these effects, those with the largest influence that are not controllable are:

- Hot, dry, windy weather;
- Rainfall;
- Soil clay content and mineralogy;
- Soil pH and buffering.

Those that are somewhat controllable are:

- Fertiliser type and application timing,
- Urine depositions through grazing management,
- Urease and nitrification inhibitors.

3. Measurement Techniques

3.1 Aspects of NH_3 Loss

The measurement of NH_3 losses from a field or farm building involves two aspects. It is necessary to determine both the flow (or exchange) of air for a given duration and also the concentration of NH_3 in that air. For an accurate estimation of the NH_3 losses, these

two measurements should be gathered reliably, which is a hard feat to accomplish. A third aspect is the up-scaling of these measurements to the field or farm scale. Typically, measurements are taken in relatively small areas and/or in conditions that are not representative of the whole field. Also, the distinction between NH_3 fluxes measured in a given place and the total net loss, which is the difference between the amount emitted and the amount re-deposited elsewhere in the field, is difficult to determine. This is especially important when the emissions are concentrated in a fraction of the area (such as urine patches in a paddock). Measurements of NH_3 volatilisation are thus often linked to relatively high degrees of uncertainty.

There is wide variety of techniques for measuring NH_3 volatilisation. These use different approaches and instruments, and are intended for distinct scales. The technique and strategy selected should therefore be tailored to the intended purpose for the data. For example, measurements might be used to evaluate different fertiliser application techniques and therefore determination of the relative differences, rather than total losses, might be sufficient. One might be interested in net losses from the whole paddock or in trying to identify the variability within it, so the temporal and spatial resolutions required may vary widely. The scale and the level of interference that a technique has on the environment being assessed will determine how representative the measurement is.

Several reviews have already been published describing most of the techniques available to determine NH_3 volatilisation (Cannavo *et al.* 2008; Misselbrook *et al.* 2005; Ni and Heber 2008; Phillips *et al.* 2001; Phillips *et al.* 2000; Shah *et al.* 2006; Sommer *et al.* 2004; Timmer *et al.* 2005). Each of these focuses on different scales and uses, such as fertiliser evaluation, losses from effluent ponds, or NH_3 concentration in buildings.

This section is divided in two parts. The first section reviews the devices available to measure NH_3 concentration in the air and the second reviews the techniques used to estimate the flux of NH_3 from a given area or building. The aspect of spatial resolution and up-scaling is treated in parallel with the estimation of NH_3 fluxes.

3.2 Determining NH_3 Concentration in the Air

3.2.1 Acid Traps

3.2.1.1 Description

Acid traps, also referred to as ammonia scrubbers, encompass several devices that have the ability to extract the NH_3 from the air into an acid medium from which the concentration can be later determined.

The typical setup uses an air pump to drive the air through a reservoir of an acidified water solution. As the air bubbles through the acidified water, ammonia is ionised to ammonium, which is non-volatile and thus is retained in the liquid. Typically, sulphuric acid (at 0.01–0.2 M) is used (Black *et al.* 1987b; Cabrera *et al.* 2001; Carey *et al.* 1997; Carran *et al.* 1982; Dawar *et al.* 2011; Di and Cameron 2004; Généromont *et al.* 1998; Lockyer and Whitehead 1990; Luo *et al.* 2006; Menneer *et al.* 2008; Ryden *et al.* 1987; Sherlock and Goh 1984; Vallis *et al.* 1982; Whitehead and Raistrick 1992; Whitehead and Raistrick 1993; Zaman and Blennerhassett 2010), although orthophosphoric acid (0.002–0.02 M) (Bussink 1994; Hatch *et al.* 1990; Lockyer and Whitehead 1990; Misselbrook *et al.* 2005; Petersen *et al.* 1998; Smith *et al.* 2007; Sommer and Jensen 1994; Velthof *et al.* 1990) and boric acid (2–4%) (Bolado Rodríguez *et al.* 2005; Gameh *et al.* 1990; Sherlock and Goh 1984; Van Der Weerden *et al.* 1996) have also been used.

The solution is exposed for a certain number of hours, depending on the flux of NH_3 in the environment, and then is analysed in the laboratory. Titrimetric and colorimetric methods are often used in the lab to determine the NH_4^+ content. pH test papers may be used for quick tests in the field (Ni and Heber 2008).

3.2.1.2 Strengths and Weaknesses

Acid traps are cheap and simple, and have been widely used. However, they need an energy source for the air pump and are labour intensive, as the traps must be replaced regularly and the solution analysed in laboratory.

It has been shown that acid traps are very efficient in removing NH_3 from the air (Genfa *et al.* 1989; Hristov *et al.* 2011; Misselbrook *et al.* 2005). Some 97% or more of the NH_3 in the passing air is typically trapped regardless of the air flow. The trapping efficiency can be enhanced by using traps in series. The NH_3 concentration in the air and the acid strength in the traps do not affect the trapping efficiency for small to medium periods (1–6 hours) (Misselbrook *et al.* 2005). It is recommended that the strength of the solution be increased when measuring over long time intervals or when NH_3 concentrations are high.

The detection limit depends on the method used to analyse the acid solution after exposition. Titrimetric methods detect concentrations in the order of 1.0 parts per million (ppm), while colorimetric methods reach values around 0.1 ppm (Ni and Heber 2008; Shah *et al.* 2006); the detection limit can be lowered to 0.01 ppm using ion chromatography. However, the acid trap technique does not distinguish between NH_3 and particulate NH_4^+ in the air, which might be high in places with high suspended NH_4^+ contents, such as in poultry farms.

3.2.2 Ammonia Denuders

3.2.2.1 Description

Several devices are grouped in the category of ammonia denuders, including filter packs, passive diffusion samplers, and gas detection tubes. They use a solid acidic medium, which is protected from air turbulence by a membrane or by being placed inside a tube, to trap NH_3 from the air.

Simple denuders, mostly for qualitative purposes, consist of a filter paper impregnated with an acid. These detectors are used for alert systems in situations where ammonia levels can reach dangerous levels or are used as an indirect measure of NH_3 fluxes. The latter is used for qualitative analysis (e.g. of the relative difference between treatments) or when budget constraints do not permit proper measurement of NH_3 fluxes (Carran *et al.* 2000; Phillips *et al.* 2001; Stiegler *et al.* 2007).

Most denuders consist of a tube which is designed such that the air flowing through is non-turbulent (Leuning *et al.* 1985; Ni and Heber 2008; Phillips *et al.* 2001; Schjoerring *et al.* 1992). The inside of the tube is coated with an acid which traps NH_3 from the passing air for later analysis. Denuders have to be carefully prepared in the lab to ensure proper acid coating and that no contamination occurs. Typically, oxalic acid, applied with an acetone solution for rapid drying, is used. However citric, tartaric, or phosphoric acids have also been used, and methanol has also been employed as a solvent (Shah *et al.* 2006). After exposure to the NH_3 -laden air, the tubes are rinsed and the solution is analysed in the laboratory. This laboratory analysis can use the same methods as described for acid traps.

Tubular denuders are also called “Ferm tubes” after the initial work by Ferm (1979), although several variations have been produced since (further description in Ni and Heber 2008; Phillips *et al.* 2001; Shah *et al.* 2006)). Most denuders can be categorised as either passive or active samplers. Passive samplers rely on natural air flow, while active samplers use a pump to force a high air flow through the tube. Passive samplers are widely used in field studies using micrometeorological methods, such as the Schjoerring passive sampler (Schjoerring *et al.* 1992; Smith *et al.* 1996; Sommer and Olesen 2000; White *et al.* 2000) and the Leuning sampler, also called a “shuttle” (Eckard *et al.* 2003; Freney *et al.* 1992; Leuning *et al.* 1985; Prasertsak *et al.* 2001; Sherlock *et al.* 1995; Sherlock *et al.* 1989; Sherlock *et al.* 2002; Smith *et al.* 1996; Turner *et al.* 2010). The shuttle’s design allows it to measure NH_3 fluxes directly, as the air flow through the sampler is directly proportional to the wind speed (Leuning *et al.* 1985).

Active samplers are commonly used in animal facilities where real-time measurements are needed. Typically, the sampling tubes are bought sealed and used only once. The

most popular device is the Dräger tube which is fully mobile. It has a manual pump for forcing the air and uses colour change to estimate NH₃ concentrations (Ni and Heber 2008). It has also been tested with reasonable success in the field (Pacholski *et al.* 2008; Roelcke *et al.* 2002).

3.2.2.1 Strengths and Weaknesses

Denuders are widely used in the field because they are easy to handle and do not need an energy source. The primary drawback is the time needed to trap a detectable amount of NH₃, which can be several hours for low concentrations. On the other hand, when concentrations are high, the acid coating can become saturated. Trapping efficiencies are normally high (>97%;(Shah *et al.* 2006). The detection limits depend on the method employed to analyse the solution used to rinse the acid coating. Passive samplers have to be calibrated in a wind tunnel and tend to have a higher variability compared to active samplers (Ni and Heber 2008; Shah *et al.* 2006). However, active samplers are much more expensive and measure NH₃ concentrations only, while passive samplers can measure the flux directly.

3.2.3 Optical Methods

3.2.3.1 Description

Devices using the optical approach measure the amount of NH₃ in the air by evaluating the interaction of NH₃ molecules and electromagnetic radiation. The devices can be grouped into three main approaches: chemiluminescence, spectroscopy, and fluorescence.

Chemiluminescence devices determine NH₃ by converting it to NO, usually using high temperatures (750–800°C), and then measuring the radiation signature (Ni and Heber 2008; Phillips *et al.* 2001). Because total NO is measured, the background NO concentration should be measured separately to improve accuracy. The detection limit for this method is in the order of 1.0 parts per billion (ppb). Chemiluminescence has been used to measure NH₃ concentrations in animal facilities, and in several field and lab studies (Aneja *et al.* 2000; Denmead *et al.* 2010; Génarmont *et al.* 1998; Mulvaney *et al.* 2008; Roelle and Aneja 2005).

Devices that use spectroscopy measure the deviation or interference caused by NH₃ molecules in the spectrum of a light beam (Ni and Heber 2008; Phillips *et al.* 2001; Shah *et al.* 2006). The light used typically has wavelengths at ultraviolet (0.001–0.4 µm) or infrared (0.7–1.0 µm) bandwidths. There are a variety of devices using spectroscopy that measure NH₃ in air passing through a small tube or even in an open path across a relatively large area. The detection limit is generally in the order of few ppb, but

increases with distance for open path measurements, up to an order of 1.0 ppm. Common examples of spectroscopy devices include:

Differential optical adsorption spectroscopy (DOAS) – This is an open-path method that is able to take measurements over distances of 0.1 m to several kilometres, and that typically employs ultraviolet light (Mount *et al.* 2002; Rumburg *et al.* 2008);

Selected ion flow tube mass spectroscopy (SIFT-MS) – This uses spectroscopic analysis to detect trace gases in the air passing through an ion-selective flow tube after chemical ionisation (Clough *et al.* 2003; Milligan *et al.* 2002);

Fourier transform infrared – This employs two mirrors to re-join a split infrared beam, and interference with the molecules in the path of the half-beams produces a pattern that can be used to determine the amount of NH₃ gas (Flesch *et al.* 2005; Loh *et al.* 2008);

Photoacoustic spectroscopy – These devices measure acoustic waves generated by the vibration of NH₃ molecules excited by a light beam (Emmenegger *et al.* 2004; Monaco *et al.* 2012; Webber *et al.* 2005).

The devices that use fluorescence to measure NH₃ typically employ absorptive paper (tapes) impregnated with a solution that can react with the ammonia in the air. The reaction changes the fluorescence intensity of the material and this can be used to determine the amount of NH₃ (Nakano *et al.* 1995; Phillips *et al.* 2001). The detection limit for these tapes is in the order of 1.0 ppm. Alternatively, the air sample can be photofragmented repeatedly using ultraviolet laser; the third fragmentation renders a fluorescence intensity that can be measured to infer the NH₃ content (Buckley *et al.* 1998; Phillips *et al.* 2001). With this procedure, the detection limit can be reduced to ppb or even parts per trillion levels.

3.2.3.2 Strengths and Weaknesses

Optical methods are interesting alternatives because of their possibility of continuous measurement and automation. For open path devices, the possibility of integrating measurements over wide distances may be appealing for situations with large variability, such as in grazed paddocks and feedlots. Also, most of the optical methods can be used to determine more than one gas species at the same time, e.g. CH₄, N₂O and NH₃ (Loh *et al.* 2008), or NO_x and NH₃ (Denmead *et al.* 2010). However, this capability also implies that measurements can suffer interference from other gases such as CO₂ or water vapour. In the case of chemiluminescence, all oxidisable N species (NH₃, NO_x) are measured together. Although there is an increase in the number of commercial available devices, with a corresponding lowering of prices, optical methods still tend to

be quite expensive, and require careful maintenance and calibration. The devices also require a supply of energy, which may limit their use in remote locations.

3.2.4 Electrochemical Methods and ‘Electronic Noses’

3.2.4.1 Description

These devices measure NH_3 concentrations by determining changes in the electric properties of a medium due to the presence of ammonia. Electronic noses are much more complex than electrochemical sensors and are still under development.

Electrochemical sensors respond to changes in electrical potential when ammonia reacts with an electrolyte (Phillips *et al.* 2001). A permeable membrane is used as an interface with the environment. These devices have been used in buildings in alerting systems for quite some time as their response time to sudden changes in NH_3 concentration is small.

Electronic noses also use changes in electrical properties to detect the presence of different molecules in the air. Their main difference from the electrochemical sensors is that these devices use a combination of several sensing elements (20 or more) to improve the range and sensitivity of the measuring system, akin to a human nose (Phillips *et al.* 2001). The device can theoretically identify a wide range of substances at varying concentrations. This technique also requires complex software to interpret the results.

3.2.4.2 Strengths and Weaknesses

Devices using this method are still in development, especially those of the electronic nose class. The interest in them is due to their fast response time and high sensitivity to a wide range of substances. However, they are still expensive and the devices presented so far suffer from saturation, that is, their sensitivity decreases with use.

3.3 Determining NH_3 Fluxes

3.3.1 Indirect Methods

3.3.1.1 Description

Indirect methods encompass any procedure where the flux of NH_3 volatilised is not directly measured. The level of flux is inferred from auxiliary measurements integrated over the time interval of interest. These methods can be clustered in two main classes: one obtains most of the fluxes of the N cycle and infers those that remain; the second measures the quantities that vary proportionally to NH_3 fluxes.

The most common indirect estimation of NH₃ volatilisation is based on mass balance. In this procedure, some of the N transformations and fluxes within a system are measured; the remaining ones are then estimated by difference, with some values sometimes being assumed. A marker, such as ¹⁵N, is often used to help identify some of the values in the mass balance, thus improving the reliability of the estimates. Typically, the estimation of NH₃ fluxes using mass balance is used when its value is of relatively low importance, and all gaseous losses are often lumped together (Bronson *et al.* 1999; Cookson *et al.* 2001; Ellington 1986; Hristov *et al.* 2009; Pakrou and Dillon 1995; Suter *et al.* 2011; Thompson and Fillery 1997; Wachendorf *et al.* 2005b).

NH₃ fluxes have also been estimated by measuring the variation in NH₄⁺ and pH in the soil, as well as the wind speed (Sherlock *et al.* 1995; Smith *et al.* 1996). The concentration of NH₃ in the soil is inferred from the NH₄⁺ and pH measurements, while wind speed is used to compute the flux off the field. An exchange coefficient, which should be inferred for each location, is used to describe the interaction between the soil and the atmosphere.

Another procedure that can be considered an indirect method for determining NH₃ volatilisation is the measurement of only the NH₃ concentration in the air (Carran *et al.* 2000; Stiegler *et al.* 2007). This does not provide values of flux but can be used in a semi-quantitative way to compare side-by-side treatments. These values can also be used as a check to the mass balance.

3.3.1.2 Strengths and Weaknesses

Employing an indirect method may be a way of reducing costs, especially when the flux of ammonia is of low interest. It is suitable for use in preliminary analyses of the N cycle in a system, or in qualitative analyses. However, these methods are highly dependent on the quality of the auxiliary measurements. Lumping all gases together or having to rely on assumptions, such as considering denitrification losses as negligible, are also factors that weaken the confidence in the estimates based on this method.

3.3.2 Enclosure Methods

3.3.2.1 Description

A wide variety of devices and procedures can be grouped together as enclosure methods. They can be divided into three main sub-groups: static closed chambers, which have no air exchange; closed dynamic chambers, where air exchange is tightly controlled; and wind tunnels, which are semi-open dynamic chambers.

The chamber technique is often used for lysimeter experiments and other experimental studies in relatively small areas, including laboratory-based studies. It involves placing

and sealing a chamber on a portion of the field or onto the lysimeter. Gas exchange is allowed only between the air in the chamber and the soil surface (a fully closed chamber), or the air is exchanged with the exterior at a known rate using a pump system (dynamic chamber). In the latter, the flowing air may pass through an acid trap for later NH_3 determination (Black *et al.* 1985; Carran *et al.* 1982; Di and Cameron 2000; Menneer *et al.* 2008; Sherlock 1984; Vallis *et al.* 1982; Whitehead and Raistrick 1990; Whitehead and Raistrick 1992; Zaman and Blennerhassett 2010) or through a measurement device for real-time measurements, which is more typical of lab studies (Monaco *et al.* 2012; Mulvaney *et al.* 2008). Measurements in static chambers are uncommon but may be done while measuring N_2O fluxes.

Wind tunnels can be regarded as large dynamic chambers where two sides of the structure are open and air exchange with the environment happens. Typical structures cover about 1 m^2 and are made of translucent material. Air is forced through the tunnel by a fan, and thus air flow can be controlled. The concentration of ammonia is measured at the entrance of the tunnel and in the outlet; as the air flow through the tunnel is known, it is therefore possible to determine the NH_3 flux (Lockyer and Whitehead 1990; Misselbrook *et al.* 2005; Petersen *et al.* 1998; Ryden *et al.* 1987; Smith *et al.* 2007; Sommer and Jensen 1994; Van Der Weerden and Jarvis 1997; Van Der Weerden *et al.* 1996; Velthof *et al.* 1990). Several of the devices described in Section 3.2 have been employed to determine NH_3 concentrations in wind tunnels.

Some systems allow the wind speed in wind tunnels or the exchange rate in dynamic chambers to be adjusted to mimic the environmental conditions in the field around the enclosures (Cabrera *et al.* 2001; Ryden and Lockyer 1985).

3.3.2.2 Strengths and Weaknesses

Chambers have been used for a long time in experiments measuring ammonia volatilisation. They are cheap and simple to operate. Because of their relatively small size, generally 0.1-0.2 m^2 , good spatial resolution can be attained. However, the environment in the chamber is greatly disturbed, which interferes with the energy, and the soil moisture and temperature regimes in the chambers can be significantly different from the surrounding environment. Also, the transport process is altered as wind speed variations are prevented during measurement. Wind tunnels experience these problems to a lesser degree, as the chamber is larger and semi-open; however, the environmental conditions are still disturbed considerably. The use of a dynamically adjustable wind speed seems to reduce interference to a limited extent. It has been shown that the placement of the device for measuring NH_3 concentration within the wind tunnel can significantly alter the estimates of ammonia fluxes (Loubet *et al.* 1999a; Loubet *et al.* 1999b). The ability to control the wind speed and temperature may be taken as an

advantage for studies of the influence of basic factors on ammonia volatilisation, e.g. studies of the effect of wind speed (Olesen and Sommer 1993; Ryden and Lockyer 1985) and temperature (He *et al.* 1999; Whitehead and Raistrick 1991).

Another cause for concern with enclosure methods is that ammonia recovery is always less than 100% (Misselbrook *et al.* 2005; Van Der Weerden *et al.* 1996). This is probably because ammonia clings to the walls of the chamber or tunnel and thus is not measured. For field experiments, deposition of dew can trap significant amounts of ammonia, which is released when the dew evaporates, thus considerably altering the timing of NH₃ fluxes.

3.3.3 Open Methods

3.3.3.1 Description

Open methods rely on measuring NH₃ concentrations in the open air plus a series of atmospheric variables that can be used to compute the net flux of ammonia from a given area. The measurement of NH₃ concentrations at different heights is typical to a number of the open methods, as volatilisation is strongly driven by concentration gradients. Several procedures have been developed to determine volatilisation losses from a field in the open air. These differ on the theory or mathematical approach used to integrate the profiles of NH₃ concentration and the atmospheric transport dynamics.

Open methods of determining ammonia fluxes, often called aerodynamic or micrometeorological methods, are typically used in field studies. They do not rely on the physical enclosure of an area, but define it by the measurement/integration approach. The open methods are quite popular, mainly because they cause very limited interference, if any, on the environmental conditions. However, some methods rely on assumptions that should be evaluated when deciding on their use. A brief description of a few methods is given below.

Micrometeorological mass balance is considered the standard method for determining ammonia volatilisation. It requires the measurement of NH₃ concentrations and wind speed at several heights (commonly 0.5, 2.0, 3.5, and 5.0 m) and in two different locations, one to obtain background levels and another within the field where the flux is to be measured. Examples and further details can be found elsewhere (Ferguson *et al.* 1988; Générmont *et al.* 1998; Jarvis *et al.* 1991; Ni and Heber 2008; Ryden and Lockyer 1985; Shah *et al.* 2006; Sherlock *et al.* 2002; Sommer *et al.* 2004).

Integrated Horizontal Flux (IHF) is a procedure that uses measurements of the horizontal NH₃ fluxes at several different heights to estimate the vertical fluxes and thus the total net ammonia transport. The fluxes can be determined directly using passive samplers, or determined by measuring wind speed and NH₃ concentrations. The

computation of the NH₃ fluxes uses mean wind speed, which may result in overestimation, as the turbulent transport terms are simplified. Nevertheless, IHF is often considered the best technique for measuring any type of gas transport through the atmosphere, not only transport of NH₃. More details and examples are given in (Black *et al.* 1989; Misselbrook *et al.* 2005; Ni and Heber 2008; Shah *et al.* 2006; Sherlock *et al.* 1995; Sintermann *et al.* 2011; Sommer *et al.* 2004; Wilson *et al.* 1983).

The Simplified Method (also known as the Z_{INST} method) is a simplified procedure based on the IHF method but uses only one height to estimate the net fluxes (Laubach *et al.* 2012; Ni and Heber 2008; Shah *et al.* 2006; Sherlock *et al.* 1989; Sommer *et al.* 2004; Turner 2010). The method is designed for circular areas and for homogeneous terrain. It is most appropriate for unstable atmospheric conditions (e.g. daytime).

The Perimeter Profile Method uses measurements of the NH₃ fluxes in four perpendicular locations around a circle. In each location, pairs of passive samplers (one inward and another outward) are placed at different heights. This configuration allows ammonia fluxes to be determined without any need for a homogeneous surface around the measured area (Schjoerring *et al.* 1992; Sommer *et al.* 2004).

The Aerodynamic Gradient Method uses transport theory to estimate NH₃ fluxes based on measurements of wind speed and ammonia concentrations at two heights. This method does not need to capture mass balance (Génermont *et al.* 1998; Shah *et al.* 2006; Sintermann *et al.* 2011; Sommer *et al.* 2004).

Eddy Covariance methods compute ammonia fluxes based on the covariance of a discrete time series of wind speed and NH₃ concentrations measured at frequent intervals and one height. This method does not rely on assumptions of, for example, atmospheric stability, but needs high-resolution measurements (10-30min), which are difficult to obtain for gases at low concentrations (Shah *et al.* 2006; Sintermann *et al.* 2011; Sommer *et al.* 2004).

The Backward Lagrangian Stochastic (BLS) model uses backward stochastic dispersion modelling to solve an ensemble of particle trajectories which are linked to a defined source area to estimate NH₃ fluxes. The method needs the NH₃ concentration to be measured at one or more points, as well as wind speed and surface roughness (Denmead *et al.* 2010; Laubach *et al.* 2012; Loh *et al.* 2008; Sintermann *et al.* 2011; Sommer *et al.* 2005; Sommer *et al.* 2004; Turner *et al.* 2010). A feature of this approach is that the N source area can have any geometry. Free software (WindTrax – www.thunderbeachscientific.com/windtrax.html) is available to help computing ammonia fluxes with this method.

There are also some variations of the dispersion model approach, such as Inverse Lagrangian Analysis (Sommer *et al.* 2004), which accounts for emitting sources other

than the soil (the plant canopy, for instance). Eulerian Inverse modelling uses a semi-analytical solution of the dispersion–diffusion theory of fluids to determine NH_3 fluxes (Sintermann *et al.* 2011).

3.3.3.2 Strengths and Weaknesses

The open methods are favoured because they consider relatively large areas to determine NH_3 fluxes and do not disturb the environment. These characteristics allow measurements in field conditions and integration over variable sources, such as animal excreta depositions. All these methods have robust results, even the simplified methods, when the assumptions used in their development are valid. The IHF method seems to be the dominant or reference method to determine NH_3 losses. It is relatively simple and cheap compared to other procedures and has consistent performance (Hristov *et al.* 2011; Misselbrook *et al.* 2005; Sintermann *et al.* 2011; Sommer *et al.* 2004). The use of simplified methods, especially BLS, has been increasing since they require fewer measurements of NH_3 concentration and their performance has been shown to be quite reliable (Denmead *et al.* 2010; Hristov *et al.* 2011; Sommer *et al.* 2005; Turner 2010).

Because the open methods integrate measurements over large area, they typically have low spatial and temporal resolution, although developments in measurement devices have made it possible to increase the temporal resolution (Hristov *et al.* 2011; Ni and Heber 2008; Timmer *et al.* 2005). The mathematical solutions for some of the methods include some assumptions that must be fulfilled to ensure the results are reliable. These solutions can be quite complex, thus requiring expert users and dedicated software tools.

4. Modelling the Volatilisation Process

There is a considerable variety of modelling approaches used to describe NH_3 volatilisation. This variation reflects the different purposes the estimates are used for and, in particular, their spatial/temporal resolution. Another distinction among them is whether the models describe the volatilisation process empirically or using a mechanistic approach. Some models describe only the volatilisation process, while others encompass the whole N cycle. A brief description of these variations is given below, followed by a short description of several pertinent models.

4.1 Process-Focussed Models

Different models that describe NH_3 volatilisation account for a variable number of other soil processes. The distinction made here is on how much focus is put on describing volatilisation as an output.

One group of models encompasses volatilisation-specific models, which focus only or primarily on estimating volatilisation losses from a given N source; the remaining processes in the N cycle are disregarded or over-simplified. Examples of this approach include the Sherlock and Goh model (Sherlock and Goh 1985a; Sherlock and Goh 1985b), Volt'Air (Garcia *et al.* 2011; Générumont and Cellier 1997), the Ammonia Loss from Field-applied Animal Manure (ALFAM) model (Søgaard *et al.* 2002) and the Swiss Empirical Model (Menzi *et al.* 1998).

Another group of models focuses on the whole N cycle, attempting to describe the fate of N in the soil–plant system more completely. All or most of the N processes are accounted for, although the level of detail may not be the same in some models. For instance, models such as those of Rachhpal-Singh and Nye (Kirk and Nye 1991; Rachhpal-Singh and Nye 1986a; Rachhpal-Singh and Nye 1986b; Rachhpal-Singh and Nye 1986c; Rachhpal-Singh and Nye 1988), Denitrification–Decomposition (DNDC) (Li *et al.* 1992; Li 2000) and the Farm Assessment Tool (FASSET) (Hutchings *et al.* 2007; Hutchings *et al.* 1996) consider the whole N cycle at similarly high levels of detail, whereas models such as DayCent (Del Grosso *et al.* 2008; Parton *et al.* 1998) and NGAUGE (Brown *et al.* 2005; Misselbrook *et al.* 2004) represent volatilisation in a much simpler approach than other N transformation processes.

4.2 Level of Detail or Resolution

Models vary considerably in the level of detail in which they describe the system and the processes within. At the system level, detail is generally related to scale. Models that describe processes at large temporal and/or spatial scales tend to be quite simple, i.e. N outputs are described by relative simple functions which, in turn, require a small number of inputs. Simple models tend to be of an empirical or semi-empirical nature. They employ either a regression model or a lookup table to estimate the amount of NH₃ volatilisation as function of total N inputs, sometimes also using ancillary variables. Typical examples are the N budgeting models such as OVERSEER (Wheeler *et al.* 2008; Wheeler *et al.* 2003; Wheeler *et al.* 2006) or the Model for Ammonia System Transfers (MAST) (Ross *et al.* 2002).

For models that work at smaller scales, the level of detail can be high. This way, subtle variations that are not as important at large scales can be captured. Models that attempt to describe the soil processes with more detail typically use a mechanistic description of the processes. Mechanistic or process-based NH₃ volatilisation modelling typically uses a mathematical depiction of the N transformations as shown in Section 2.2. In general, mechanistic models require a much greater level of information than empirical models. They also need more computing power. Examples include Volt'Air (Garcia *et al.* 2011; Générumont and Cellier 1997), DNDC (Li *et al.* 1992; Li 2000),

FASSET (Hutchings *et al.* 2007; Hutchings *et al.* 1996) and the Agricultural Production Systems Simulator (APSIM) (Keating *et al.* 2003b; Vogeler *et al.* 2010).

It is important to remember that a more detailed model will not necessarily be more accurate, as increased error in model inputs often substitutes for reduced error in the process description (Cichota and Snow 2008). It is therefore important to consider the intended use when selecting a model for a task. Within the context of this review, a simpler model might be more appropriate for assessing whole-farm implications but useless if considering what management interventions or technologies might reduce volatilisation because for the latter, a more process-based model is needed.

4.3 Model Comparison Studies

Few publications focus on the comparison of some of the available models or modelling approaches used for determining N volatilisation (Cannavo *et al.* 2008). For example Roelle and Aneja (2005) and Corstanje *et al.* (2008) evaluated models that simulate the N cycle and volatilisation with different levels of detail. The results indicate that matching the scale and the model is the best way to get reliable results, thus suggesting there is no model or modelling approach that is suited for all uses. Other comparisons, such as Watson and Atkinson (1999) and Jarvis and Ledgard (2002), focussed on models developed at a relatively similar level of detail but with differing approaches. These variations often reflect the different purposes for the models as well as the different systems the models have been developed to simulate.

4.4 Models for Estimating Volatilisation in Pastoral Systems

A list of several models, with a brief description, is presented below. The list does not include all models available, but presents an overview of the variety, with a focus on tools that may be of interest for use in research or as management tools in the dairy systems typical of Australia or New Zealand. The list starts with simpler models, focussed on volatilisation only, then goes into N budget models which describe the whole farm in a relatively simple way, and finishes with the highly detailed mechanistic models typically used in research and for case studies.

4.4.1 ALFAM

This model is derived from the ALFAM project (www.alfam.dk). It is a semi-empirical model developed based on an extensive dataset of NH₃ volatilisation from slurry and manure collected in several European countries (Søgaard *et al.* 2002). ALFAM uses the Michaelis–Menton equation for describing the variation of NH₃ volatilisation as a function of the TAN content in the slurry. The model is sensitive to slurry type and dry matter content as well as the air temperature, water vapour pressure, and wind speed.

The ALFAM model has been developed using a wide variety of data and the performance of the model has been shown to be good (Søgaard *et al.* 2002). However, the model considers only slurry or manure applications. Being an empirical model calibrated for Europe, ALFAM cannot be readily used elsewhere. The possibility of using it for other N sources and locations needs to be studied further.

4.4.2 Swiss Empirical Model

This model has been developed using regression analyses of data from several studies with slurry in Switzerland (Menzi *et al.* 1998). It uses an empirical relationship between volatilisation and TAN, which is further modified by air temperature and humidity.

It is based on data from Switzerland only and on a limited variation of environmental conditions. It also accounts for slurry or manure applications only.

4.4.3 MAST

MAST (mast.unican.es) is an empirical model developed in the United Kingdom (UK) to examine the impact on N volatilisation losses of changing farm management practices (Ross *et al.* 2002). It is a simple model and accounts for all N sources in dairy farms (slurry, fertilisers, and excreta). However, being an empirical model, its applicability elsewhere is questionable.

4.4.4 OVERSEER

OVERSEER (www.overseer.org.nz) is a nutrient budget model that was developed in New Zealand in the late 1990s as a fertiliser decision support tool. It has evolved since then to become an on-farm resource accounting system (Carey and Metherell 2002; Ledgard *et al.* 2004; Ledgard *et al.* 2001; Ledgard *et al.* 1999b; McDowell *et al.* 2005; Wheeler *et al.* 2003). More recently, OVERSEER has been used for evaluating the environmental impacts of current farming activities, as well as for investigating the effects in changes of farm management (Dragten and Thorrold 2005; Wheeler 2009; Wheeler *et al.* 2008; Wheeler *et al.* 2006). Although several nutrients are accounted for, the N cycle has received the greatest development within OVERSEER. The model's outputs are on an annual basis. In its calculations, OVERSEER includes the effects of nitrification inhibitors. NH₃ emissions from different sources (fertiliser, urine, effluent, etc) are computed using specific empirical factors and are corrected based on location as a proxy for environmental conditions.

The OVERSEER model computes the N budgets for the whole farm, including transfers within the farm. There is a lot of experience behind the model, as it has been developed and used for several years in New Zealand. However, the model is not readily transferable to other countries without a revision of the main location factors. As the

model works primarily on an annual basis, it has a limited capacity to capture processes with significant short-term temporal variation.

4.4.5 Nitrogen Leaching Estimation

The Nitrogen Leaching Estimation (NLE) model was developed in New Zealand (Di and Cameron 2000). It uses semi-empirical relationships to compute a farm N budget and aims to estimate N leaching. Volatilisation is only considered implicitly in the model. The model is based mostly on datasets obtained from experimental work conducted by researchers at Lincoln University and does not appear to have been used elsewhere.

4.4.6 NGAUGE

NGAUGE is a nutrient budget/decision support tool developed for grassland systems in the United Kingdom (Brown *et al.* 2005). The model chiefly focuses on the N cycle at an annual basis, although some of the processes consider within-year variation caused by interactions with weather conditions. The values for NH₃ volatilisation are computed using specific factors for different sources (fertiliser, urine, effluent, etc), which are further adjusted using factors based on environmental conditions (Misselbrook *et al.* 2004).

The model considers the whole farm system, thus allowing the effects of management changes in several aspects of the farm to be investigated. However, the model works mainly on an annual basis at the cost of some sensitivity. The volatilisation module uses a series of factors that have been developed based on data for conditions in the UK. Its applicability to other countries would require investigation.

4.4.7 SimsDAIRY

SimsDAIRY is a modular farm system model developed in the UK with N processes description derived from the NGAUGE model (Brown *et al.* 2005; del Prado *et al.* 2006; del Prado *et al.* 2011). It is thus an empirical model that attempts to simulate the N balance over the whole farm. N volatilisation is estimated using factors which are sensitive to N source and loads.

SimsDAIRY is parameterised for the farm systems of the UK, and thus its use elsewhere requires further investigation. However, it is very sound, being built on extensive work done using several particular models. It also encompasses the whole N cycle over the whole farm, thus being better suited to evaluate trade-offs and pollution swapping.

4.4.8 Sherlock and Goh Model

The Sherlock and Goh model is a mechanistic model that focuses primarily on the volatilisation process. It considers the ion equilibrium in the soil solution, and the

exchange of gases between the soil and the atmosphere (Sherlock and Goh 1984; Sherlock and Goh 1985a; Sherlock and Goh 1985b). The model uses a mechanistic approach that has been used as base for several other models. However, it only focuses on volatilisation, ignoring other aspects of the N cycle that may work in parallel and affect the total N volatilised. The model also requires the pH as an input, which restricts its usability.

4.4.9 Volt'Air Model

Volt'Air is a detailed mechanistic model of the energy balance on the soil surface that focuses heavily on the volatilisation process (Garcia *et al.* 2011). The adsorption of NH_4^+ and ionic equilibrium with NH_3 are considered but transformations such as nitrification are not. Besides the ion equilibrium, the model computes water and heat balances at the soil surface, with which the gas exchange with the atmosphere is calculated (Génermont and Cellier 1997). The model considers the energy balance at the soil surface, thus mechanistically estimating evaporation, which is related to the gas exchange between the soil and the atmosphere. However, the model does not consider N transformations in the soil and it requires pH changes to be supplied as an input (Génermont and Cellier 1997).

4.4.10 APSIM

The APSIM model (www.apsim.info) is a modular framework developed in Australia (Keating *et al.* 2003a). It has been primarily used for cropping systems, and pasture and grazing systems have only recently been included in APSIM. The soil model is mechanistic, based on the CERES model (Probert *et al.* 1998), but not all the N cycle processes are simulated at the same level of detail. In the standard version, volatilisation is not expressly computed. The N inputs are assumed to be 'effective inputs', where volatilisation has been removed *a priori*. However, a volatilisation module has been produced and used to simulated the fate of N in urine-affected areas (Cichota *et al.* 2010a; Cichota *et al.* 2010b). Specific validation of this model is still required. The model accounts for all the major processes in soil as well as plant growth, and paddock and farm management. APSIM has been well tested and successfully used in Australian conditions as well as in many other countries.

4.4.11 FASSET

The FASSET model (www.fasset.dk) uses a mechanistic approach to describe the whole farm system. The description of the volatilisation process is based on the Sherlock and Goh model (Hutchings *et al.* 2007; Hutchings *et al.* 1996). The model considers the whole N cycle, thus enabling the effect of N transformations on NH_3

volatilisation to be accounted for. The model considers the effect of initial pH, but variation in pH after the deposition of an N source to the soil is not simulated.

4.4.12 DNDC

The DNDC model (www.dndc.sr.unh.edu) describes the N and carbon transformation using a mechanistic microbial-oriented approach. Detailed functions compute the biochemical conversion of N in the soil as well as the chemical equilibrium between NH_4^+ and NH_3 , and finally the transport of NH_3 from the soil to the atmosphere (Li *et al.* 1992; Li 2000). The model is quite detailed, with mechanistic descriptions of the N transformation processes in the soil, and has been tested and used extensively. However, the transport processes in the soil and plant growth are treated at a much lower level of detail.

4.4.13 The Water and Nitrogen Management Model

The Water and Nitrogen Management Model (WNMM; www.wnmm.org) was developed to simulate intensive cropping systems in China (Li *et al.* 2005; Li *et al.* 2007). It is a mechanistic model, with N routines based on the CERES model, which was designed to work with a GIS interface. The NH_3 volatilisation process is described using a first-order kinetic decay of TAN at the soil surface (Li *et al.* 2007; Reddy *et al.* 1979).

The model is developed based on well-known models and encompasses the entire N cycle process. It also is linked to a GIS interface which can be used for analyses of spatial variability. The model is dedicated to cropping systems. Tests and development would be required for its use in pastoral systems.

4.4.14 DairyMod/EcoMod

DairyMod (or EcoMod in New Zealand; www.imj.com.au/consultancy/wfsat/wfsat.html) is a farm system model developed for Australian and New Zealand pastoral systems (Johnson 2005; Johnson *et al.* 2008). This model uses mechanistic descriptions of most of the N cycle processes. For NH_3 volatilisation, however, the calculation is simplified. The model considers that a given fraction of the urea in the soil is volatilised. The occurrence of rain can deter the process. The model has a whole-farm approach, and has been successfully used in Australian and New Zealand pastoral systems. However, the volatilisation procedure is much simpler than other processes.

4.4.15 DayCent

DayCent is a daily time-step mechanistic model developed based on the Century model (Parton *et al.* 1998; Parton *et al.* 1994). The volatilisation process is simulated in a greatly simplified way, using a soil texture-dependent proportion of the applied NH_4^+ (Del Grosso *et al.* 2008). The model is built from long-term experimentation and model

development. Its strength lies in the C cycle and on N₂O emissions. Volatilisation has only recently been included in the model and may require additional validation and/or development.

4.4.16 AGRIN

AGRIN is a detailed model developed by Agriculture and Agri-Food Canada that computes gaseous losses from soils on an hourly basis. Its focus is on monitoring NH₃ emissions from slurry applied to bare soil (Beuning *et al.* 2008). AGRIN uses descriptions of microbiological activity and chemical kinetics to estimate the amount of NH₃ in the soil, and uses gas transport theory to compute the amount volatilised. This is a mechanistic model with high temporal resolution, which is thus able to capture variations in the volatilisation process within a day. However, the model focuses on slurry and the soil processes only; plant growth is not considered.

4.4.17 Rachhpal-Singh and Nye Model

The mechanistic Rachhpal-Singh and Nye model has a large degree of complexity, developed to simulate the physical and biochemical processes in the soil at a high temporal resolution in order to estimate NH₃ volatilisation (Kirk and Nye 1991; Rachhpal-Singh and Nye 1986a; Rachhpal-Singh and Nye 1986b; Rachhpal-Singh and Nye 1986c; Rachhpal-Singh and Nye 1988). This is a very detailed model that requires a large amount of inputs and considerable computing power. It may be appropriate for proof of concept and other research studies.

5. Experimental Information and Potential Data Sources

A selection of datasets that have the potential to be further used for testing and development of models is listed below. Compiling data from different experiments could provide further insights into the volatilisation process and may identify the gaps in the description of this process. The focus here is on experiments that collected data over time, thus capturing N dynamics, and in the pastoral systems of Australia and New Zealand. The list is not large, reflecting the limited amount of work as well as the uncertainty about the reliability of some older datasets (mostly related to the measuring technique). To the list is added a series of international papers which contain information about the base processes and drivers of N volatilisation and thus can be used independently of the farming system.

5.1 Australian and New Zealand Agricultural Systems

5.2 Overview

There is only a limited amount of data for NH₃ volatilisation from pastoral systems in Australia, and only a bit more for cropping systems. The lack of data is also a reality for New Zealand, although measurements from pastures are more prominent. In Australia, values of NH₃ volatilisation have been obtained using indirect estimation or, more recently, micrometeorological methods. The latter methods are considered to be the most reliable by far. For New Zealand, most of the data were obtained using chamber methods and only more recently have micrometeorological methods been used. Although chamber methods can be considered adequate for comparative tests, the estimation of actual ammonia losses is not as reliable as for the open methods.

Data for total ammonia losses estimates in Australia can be found in various papers (Freney *et al.* 1992; Pakrou and Dillon 1995; Suter *et al.* 2011; Thompson and Fillery 1997; Thompson and Fillery 1998; Vallis *et al.* 1982; Vallis *et al.* 1985), but datasets that have time series as well as soil and environmental measurements are rare. These detailed datasets are of interest, as they can be used for understanding the factors affecting volatilisation as well as for supporting model development. A summary of the main publications with promising datasets are given below.

5.2.1 Prasertsak *et al.* (2001)

This consists of data from an experiment conducted in a dairy farm close to Millaa Millaa, Northern Queensland (Prasertsak *et al.* 2001). Nitrogen mass balance was followed in a paddock without grazing after a fertiliser application in August. NH₃ volatilisation was determined by the micrometeorological mass balance method.

5.2.2 Eckard *et al.* (2003)

Field experiments were performed at a dairy farm in Ellinbank, Victoria, Australia, between May 1998 and March 2001 (Eckard *et al.* 2003). Plots with grazing cows were subjected to three fertiliser treatments (0 and 200 kg N/ha as urea or ammonium nitrate). Basic soil and plant variables were recorded as well as gaseous losses. NH₃ volatilisation was measured using the micrometeorological mass balance method.

5.2.3 Turner *et al.* (2010)

The work for Turner's PhD thesis covers at least five trials where NH₃ measurements were made. These trials included testing different measuring methods as well as the determination of ammonia losses from fertiliser and animal excreta (Turner 2010; Turner *et al.* 2010). Two experiments were conducted on pastures at Kyabram Dairy Centre,

Victoria. In one experiment, in February 2004, a grazed paddock received 50 kg N/ha of urea followed by 50 mm of irrigation. In the other experiment, the paddock received 50 kg N/ha after grazing and irrigation three days after the fertiliser was applied. Measurements of NH₃ volatilisation were calculated following the BLS model. A mass balance using ¹⁵N was also performed on pasture, litter, and soil.

5.2.4 Sherlock *et al.*

This work groups a series of publications with data obtained at field or in lysimeter experiments, most of which were conducted in pastoral systems, using animal excreta, fertiliser, and effluent (Black *et al.* 1987a; Black *et al.* 1987b; Black *et al.* 1989; Black *et al.* 1985; Sherlock 1984; Sherlock *et al.* 1995; Sherlock and Goh 1984). These experiments were performed at Lincoln University, New Zealand, in the mid-1980s and early 1990s, and most of them used the dynamic chamber technique to measure NH₃ volatilisation.

5.2.5 Ledgard *et al.*

A series of farmlet trials were run where the fate of N in dairy farms was assessed (Ledgard 2001; Ledgard *et al.* 1999a; Ledgard *et al.* 1996). The treatments included different land use intensities and were conducted over three years. However, most of the published results are summarised in terms of the N budget (annual totals). Volatilisation was determined by a micrometeorological method.

5.2.6 Meneer *et al.* (2005)

This was a lysimeter experiment simulating urine depositions of dairy cows in a pumice soil. The experiment was performed in Hamilton, New Zealand, in the autumn of 2004 (Meneer *et al.* 2008). It included the addition of nitrification and urease inhibitors. Measurements of ammonia were performed using the dynamic chamber technique.

5.2.7 Zaman *et al.*

The objective of these experiments was to test the viability of employing urease and/or nitrification inhibitors to reduce N losses from fertiliser and urine deposited in the soil (Dawar *et al.* 2011; Zaman and Blennerhassett 2010; Zaman *et al.* 2008; Zaman *et al.* 2009). NH₃ volatilisation was determined using dynamic chambers.

5.2.8 Laubach *et al.* (2012)

Laubach *et al.* (2012) combined measurement of NH₃ losses from a pastoral field using micrometeorological methods and modelling. The experiment was conducted at Lincoln University, New Zealand, in February and March 2010.

5.2.9 Smith *et al.* (1996)

Experiments performed in New South Wales in the mid-1990s looked at the application of urban sewage and urea (Smith *et al.* 1996). Data were measured using a micrometeorological technique as well as being determined indirectly based on pH and soil N concentrations.

5.3 International Agricultural Systems

5.3.1 Singurindy *et al.*

(Singurindy *et al.* 2008; Singurindy *et al.* 2006) performed laboratory experiments at Cornell University, NY, USA, to study the effect of soil texture on gaseous emissions from urine-treated soils.

5.3.2 Saarijärvi *et al.* (2006)

(Saarijärvi *et al.* 2006) studied the emission of NH₃ from pastures affected by dung or urine depositions. Two experiments were conducted in Finland and volatilisation was measured over 5–6 days at sub-daily time-steps.

5.3.3 Whitehead *et al.*

Several experiments were conducted at the Institute of Grassland and Environmental Research, England, during the late 1980s and early 1990s. The experiments measured N transformations and losses, including NH₃ volatilisation, from grassland after the application of urine, slurry, and fertiliser (Lockyer and Whitehead 1990; Whitehead and Bristow 1990; Whitehead and Raistrick 1990; Whitehead and Raistrick 1991; Whitehead and Raistrick 1992; Whitehead and Raistrick 1993).

5.3.4 Reviews with Data Compilation

These are published papers that review, with different levels of detail, the amount of N loss from several farming systems, including NH₃ volatilisation. In general, they include data from several countries and might be of interest to compare a broad set of data with agricultural-based measurements. These papers include Ball and Ryden (1984) and Fillery (2001) for Australia/New Zealand; Sommer *et al.* (2004) and Sintermann *et al.* (2011) for Europe; and Hristov *et al.* (2011) for the USA.

6. Recommendations for Further Work

A considerable number of studies have focussed, at least in part, on NH₃ volatilisation from pastoral systems. However, the information is patchy, with lots of data about slurry or manure application in Europe, and sporadic measurements of losses from pastoral systems in Australia or New Zealand. The basic processes leading to volatilisation

losses are reasonably well understood and the factors directly affecting the rate of N losses are known. However, the dynamics and the controls of some of these factors and how they interact quantitatively require more clarification.

Our recommendations for further work, which we will elaborate on below, are for:

1. Better quantitative understanding of the dynamics of pH in the soil;
2. Better quantitative understanding of the controls of transfer from the soil to the atmosphere;
3. More information about the re-deposition processes;
4. Obtaining and compiling the experimental results from Eckard *et al.* (2003), Turner (2010), and the series published by Sherlock *et al.* in such a form as to make the data available for model development or validation;
5. Additional targeted experimental work where the complete N cycle is accounted for;
6. The further development and testing of two models:
 - a. one model that accounts for the processes at a relatively high level of detail for use in research and case studies to develop or test new farming practices, and
 - b. a second model (which may be developed from the more detailed model) that would be a simpler decision support tool to aid management decisions and policy making;
7. Further experimental work to employ open methods for measurement at the field scale and chamber methods for more detailed studies, e.g. at small spatial scales or in the laboratory.

To describe the emission process properly, we still need to improve our understanding of the controls on soil pH, especially following the addition of urea/urine and slurry. The dynamics of pH in the soil are a major determinant of the magnitude and duration of NH₃ emissions and we still do not have a reliable way to simulate the variation of these dynamics in different soils after application of urine/urea.

Another factor we need to better understand the controls of is the transfer coefficient of NH₃ from the soil surface to the atmosphere. This would include determining the thickness of the top layer of the soil that is the active NH₃ emitter and the effect of soil cover by plants or residues on the exchange rate. The exchange process has been described by Equations 6 or 7, where the parameter k_v controls the exchange between the soil and the atmosphere. This parameter combines the transport controls created by atmospheric resistance and diffusion through the soil. The influencing factors are not understood well, which makes finding values for this parameter somewhat difficult.

It is also necessary to understand the controls on the deposition of atmospheric NH₃ better. This may be important to determine net losses and transfers over large areas (at the whole-farm or catchment level) and thus improve our estimates of the indirect greenhouse gas emissions from volatilisation. Another reason why we need a better understanding of the balance between NH₃ emission and deposition is to better describe the N dynamics on areas affected by urine patches. Emissions from the patch area, which tend to be high, may be deposited in nearby areas that are still within the paddock, so the overall loss might not be so large.

A limited number of experiments have been conducted on NH₃ volatilisation and in only relatively few locations. These represent only snapshots of the range of management and environmental conditions that farm systems are subject to. This paucity of data makes it difficult to extrapolate results and may hinder the development of better management practices to avoid volatilisation losses. Modelling can help substantially with this issue when undertaken in collaboration with a measurement effort to ensure and prove their reliability. Regarding the farm systems of Australia and New Zealand, the works by Eckard *et al.* (2003), Turner (2010), and the series published by Sherlock *et al.* are the best potential data sources for model validation available at the moment.

As well as carrying out experiments to resolve the issues discussed above, it would be desirable to have some experiments where the complete N cycle is accounted for. This is because volatilisation is usually a small flux within the total cycle, and it is plausible that, during modelling a good simulation of N volatilisation is at the cost of a poor simulation of another process. The use of a ¹⁵N tracer with the experiments would certainly help constrain these types of errors.

Most experiments where volatilisation was determined do not have measurements of other gaseous losses, leaching, and storage in the soil and plant uptake. Accounting for all the pools and flows of the N cycle is essential to understand trade-offs at the paddock/farm scale as well as to understand pollution swapping better. This is important when changing management or implementing mitigation actions (nitrification inhibitors, for instance). This is necessary to ensure that optimising the farm system to reduce volatilisation losses will not cause an increase in other losses.

To obtain full benefit from these experiments, they should be coupled with modelling development and validation. Tested models with the right level of complexity can then be used to investigate potential ways to reduce losses and increase N use efficiency. It would be interesting – or even necessary – to have models developed at a minimum of two levels of complexity: one model would account for the processes at a relatively high level of detail for use in research and case studies to develop or test new farming practices; the second model would be for simpler decision support tools to aid

management and policy making. This second model may be developed from the more detailed model as well as from experimental data. It is not essential that only one or two models should be favoured exclusively, but a coordinated effort would make better use of resources. We would advocate for development or improvement of models that account for the processes, at the patch or whole-farm scale, that affect volatilisation rather than just the volatilisation process itself. Such models will be more suited for exploring management options that lower the losses by volatilisation and the losses from the whole farm.

Based on the literature, the open methods are better suited for determining NH₃ losses from the field. They have been reliably used in different systems and conditions, and can cope well with the spatial variability of pastoral systems. Employing the IHF or BLS methods using ammonia denuders seems to be the best technique at present. However, the use of optical methods to determine NH₃ concentrations is highly appealing and their development should be encouraged. These methods have a high temporal resolution and can measure different gases at once, which is very important to understand whole systems and pollution swapping. The use of optical methods can also improve the study of relatively small areas and thus capture the variability within a paddock (e.g. urine patches), which is not possible using other open methods. The use of the chamber technique may not be ideal for field determination of volatilisation losses but can be very useful for more detailed studies, such as in the laboratory. This is also the case when capturing spatial variability, such as that derived from the deposition of urine patches.

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Appendix – Summary of the Literature Consulted

For reference, a table listing the pertinent literature on NH₃ volatilisation, encompassing reviews, measurements and modelling, is given below. The table contains a short summary of the main subject of each paper, and the locations of the experiments or modelling or the origin of most literature reviews. The table also indicates the N source and loads used in the articles, the land use, and the scale to which the measurements or the modelling were tuned. Finally, there is an indication of the main measurement technique or the modelling approach; this column is simplified to give only an indication of the methodology used. To shorten the table, some contractions have been used in addition to those already explained in the main text (e.g. IHF):

- For the subject of the article:
 - loss meas: measurements of N losses;
 - meas tech: presentation of measurement technique;
 - tech comp: comparison between measurement techniques;
 - model: presentation or testing of models;
 - review: literature review;
- For N source:
 - fert: N fertiliser
 - UAN: urea–ammonium nitrate;
 - AN: ammonium nitrate;
 - CAN: calcium–ammonium nitrate;
 - AS: ammonium sulphate;
 - MAP: mono-ammonium phosphate;
 - DAP: di-ammonium phosphate;
 - ABC: ammonium bicarbonate;
- For location:
 - Palm Nth: Palmerston North, New Zealand;
 - Qld: Queensland, Australia;
 - NZ: New Zealand;
 - Aus: Australia;
 - NT: Northern Territory, Australia;
 - Vic: Victoria, Australia;
 - SA: South Australia
 - WA: Western Australia;
- For technique:
 - dyn. chamber: dynamic chamber;
 - micromet: micrometeorological;
 - atm mass balance: atmospheric mass balance;

- eq. conc.: equilibrium concentration;
- General abbreviations:
 - n/a: not available;
 - n/r: non relevant;
 - n/s: not stated;

In general, volatilisation measurements made using dynamic chambers used acid traps to obtain NH₃ concentrations; thus whenever dynamic chambers were used, the acid employed in the traps is stated. Similarly, for Ferm tubes and shuttles, the acid type is stated in the last column of the table.

Table 1. Summary of the literature consulted

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Doak 1952)	Palm Nth	loss meas	urine	484 kg/ha	pasture	field, plot, lab	n/a
(Ball <i>et al.</i> 1979b)	Palm Nth	loss meas	urine	300, 600 kg/ha	pasture	plot	dyn. chamber (H ₂ SO ₄)
(Ferm 1979)	Sweden	meas tech	NH ₃ and NH ₄	n/r	n/r	lab	Ferm tubes (oxalic acid)
(Reddy <i>et al.</i> 1979)	USA	model	slurry	n/r	n/r	plot, field	mechanistic
(Carran <i>et al.</i> 1982)	Gore, NZ	loss meas	urine	0, 300 kg/ha	pasture	plot	dyn. chamber (H ₂ SO ₄)
(Vallis <i>et al.</i> 1982)	south Qld, Aus	loss meas, meas tech	urine	370–480 kg/ha	pasture	plot	dyn. chamber (H ₂ SO ₄)
(Wilson <i>et al.</i> 1983)	Aus	meas tech	fert (urea)	n/s	pasture	field	micromet (IHF; TPS), acid trap (H ₂ SO ₄)
(Ball and Ryden 1984)	NZ mostly	review, compilation	urine, dung	n/r	pasture	field	n/r
(Black <i>et al.</i> 1984)	Lincoln, NZ	loss meas	fert (urea, DAP, ; AS) and urine	30 kg/ha for fert	pasture	plot	dyn. chamber (H ₂ SO ₄)
(Sherlock 1984)	Lincoln, NZ	loss meas, model	urine, urea	500 kg/ha	pasture	plot	dyn. chamber (H ₃ BO ₃)
(Sherlock and Goh 1984)	Lincoln, NZ	loss meas	urine, urea	500 kg/ha	pasture	plot	dyn. chamber (H ₃ BO ₃)
(Theobald and Ball 1984)	Palm Nth	loss meas	fert (urea, AS)	50, 200 kg/ha	pasture	plot	n/s
(Black <i>et al.</i> 1985)	Lincoln, NZ	loss meas	fert (urea, DAP; AS, CAN)	30 kg/ha	pasture	plot	dyn. chamber (H ₂ SO ₄)
(Leuning <i>et al.</i> 1985)	Canberra, Aus	meas tech	NH ₃ , urea	50 kg/ha	pasture	field, lab	micromet, shuttle (oxalic acid) and IHF
(Ryden and Lockyer 1985)	UK	tech comp	urea	200 kg/ha	pasture	plot, field	micromet (atm mass balance), wind tunnel (n/s)
(Sherlock and Goh 1985a)	NZ	model	urine, urea	n/r	non-specific	plot, field	mechanistic, semi-empirical
(Sherlock and Goh 1985b)	NZ	loss meas, model	urine	n/s	pasture	plot	n/r
(Vallis <i>et al.</i> 1985)	NT, Aus	loss meas	urine	150 kg/ha	pasture	plot	indirect – N mass balance
(Ellington 1986)	Vic, Aus	loss meas	fert (urea, AS)	0, 56, 112 kg/ha	bare	plot	indirect – mass balance

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Rachhpal-Singh and Nye 1986a)	UK	model	urea/urine	n/r	non-specific	plot	mechanistic
(Rachhpal-Singh and Nye 1986b)	UK	loss meas; model	fert (urea)	n/a	bare	pot, lab	n/a
(Rachhpal-Singh and Nye 1986c)	UK	model	fert (urea)	n/a	non-specific	plot	n/r
(Black <i>et al.</i> 1987b)	Lincoln, NZ	loss meas	fert (urea)	100 kg/ha	pasture	plot	dyn. chamber (H ₂ SO ₄)
(Black <i>et al.</i> 1987a)	Lincoln, NZ	loss meas	fert (urea)	30 kg/ha	pasture	plot	dyn. chamber (H ₂ SO ₄)
(Hargrove <i>et al.</i> 1987)	USA	loss meas, tech comp	fert (urea)	100 kg/ha	bare, mulch	plot	dyn. chamber (¹⁵ N balance)
(Rachhpal-Singh 1987)	India	loss meas, model	fert (urea)	n/s	bare	pot, lab	n/s
(Ryden <i>et al.</i> 1987)	UK	loss meas, meas tech, review	urine, dung, slurry, fert (urea, AN)	various	pasture, pond, building	plot, field, country	micromet (atm mass balance); wind tunnel – acid trap (H ₂ SO ₄)
(Ferguson <i>et al.</i> 1988)	USA	loss meas; tech comp	fert (urea; UAN)	120, 200 kg/ha	bare	plot, field	micromet (atm mass balance); dyn. chamber (H ₂ SO ₄)
(Rachhpal-Singh and Nye 1988)	UK	loss meas, model	fert (urea)	n/a	bare	plot	n/a
(Thomas <i>et al.</i> 1988)	UK	loss meas	urine	400–520 kg/ha	pasture	field	indirect – mass balance
(Black <i>et al.</i> 1989)	Lincoln, NZ	loss meas, tech comp	fert (urea, AS)	100 kg/ha	wheat	plot, field	micromet (IHF), dyn. chamber (H ₂ SO ₄)
(Genfa <i>et al.</i> 1989)	USA	meas tech	NH ₃	n/r	n/r	lab	denuder – diffusion scrubber
(Sherlock <i>et al.</i> 1989)	Lincoln, NZ	loss meas, tech comp	fert (urea)	100kg/ha	pasture	field	micromet, IHF, ZINST + shuttle
(Gameh <i>et al.</i> 1990)	USA	loss meas	fert (urea)	120 kg/ha	bare	pot, lab	dyn. chamber (H ₃ BO ₃)
(Hatch <i>et al.</i> 1990)	UK	loss meas, tech comp	graze + urea	various	pasture	field	micromet – acid trap (H ₃ PO ₄), Ferm tubes (oxalic acid)
(Lockyer and Whitehead 1990)	UK	loss meas	urine	192–738 kg/ha	pasture	plot	wind tunnel (H ₃ PO ₄ or H ₂ SO ₄)

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Velthof <i>et al.</i> 1990)	Netherlands	loss meas	fert (urea, CAN)	various	pasture	plot	wind tunnel (H ₃ PO ₄)
(Whitehead 1990)	UK	review, compilation	urine, dung, fert (various)	n/r	pasture	field, farm	n/r
(Whitehead and Bristow 1990)	UK	loss meas	urine	740 kg/ha	pasture	plot	wind tunnel (¹⁵ N balance)
(Whitehead and Raistrick 1990)	UK	loss meas	fert (urea, DAP, AN, AS, MAP)	n/s	bare	pot, lab	dyn. chamber (n/a)
(Jarvis <i>et al.</i> 1991)	UK	loss meas	graze, clover, urea	n/r	pasture	field	micromet, atm mass balance (H ₃ PO ₄)
(Kirk and Nye 1991)	UK	model	fert (urea)	n/s	n/r	plot, field	mechanistic
(Sommer <i>et al.</i> 1991)	Denmark	loss meas	slurry	various	various	plot, field	n/a
(Whitehead and Raistrick 1991)	UK	loss meas	urine	~22 kg/ha (?)	bare	pot, lab	dyn. chamber (H ₂ SO ₄)
(Bussink 1992)	Netherlands	loss meas	graze + fert (CAN)	various	pasture	field; farm	micromet- trap (H ₃ PO ₄)
(Freney <i>et al.</i> 1992)	Qld, Aus	loss meas	fert (urea, AS)	160 kg/ha	sugarcane	field	micromet, shuttle (oxalic acid)
(Li <i>et al.</i> 1992)	USA	model	fert (various); residues	n/r	various	plot, field	mechanistic
(Schjoerring <i>et al.</i> 1992)	Denmark	meas tech	NH ₄ solution	n/r	n/r	field	passive flux sampler (oxalic acid); acid trap (H ₂ SO ₄)
(Sugimoto <i>et al.</i> 1992)	Palm Nth	loss meas	dung	0, 65, 130, 200 kg/ha	pasture	plot	dyn. chamber (H ₂ SO ₄)
(Whitehead and Raistrick 1992)	UK	loss meas	urine	~22 kg/ha (?)	bare, pasture	pot, lab	dyn. chamber (H ₂ SO ₄)
(Haynes and Williams 1993)	NZ	review, compilation	urine, dung, slurry	various	pasture	plot, field	n/r
(Olesen and Sommer 1993)	Denmark	loss meas, model	slurry	n/r	tank	n/r	semi-mechanistic model, wind tunnel – acid trap (H ₃ PO ₄)
(Whitehead and Raistrick 1993)	UK	loss meas	urine	265 kg/ha	bare	pot, lab	dyn. chamber (H ₂ SO ₄)

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Bussink 1994)	Netherlands	loss meas, upscale	graze + fert (CAN)	various	pasture	field, farm, country	micromet – acid trap (H ₃ PO ₄)
(Parton <i>et al.</i> 1994)	USA	model	n/r	n/r	n/r	field	n/r
(Sommer and Jensen 1994)	Denmark	loss meas	urea, DAP, AS, CAN	80–120 kg/ha	wheat	plot	wind tunnel (H ₃ PO ₄)
(Svensson 1994)	Sweden	meas tech	manure, fert (n/a)	n/a	various	plot, field	dyn. chamber (n/s), passive diffusion, denuder
(Watson <i>et al.</i> 1994)	Ireland	loss meas	fert (urea)	100 kg/ha	bare	pot, lab	dyn. chamber (H ₃ PO ₄)
(Weier 1994)	Aus	review	various	n/r	various	various	n/r
(Hutchings and Kristensen 1995)	UK, Denmark	model	graze; urine	n/r	pasture	field	semi-mechanistic
(Nakano <i>et al.</i> 1995)	Japan	meas tech	NH ₃	various	n/r	lab	optical method – fluorescent tape
(Pakrou and Dillon 1995)	SA	loss meas	urine	653–1366 kg/ha	pasture	field, lysimeter	indirect (¹⁵ N mass balance)
(Sherlock <i>et al.</i> 1995)	Lincoln, NZ; NSW	loss meas, tech comp	urine; urea	500, 100 kg/ha	crop, pasture	field	micromet, IHF (shuttle – oxalic acid indirect method (pH, TAN, wind))
(Fox <i>et al.</i> 1996)	USA	loss meas, tech comp	fert (urea, UAN)	134 kg/ha	crop	field	micromet, shuttle (oxalic acid)
(Hutchings <i>et al.</i> 1996)	UK, Denmark	model	NH ₄	n/r	generic	plot, field	semi-mechanistic
(Ledgard <i>et al.</i> 1996)	Hamilton, NZ	loss meas	graze + urea	various	pasture	field	micromet, shuttle (oxalic acid)
(Smith <i>et al.</i> 1996)	NSW	loss meas, tech comp	sewage	80 kg/ha	pasture	field	micromet, with shuttle or passive sampler; indirect method (TAN, pH, wind)
(Van Der Weerden <i>et al.</i> 1996)	UK, France	loss meas, tech comp	NH ₄ Cl	n/r	n/r	lab	wind tunnel (H ₃ PO ₄ or H ₃ BO ₃)
(Carey <i>et al.</i> 1997)	Lincoln, NZ	loss meas	slurry	0, 200, 400 kg/ha	pasture	lysimeter	dyn. chamber (H ₂ SO ₄)
(Crespo <i>et al.</i> 1997)	Cuba	loss meas	dung	n/a	n/a	n/a	n/a
(Génemont and Cellier 1997)	France	model	slurry	n/r	pasture, bare	plot, field	mechanistic

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Hack-ten Broeke and van der Putten 1997)	Netherlands	review	graze + fert	n/r	pasture, crop	farm	N budget; ups cale
(Thompson and Fillery 1997)	WA	loss meas	urine, dung, stubble	150, 300, 46, 18 kg/ha	pasture, wheat	plot	indirect (¹⁵ N mass balance)
(Van Der Weerden and Jarvis 1997)	UK	loss meas	fert (urea, AN, CAN)	90, 70, 120 kg/ha	pasture	plot	wind tunnel (H ₃ PO ₄)
(Buckley <i>et al.</i> 1998)	USA	meas tech	NH ₃	n/r	n/r	lab	optical method – fluorescence
(Bussink and Oenema 1998)	Netherlands	review	various	n/r	various	farm, field	N budget
(Génemont <i>et al.</i> 1998)	France	loss meas, tech comp	slurry	114 kg/ha	bare	field	micromet (atm mass balance; AGM), acid trap (H ₂ SO ₄ , chemiluminescence)
(Menzi <i>et al.</i> 1998)	Switzerland	loss meas, model	slurry	~50–70 kg/ha	pasture, crop	field	micromet, passivel sampler (HCl), empirical model
(Parton <i>et al.</i> 1998)	USA	model	n/r	n/r	various	field	semi-mechanistic
(Petersen <i>et al.</i> 1998)	Denmark	loss meas	urine, dung	n/s	pasture	plot, field	wind tunnel (H ₃ PO ₄)
(Probert <i>et al.</i> 1998)	Aus	model	n/r	n/r	n/r	plot, field	mechanistic
(Thompson and Fillery 1998)	WA	loss meas	urine	46–460 kg/ha	pastur,; wheat	plot	indirect (¹⁵ N mass balance)
(Vandré and Kaupenjohann 1998)	Germany	loss meas, meas tech	slurry	various	crop	plot; field	passive sampler with standard emitter, acid trap (H ₂ SO ₄)
(Bronson <i>et al.</i> 1999)	WA	loss meas	urine	205 kg/ha	bare	plot	indirect (¹⁵ N mass balance)
(He <i>et al.</i> 1999)	USA	loss meas	fert (urea, ABC, AS, AN)	100–300 kg/ha	bare	pot, lab	dyn. chamber (sponge with H ₃ PO ₄)
(Ledgard <i>et al.</i> 1999a)	Hamilton, NZ	loss meas	graze + urea	various	pasture	field	micromet, shuttle (oxalic acid)
(Ledgard <i>et al.</i> 1999b)	NZ	model	various	n/r	various	field, farm	semi-empirical
(Loubet <i>et al.</i> 1999a)	France	meas tech	CO ₂	various	n/r	plot	wind tunnel
(Loubet <i>et al.</i> 1999b)	France	meas tech	CO ₂	n/r	n/r	lab	wind tunnel
(Silva <i>et al.</i> 1999)	Lincoln, NZ	loss meas	urine, slurry, urea	200–1400 kg/ha	pasture	lysimeter	none

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Watson and Atkinson 1999)	UK	model	various	n/r	various	farm	N budget
(Aneja <i>et al.</i> 2000)	USA	loss meas	slurry	n/r	pond	plot	dyn. chamber, chemiluminescence
(Carran <i>et al.</i> 2000)	Palm Nth	meas tech	urine, urea	various	pasture	plot	passive sampler (oxalic acid)
(Di and Cameron 2000)	Lincoln, NZ	model	various	n/r	pasture	farm, field	empirical
(Li 2000)	USA	model, loss meas	fert (various), residues	n/r	crop	plot, field	mechanistic
(Misselbrook <i>et al.</i> 2000)	UK Europe	model, inventory	various	n/r	various	farm, country	inventory, emission factors
(Paramasivam <i>et al.</i> 2000)	USA	model, loss meas	fert (AN)	n/a	bare	plot	none
(Phillips <i>et al.</i> 2000)	UK	review, meas tech	slurry, building	various	building	field	various
(Sommer and Olesen 2000)	Denmark	loss meas, model	slurry	various	pasture, crop; bare	field	micromet, passive flux sampler (oxalic acid)
(White <i>et al.</i> 2000)	SA	loss meas	graze	n/r	pasture (annual and perennial)	field	passive flux sampler
(Cabrera <i>et al.</i> 2001)	USA	meas tech	NH ₄ Cl	n/r	bare	plot	dyn. chamber/wind tunnel, acid trap (H ₂ SO ₄)
(Cookson <i>et al.</i> 2001)	Lincoln, NZ	loss meas	fert (urea)	50–200 kg/ha	grass seed	lysimeter	indirect (mass balance)
(Fillery 2001)	Aus	review	graze	n/r	pasture	field	n/r
(Harrison and Webb 2001)	UK	review	fert (various)	n/r	various	n/r	n/r
(Huijsmans <i>et al.</i> 2001)	Netherlands	review, loss meas	manure	various	various	plot, field	n/r
(Kebreab <i>et al.</i> 2001)	UK	model	animal	n/r	various	n/r	mechanistic
(Ledgard 2001)	NZ mostly	review	graze	n/r	pasture	field, farm	n/r
(Ledgard <i>et al.</i> 2001)	NZ	model	graze	n/r	pasture	field, farm	semi-empirical
(Misselbrook and Hansen 2001)	UK, Denmark	loss meas, tech comp	urea; slurry; manure	138, 50, 4.3kg/ha	pasture	field	micromet, JTI (with PDS) and IHF (oxalic or tartaric acid)

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Ni and Heber 2001)	USA	review, meas tech	various	n/r	building	n/r	various
(Phillips <i>et al.</i> 2001)	UK	review, meas tech	slurry, manure, etc	n/r	building	field	various
(Prasertsak <i>et al.</i> 2001)	North Qld	loss meas	fert (urea)	115 kg/ha	pasture	plot, field	micromet, shuttle (oxalic acid)
(Smith <i>et al.</i> 2001)	SA	loss meas	slurry + fert (urea)	15–2500 kg/ha	crop	field	micromet (n/s)
(Sommer <i>et al.</i> 2001)	Denmark	loss meas, tech comp	slurry + pigs	n/s	pasture	plot, field	micromet, dyn. chamber, active and passive denuders (n/s)
(Cameron <i>et al.</i> 2002)	Lincoln, NZ	loss meas	effluent, urine	300, 600 kg/ha (effluent); 1000 kg/ha (urea)	pasture	lysimeter	dyn. chamber (H ₂ SO ₄)
(Carey and Metherell 2002)	NZ	model	various	n/r	nr	field	Ca and Mg model
(Delgado 2002)	USA mostly	review	fert (various)	n/r	crop, pasture	n/r	n/r
(Di <i>et al.</i> 2002)	Lincoln, NZ	loss meas	effluent, urine	400 kg/ha (effluent); 1000 kg/ha (urea)	pasture	lysimeter	dyn. chamber (H ₂ SO ₄)
(Follett and Delgado 2002)	USA	review, inventory	various	n/r	various	field, farm, country	n/r
(Jarvis and Ledgard 2002)	UK, NZ	model	graze	n/r	pasture	farm	N budget, inventory
(Kebreab <i>et al.</i> 2002)	Netherlands	model	animal	n/r	n/r	animal	mechanistic
(Milligan <i>et al.</i> 2002)	NZ	meas tech	synthetic urine	1000 kg/ha	pasture	lab	dyn. chamber, SIFT-MS
(Mount <i>et al.</i> 2002)	USA	meas tech	various, slurry	various	pasture; building	plot, field	optical method – DOAS
(Roelcke <i>et al.</i> 2002)	China	loss meas, meas tech	fert (urea, ABC)	100, 200 kg/ha	crop	plot	Dräger tube
(Ross <i>et al.</i> 2002)	UK	model	various	n/r	various	farm	N budget
(Sherlock <i>et al.</i> 2002)	Lincoln, NZ	loss meas, tech comp	slurry	366 kg/ha	pasture	field	micromet, atm mass balance + shuttle (oxalic acid), also Fem tubes

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Søgaard <i>et al.</i> 2002)	Europe	model	slurry, manure	n/r	various	field	empirical; semi-mechanistic
(Bowatte 2003)	Palm Nth	loss meas	urine	200, 400; 280, 560 kg/ha	pasture	plot	passive sampler (oxalic acid)
(Clough <i>et al.</i> 2003)	NZ	loss meas	synthetic urine	0–1000 kg/ha	bare	pot., lab	spectroscopy (SIFT-MS)
(Dalal <i>et al.</i> 2003)	Aus	review	various	n/r	various	n/r	n/r
(de Vries <i>et al.</i> 2003)	Netherlands	review	various	n/r	various	farm, country	n/r
(Eckard <i>et al.</i> 2003)	Vic	loss meas	graze, fert (urea, AN)	various	pasture	field; farm	micromet, shuttles (oxalic acid)
(Keating <i>et al.</i> 2003a)	Aus	model	n/r	n/r	n/r	plot, field	mechanistic
(Kroeze <i>et al.</i> 2003)	Netherlands	review	various	n/r	various	field, farm	n/r
(Leteme <i>et al.</i> 2003)	France	loss meas	urine, fert (n/s)	n/s (urine); 100, 300 kg/ha (fert)	pasture	field	n/a
(Stout 2003)	USA	loss meas	urine	440, 880, 1320 kg/ha	pasture	lysimeter	none
(Wheeler <i>et al.</i> 2003)	NZ	model	various	n/r	pasture	field, farm	N budget
(Bolan <i>et al.</i> 2004)	NZ mostly	review	graze	n/r	pasture	various	n/r
(Di and Cameron 2004)	Lincoln, NZ	loss meas	urine, urea	1000 kg/ha (urine), 25kg/ha (fert)	pasture	lysimeter	dyn. chamber (H ₂ SO ₄)
(Edmeades 2004)	NZ	review	urine; urea	n/r	pasture	various	n/r
(Emmenegger <i>et al.</i> 2004)	Switzerland	tech comp	car exhaust	n/r	n/r	field	various (acid traps, denuders, optical devices)
(Ferreira <i>et al.</i> 2004)	Brazil	review	urine	n/r	pasture	plot	none
(Ledgard <i>et al.</i> 2004)	NZ	model	various	n/r	pasture	field, farm	N budget
(Misselbrook <i>et al.</i> 2004)	UK	model	fert (various)	n/r	various	field, farm, country	empirical 'process-based'
(Saggar <i>et al.</i> 2004)	NZ	review	urine, dung	n/r	pasture	plot	n/r
(Singh <i>et al.</i> 2004)	NZ	loss meas	urine, urea	600, 100 kg/ha	pasture	lysimeter	dyn. chamber (H ₂ SO ₄)
(Sommer <i>et al.</i> 2004)	Europe mostly	review	fert (various)	n/r	crops	various	n/r

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Bolado Rodríguez <i>et al.</i> 2005)	Spain	loss meas, model	fert (urea)	0.2, 2 g/kg soil	bare	pot; lab	dyn. chamber (H ₃ BO ₃)
(Brown <i>et al.</i> 2005)	UK	model	various	n/r	various	field, farm	empirical
(Flesch <i>et al.</i> 2005)	USA	meas tech	slurry	n/r	building	field	BLS – laser
(Gates <i>et al.</i> 2005)	USA	meas tech	poultry	n/r	n/r	building	Dräger PAC
(Johnson 2005)	Aus	model	various	various	pasture	field	semi-mechanistic
(Li <i>et al.</i> 2005)	China	model comp, loss meas	fert (urea)	400 kg/ha	crop	field	mechanistic
(McDowell <i>et al.</i> 2005)	NZ	model	various	various	pasture	plot; field	P model
(McNeill <i>et al.</i> 2005)	Aus; Europe	review	manure, slurry	n/r	various	n/r	n/r
(Misselbrook <i>et al.</i> 2005)	UK	loss meas, tech comp	manure	n/s	n/s	lab; plot; field	micromet, IHF, eq conc. (acid trap (H ₃ PO ₄), PDS, shuttle), wind tunnel
(Pervanchon <i>et al.</i> 2005)	France	model	various	n/r	various	n/r	empirical, inventory
(Roelle and Aneja 2005)	USA	loss meas, model, model comp	slurry	n/a	lagoon, crop	plot; field	dyn. chamber, chemiluminescence; empirical model; mechanistic model
(Silva <i>et al.</i> 2005)	Lincoln, NZ	loss meas	effluent, urine, urea	400, 1000 kg/ha	pasture	lysimeter	dyn. chamber (H ₂ SO ₄)
(Sommer <i>et al.</i> 2005)	Canada	loss meas, meas tech	urea	79 kg/ha	n/s	field	micromet, IHF, BLS, shuttle (oxalic acid)
(Timmer <i>et al.</i> 2005)	Netherlands	review, meas tech	various	n/r	various	n/r	various
(Wachendorf <i>et al.</i> 2005b)	Germany	loss meas	cow urine, dung	1030, 1050 kg/ha	pasture	lysimeter	indirect (¹⁵ N mass balance)
(Webber <i>et al.</i> 2005)	USA	meas tech	n/r	n/r	n/r	n/r	optical – diode laser and photo-acoustic
(Alva <i>et al.</i> 2006)	USA	review	fert (various)	n/r	n/r	field, farm	n/r
(Barbieri <i>et al.</i> 2006)	Argentina	loss meas	fert (urea)	0, 90, 180 kg/ha	pasture	plot, field	semi-open static (H ₂ SO ₄)
(del Prado <i>et al.</i> 2006)	UK	model	various	n/r	various	field, farm	semi-empirical

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Laurenson <i>et al.</i> 2006)	NZ	review	slurry	n/r	various	n/r	n/r
(Luo <i>et al.</i> 2006)	Hamilton, NZ	loss meas	manure, dung, urine	4030 kg/ha	standoff pads	lab	dyn. chamber (H ₂ SO ₄)
(Parfitt <i>et al.</i> 2006)	NZ	review, model	various	n/r	various	region, country	inventory
(Rodhe <i>et al.</i> 2006)	Sweden	loss meas	slurry	67 kg/ha	pasture	field	eq. conc., PDS
(Saarijärvi <i>et al.</i> 2006)	Finland	loss meas	urine, dung	~490, 100 kg/ha	pasture	field	eq. conc., PDS
(Shah <i>et al.</i> 2006)	USA	review, meas tech	various	n/r	various	field	various
(Singurindy <i>et al.</i> 2006)	USA	loss meas	urine	592 kg/ha	bare	pot, lab	static and dyn. chambers (H ₂ SO ₄)
(Wheeler <i>et al.</i> 2006)	NZ	model	graze	n/r	pasture	field, farm	n/r
(Dueri <i>et al.</i> 2007)	Switzerland	model	manure, slurry	n/r	pasture, crop	field; farm	empirical
(Eckard <i>et al.</i> 2007)	Vic	model; review	graze	n/r	pasture	farm	N budget
(Hutchings <i>et al.</i> 2007)	Denmark	model	graze	n/r	pasture	field	mechanistic
(Li <i>et al.</i> 2007)	Aus, China	model	various	various	various	field	semi-mechanistic
(Núñez <i>et al.</i> 2007)	Chile	review	various	various	pasture	plot, field	n/r
(Payraudeau <i>et al.</i> 2007)	France	review	various	various	various	farm	n/r
(Smith <i>et al.</i> 2007)	Canada	tech comp	manure	230 kg/ha	bare	plot; field	static chamber (foam – H ₃ PO ₃); dyn. chamber (acid trap – H ₃ PO ₄), micromet, TPS (silica gel)
(Stiegler <i>et al.</i> 2007)	USA	meas tech	foliar fert (urea)	5000, 12,500 kg/ha (0.1, 0.25 lb/ft ²)	pasture	plot	indirect, passive sampler (H ₃ BO ₃)
(Aneja <i>et al.</i> 2008)	USA	review	various	various	various	n/r	n/r
(Asing <i>et al.</i> 2008)	Palm Nth	loss meas	fert (urea), manure	90 kg/ha	crop	pot, lab	dyn. chamber (H ₂ SO ₄)
(Beuning <i>et al.</i> 2008)	Canada	model	various	various	various	field	semi-mechanistic
(Cannavo <i>et al.</i> 2008)	USA	review, model	various	various	various	field, farm	semi-mechanistic
(Chen <i>et al.</i> 2008)	Aus	review	various	n/r	various	field; farm	n/r

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Corstanje <i>et al.</i> 2008)	UK	model	fert (urea)	various	various	field, plot, lab	mechanistic, semi-empirical
(Cortus <i>et al.</i> 2008)	Canada	model	pig urine	various	building	plot	mechanistic
(Del Grosso <i>et al.</i> 2008)	USA	model	various	n/r	various	farm, country	semi-mechanistic
(Delgado <i>et al.</i> 2008)	USA	model, review	various	n/r	various	country	inventory
(Fraser and Stevens 2008)	UK	model	various	n/r	pasture	farm	N budget, inventory
(Humphreys 2008)	Ireland	review	various	n/r	pasture, crop	farm	n/r
(Johnson <i>et al.</i> 2008)	NZ, Aus	model	graze	n/r	pasture	field, farm	mechanistic
(Loh <i>et al.</i> 2008)	north Qld, Vic,	loss meas	dung, urine, manure	n/r	feedlot	field	BLS, near-infrared diode laser
(Martin <i>et al.</i> 2008)	Canterbury, NZ	loss meas	fert (urea)	25, 50, 75, 100 kg/ha	pasture	field, plot	none
(Menneer <i>et al.</i> 2008)	Hamilton, NZ	loss meas	urine	775 kg/ha	pasture	lysimeter	dyn. chamber (H ₂ SO ₄)
(Mulvaney <i>et al.</i> 2008)	USA	loss meas	urine, dung	n/s	pasture	plot	static chamber – NH ₃ selective electrochemical cell
(Ni and Heber 2008)	USA	review	various	n/r	various	various	various
(Pacholski <i>et al.</i> 2008)	China	tech comp	fert (urea)	75, 120, 150, 200 kg/ha	crop, bare	field, plot	micromet (simplified IHF – oxalic acid), dyn. chamber (Dräger tube), ¹⁵ N balance
(Pu <i>et al.</i> 2008)	south Qld	loss meas	urban biosolids	~180 kg/ha	pasture	field, plot	indirect (N mass balance)
(Rumburg <i>et al.</i> 2008)	USA	loss meas, model	dung, urine, manure	n/r	building	building	DOA, mechanistic, semi-empirical
(Singurindy <i>et al.</i> 2008)	USA	loss meas	urine	592 kg/ha	bare	pot, lab	dyn. chamber (H ₂ SO ₄)
(Thorman <i>et al.</i> 2008)	UK, Denmark	model	slurry	various	crop	field	semi-empirical
(van Groenigen <i>et al.</i> 2008)	Europe mostly	review, model	various	n/r	various	various	n/r
(Wheeler <i>et al.</i> 2008)	NZ	model, review	graze	n/r	pasture	field; farm	semi-empirical, N budget, inventory
(Zaman <i>et al.</i> 2008)	Hamilton, NZ	loss meas	fert (urea, DAP)	150 kg/ha	pasture	field	n/s
(David <i>et al.</i> 2009)	Germany	loss meas, meas tech	fertilised soil, litter, plant	n/r	pasture	plot	dyn. chamber (citric acid)

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Hristov <i>et al.</i> 2009)	USA	loss meas	dung, urine, manure	various	bare, building	pot, lab	indirect (¹⁵ N mass balance)
(Milford <i>et al.</i> 2009)	Germany	loss meas, tech comp	fert (CAN)	105 kg/ha	pasture	field	micromet (aerodynamic gradient), three wet denuders
(Orwin <i>et al.</i> 2009)	Lincoln, NZ	loss meas	urine	n/r	pasture	field, plot	none
(Singh <i>et al.</i> 2009)	Palm Nth	loss meas	urine	144, 290, 570 kg/ha	pasture	pot, lab	dyn. chamber (H ₂ SO ₄)
(Sommer <i>et al.</i> 2009)	Denmark	model, loss meas	manure	various	building	field	PDS, circulation model
(Stevens and Quinton 2009)	UK	review	various	n/r	crop	field, farm	n/r
(Wheeler 2009)	NZ	model, review	graze	n/r	pasture	field, farm	n/r
(Zaman <i>et al.</i> 2009)	Palm Nth	loss meas	urine	600 kg/ha	pasture	field	dyn. chamber (H ₂ SO ₄)
(Cichota <i>et al.</i> 2010a)	NZ	model	urine	1000 kg/ha	pasture	lysimeter	n/r
(Cichota <i>et al.</i> 2010b)	NZ	model	urine + DCD	1000 kg/ha	pasture	lysimeter	n/r
(Clough <i>et al.</i> 2010)	Lincoln, NZ	loss meas	urine	760 kg/ha	bare	pot; lab	stat chamber (H ₃ PO ₃)
(Denmead <i>et al.</i> 2010)	China	loss meas	fert (urea)	60 kg/ha	crop	field	BLS, chemiluminescence analyser
(Loubet <i>et al.</i> 2010)	France, Italy	meas tech, model	slurry, fert (AN)	57–232 kg/ha	bare, pasture	field	analytical (inverse dispersion modelling)
(Turner 2010)	Aus	review, meas tech	various	n/r	pasture, crop	n/r	various
idem, chapter 4	Vic	tech comp	fert (urea)	80 kg/ha	crop	field	micromet (atm mass balance, ZINST, BLS), shuttle
idem, chapter 5	Vic	loss meas	graze, urea	~600–700 kg/ha (excreta); 50 kg/ha (urea)	pasture	field	BLS, shuttle
idem, chapter 6	Vic	loss meas	fert (urea, UAN, AS)	46 or 92 kg/ha	crop	field	micromet (ZINST)
idem, chapter 7	China	loss meas	fert (urea)	60 kg/ha	crop	field	BLS, chemiluminescence analyser
idem, chapter 8	Vic	loss meas	fert (urea)	80 kg/ha	crop	field	micromet, atm mass balance, shuttle

Article citation	Main location	Main subjects	N source	N loads	Soil use	Scale	Meas. technique/model approach
(Turner <i>et al.</i> 2010)	Vic	loss meas, tech comp	fert (urea)	80 kg/ha	crop	field	micromet (simplified mass balance), BLS; shuttle
(Wang <i>et al.</i> 2010)	China	model, GIS	n/r	n/r	various	region	semi-mechanistic
(Zaman and Blennerhassett 2010)	Lincoln, NZ	loss meas	urine	600 kg/ha	pasture	lysimeter	dyn. chamber (H ₂ SO ₄)
(Dawar <i>et al.</i> 2011)	Lincoln, NZ	loss meas	fert (urea)	100 kg/ha	pasture	lysimeter	dyn. chamber (H ₂ SO ₄)
(del Prado <i>et al.</i> 2011)	UK, Spain	model	various	n/r	various	field, farm	semi-empirical
(Flysjö <i>et al.</i> 2011)	Sweden, NZ	model; review	various	n/r	pasture, building	field, farm	Inventory, system comparison
(Garcia <i>et al.</i> 2011)	France	model	various	n/r	pasture, crop	field, farm	mechanistic, N budget
(Hristov <i>et al.</i> 2011)	USA	review	various	various	various	field, farm	various
(Junejo <i>et al.</i> 2011)	Malaysia	review	various	n/r	various	n/r	n/r
(McGinn <i>et al.</i> 2011)	North Qld	meas tech	n/r	n/r	n/r	field	point source dispersion (BLS?), open path laser
(Sheppard and Bittman 2011)	Canada	model; review	various	n/r	n/r	field, farm	inventory
(Sherlock <i>et al.</i> 2011)	NZ	review	urine, urea	various	various	field,, farm	n/r
(Sintermann <i>et al.</i> 2011)	Europe	review; meas tech	slurry	n/r	various	field; farm	various
(Suter <i>et al.</i> 2011)	Vic	loss meas	urea	100, 160 kg/ha	bare	pot, lab	indirect (N mass balance)
(Gourley <i>et al.</i> 2012)	Vic; USA	loss meas, review	various	n/r	n/r	farm	inventory, N budget
(Laubach <i>et al.</i> 2012)	Lincoln, NZ	loss meas, tech comp, model	urine	~600 kg/ha	pasture	field	micromet (atm mass balance, BLS, ZINST), shuttle
(Monaco <i>et al.</i> 2012)	Italy	loss meas	slurry	91 kg/ha	bare	pot, lab	dyn. chamber – photoacoustic infrared analyser +acid trap (H ₂ SO ₄)
(Taghizadeh-Toosi <i>et al.</i> 2012)	Lincoln, NZ	loss meas	NH ₃	n/r	pasture	lysimeter	indirect (N mass balance)