# Review of New Zealand specific $FRAC_{GASM}$ and $FRAC_{GASF}$ emissions factors

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# Final Report:

# Review of New Zealand Specific $Frac_{GASM}$ and $Frac_{GASF}$ Emissions Factors

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**to**

**Ministry of Agriculture and Forestry**

**October 2008**

**(Reprinted post peer review, January 2009)**

***Prepared by***

**R. Sherlock, P. Jewell, T. Clough**

**Centre for Soil and Environmental Quality**
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# Executive Summary

$Frac_{GASM}$ and $Frac_{GASF}$ are important factors within national nitrous oxide ($N_2O$) emissions inventories. These factors represent the proportions of manure-N and fertiliser-N respectively that are released into the atmosphere, principally as ammonia, $NH_3$, to become indirect sources of $N_2O$ when re-deposited on land surfaces elsewhere. Currently the NZ $N_2O$ inventory uses the IPCC defaults of 0.2 and 0.1 for $Frac_{GASM}$ and $Frac_{GASF}$ respectively. The use of 0.2 for $Frac_{GASM}$ in New Zealand's $N_2O$ inventory recently came under the scrutiny of the 'Expert Review Team' (ERT) of the United Nations Framework Convention on Climate Change (UNFCCC) secretariat. Amongst other things, the ERT encouraged NZ to: "***investigate a country-specific*** $\boldsymbol{Frac_{GASM}}$ ***or document why the IPCC default value is considered appropriate for New Zealand conditions".*** This current review forms part of that investigation.

In this review we have attempted to locate and scrutinise all (mostly field-based) studies of relevance to the magnitudes of $Frac_{GASM}$ and $Frac_{GASF}$ as used in NZ's current $N_2O$ inventory. Following a brief introduction (section1) sections 2 and 3 focus on the factors influencing the production and emission of $NH_{3(g)}$ and $NOx_{(g)}$[1] from soils and also provide an overview of the techniques employed for their measurement. Sections 4 and 5 then focus respectively on international and local (NZ) studies of relevance to $Frac_{GASM}$. In section 6 we review international and NZ data on $NH_{3(g)}$ emissions from mainly urea and diammonium phosphate fertilisers and then follow that in section 7 with a review of NOx emissions from animal excreta and fertiliser applied to pasture. Section 8 summarises all major findings and recommendations.

We found that overseas (especially European) studies of $NH_{3(g)}$ emissions during grazing, can be used to assist in the re-evaluation of a country-specific $Frac_{GASM}$ for NZ. In most European countries, $NH_{3(g)}$ emitted from pasture soils following grazing is just one of several sources contributing to their reported $Frac_{GASM}$ inventory values, whereas in NZ, 97 % of all livestock urine and dung is deposited directly on soils during grazing and the $NH_{3(g)}$ derived from that source dominates NZ's $Frac_{GASM}$. Using mean international $NH_3$-N emission data from urine and dung affected pasture soils (obtained from 45 separate chamber

[1] Nitric oxide gas, $NO_{(g)}$, and nitrogen dioxide gas, $NO_{2(g)}$ are collectively referred to as 'NOx'.

and wind tunnel studies) the proportion of excreted-N emitted as $NH_3$-N was estimated as 9.3 (SD ~ 4.5) %. This equates to a $Frac_{GASM}$ value of 0.093 (or 0.094 if the very minor contribution due to NOx is included). The same calculation performed on the 23 reported chamber measurements of urine and dung carried out in NZ indicates 12.3 % of excreted-N is emitted as $NH_3$-N. That value equates to a $Frac_{GASM}$ of 0.123 (or 0.124 when the very minor contribution due to NOx emissions is included). On the basis of these two values alone (0.094 and 0.124; the weighted mean of which is 0.10) the first of four recommendations is made:

**Recommendation 1:**

**A New Zealand specific value of 0.1 for $Frac_{GASM}$ be considered for adoption.**

Note that changing $Frac_{GASM}$ from 0.2 to 0.1 reduces NZ's 2006 $N_2O$ inventory by *ca* 6% from 41.075 to 38.620 Gg $N_2O$. This difference of 2.455 Gg $N_2O$ equates to 761.05 Gg $CO_2$-e.

Recommendation 1 is based on chamber and wind tunnel measurements only which some researchers maintain tend to maximise potential emissions of $NH_{3(g)}$. When we examine instead the dataset of international "whole system" non-chamber measurements of $NH_{3(g)}$ emissions from grazed pastures we show that a case can be made for an even larger reduction in NZ's $Frac_{GASM}$ value. From 47 grazing events by cattle on heavily fertilised perennial ryegrass mainly in England and Holland, a weighted mean value of 9.6 % of the excreta-N was emitted as $NH_3$-N. While this is remarkably similar to the two values derived independently above (i.e. 9.3 & 12.3 %), at lower rates of fertilisation more typical of what might be encountered in NZ, 23 documented grazing events gave a weighted mean value of just 4.2 % of the excreta-N emitted as $NH_3$-N. And from 9 studies involving beef cattle or dairy cows grazing unfertilised grass/clover pastures a slightly lower weighted mean of 3.3 % was obtained. These last two values bracket the only similar study carried out on unfertilised ryegrass-clover pasture in NZ (4.0 %). From these "whole system", non-chamber studies, it could be argued that a NZ specific value of ~ 0.04 for $Frac_{GASM}$ might be even more appropriate than the value (0.1) based on chamber and wind tunnel data alone. But such a recommendation is premature at this time since the number of local non-chamber based studies of $NH_{3(g)}$ emissions from grazed pastures are very limited. We therefore make our second recommendation:

**Recommendation 2:**

**Research be supported on "whole system" non-chamber measurements of grazed pasture systems to further refine the New Zealand specific value for $Frac_{GASM}$**

Should future research justify a reduction of $Frac_{GASM}$ to ~ 0.04, the 2006 inventory would reduce by 3.928 Gg $N_2O$ which equates to 1,218 Gg $CO_2$-equivalents.

With regard to $Frac_{GASF}$ we note that urea is the dominant N-fertiliser used in NZ (~ 80 %) with the remaining 20 % being mainly diammonium phosphate (DAP). In addition, most N-fertiliser is used to boost pasture production in dairying. Our review of international and local studies of relevance to NZ's $Frac_{GASF}$ revealed a 'rate of application effect' for urea whereby $NH_{3(g)}$ emissions increased from ~ 11 % of the urea-N applied at 30 kgN/ha to 33 % of the urea-N applied at (albeit unrealistically high) rates of 300 kgN/ha. At the rates of N-fertiliser typically applied in single applications to NZ pasture ($\leq$ 45 kgN/ha) the weighted mean value for the $NH_{3(g)}$ emissions from 19 separate studies following urea-N application to pasture soil was 10.8 % (SD ~ 2.9 %). Under NZ conditions, allowing for the (~ 20 %) use of DAP and its lower potential emission factor (4.6 %), the weighted mean $NH_{3(g)}$ emission from these two fertilisers is estimated as 9.6 % of the applied fertiliser-N. This equates to a $Frac_{GASF}$ value for NZ of 0.096 (or 0.099 when the minor contribution due to NOx emissions is included). That final value is essentially identical to the value for $Frac_{GASF}$ that NZ currently uses (0.1). We believe these findings from the international and NZ studies reviewed here, provide sufficient justification for this third recommendation:

**Recommendation 3:**

**A New Zealand specific value of 0.1 for $Frac_{GASF}$ be considered for adoption.**

Finally we note that reductions in $NH_{3(g)}$ emissions from urea fertiliser are possible through the use of urease inhibitors. Use of that technology could probably contribute further, modest (e.g. 32 Gg $CO_2$-e) reductions to NZ's GHG emissions inventory. However, more local measurements would be needed to underpin and support any move to include urease inhibitor use within NZ's GHG inventory. We therefore suggest a fourth and final recommendation:

**Recommendation 4:**

**Research be supported to explore the efficacy of urease inhibitors to reduce $NH_{3(g)}$ emissions from urea fertiliser in New Zealand, with a view of further refining NZ's $Frac_{GASF}$ value.**

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# Section 1. Introduction

## 1.1 UUContext of the Project:

Frac$_{GASM}$ and Frac$_{GASF}$ are important factors within national nitrous oxide ($N_2O$) emissions inventories. These factors represent the proportions of manure-N and fertiliser-N respectively that are released into the atmosphere as chemically reactive ammonia gas ($NH_3$) and nitrogen oxides other than $N_2O$ (essentially NO and $NO_2$ which collectively are referred to as NOx). Volatilised $NH_3$ dominates these non-$N_2O$ source emissions with NOx being typically only a minor contributor. Collectively these reactive nitrogenous gases serve as indirect sources of $N_2O$ when re-deposited on land surfaces elsewhere. Currently the NZ $N_2O$ inventory uses the IPCC defaults of 0.2 and 0.1 for Frac$_{GASM}$ and Frac$_{GASF}$ respectively[2]. The use of 0.2 for Frac$_{GASM}$ in New Zealand's $N_2O$ inventory has recently come under the scrutiny of the 'Expert Review Team' (ERT) of the United Nations Framework Convention on Climate Change (UNFCCC) secretariat[3]. That review noted:

***"The ERT encourages New Zealand to investigate a country-specific Frac$_{GASM}$ or document why the IPCC default value is considered appropriate for New Zealand conditions".*** This current review forms part of that investigation.

NZ's national $N_2O$ inventory is sensitive to changes in these factors, especially to changes in Frac$_{GASM}$. For example, setting Frac$_{GASM}$ equal to Frac$_{GASF}$ by halving it to 0.1 reduces the calculated annual agricultural $N_2O$ emissions by ~ *ca*. 2.45Gg $N_2O$ (~ 760Gg $CO_2$-e). At $22 per tonne of $CO_2$ this equates to ~ $17 million.

While some NZ research has investigated Frac$_{GASF}$ there appear to be relatively few published NZ studies which have attempted to quantify Frac$_{GASM}$. This is in strong contrast to other jurisdictions. Mitigation of $NH_3$ emissions from applied manure-N is subject to regulation in many parts of Europe. This is certainly not the case in NZ where trans-boundary (trans-national) air pollutant effects are minimal and where ammonia volatilisation research appears not to have received the same attention as it has in Europe, North America and Asia. This project brings together and reviews all NZ peer-reviewed published and

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2 Frac$_{GASM}$ and Frac$_{GASF}$ are referred to in this report either as fractions (e.g. 0.2) or more conveniently as percentages (e.g. 20%). It should be clear from the context, which representation is being employed.

3 From the in-country review, coordinated by an 'Expert Review Team (ERT) of the United Nations Framework Convention on Climate Change (UNFCCC) secretariat, Wellington, February 2007.

unpublished work relating to $Frac_{GASM}$ and $Frac_{GASF}$ and compares it with reputable published studies carried out on comparable pasture systems overseas. From this an informed recommendation is made as to whether the currently available NZ data support retention of the current IPCC defaults and what action would be needed to develop NZ specific factors for $Frac_{GASM}$ and $Frac_{GASF}$.

Figure 1 below[4], depicts the various routes for both direct and indirect $N_2O$ emissions arising from pastoral agriculture in New Zealand. The vast majority of both direct and indirect anthropogenic $N_2O$ emissions from New Zealand agriculture arises from the nitrogen excreted directly onto pasture by our grazing ruminants (dairy cows, beef cattle and sheep). This is depicted to the left of the dashed vertical line in the figure below. Only that nitrogen excreted and captured during milking, utilisation of stand-off pads, feedpads and herdhomes, or in piggeries or poultry production is accounted for by the pathways depicted to the right of the dashed line.

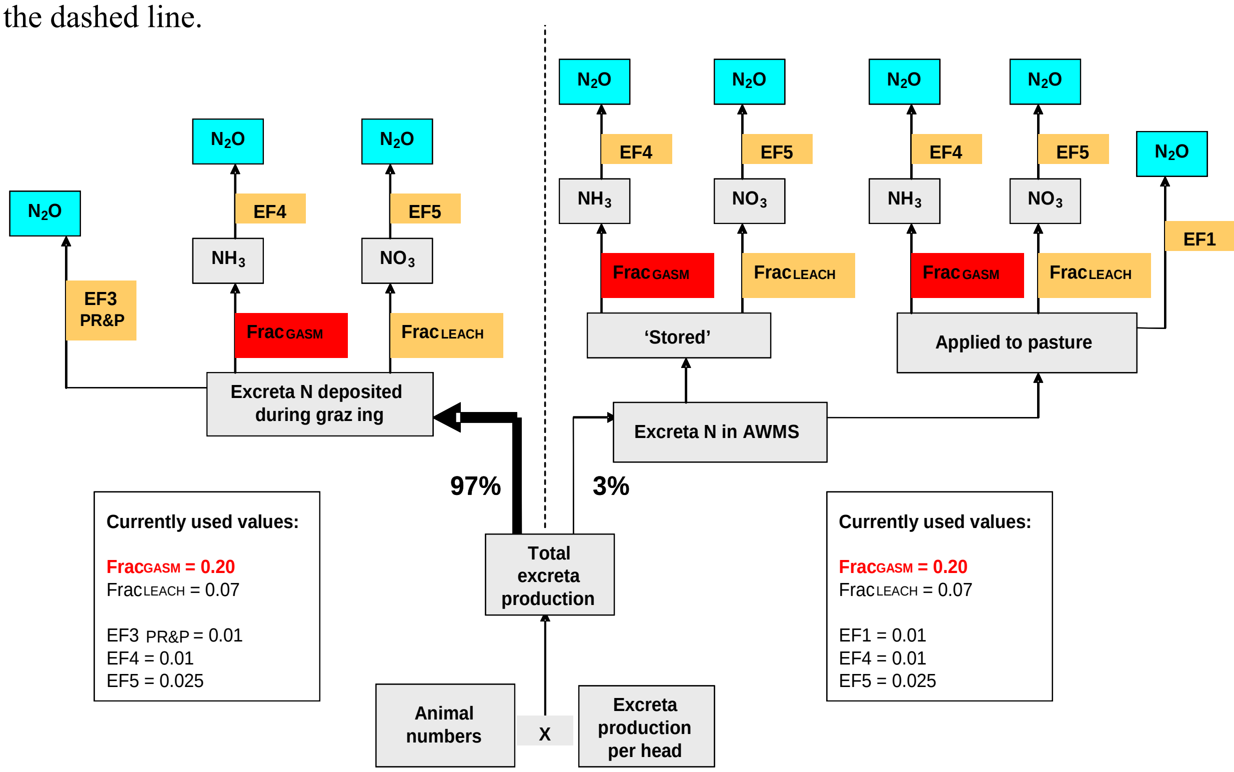


Figure 1. Flow chart of the current IPCC national $N_2O$ inventory methodology for pastoral agriculture in NZ.

[4] Referred to informally within the NzOnet group of scientists as the "horrendogram"

As can be seen, $Frac_{GASM}$ is applied in both contexts, but since excreta-N deposited directly during grazing is the major source of NZ's indirect $N_2O$ this report will review work principally from that source.

A smaller, but still significant source of anthropogenic $N_2O$ emissions, is the nitrogen-containing fertiliser used by NZ's farmers. Most of this fertiliser is in the form of urea and most is used to boost pasture production within the dairy industry. The direct and indirect $N_2O$ emissions arising from that source are depicted in Figure 2 below.

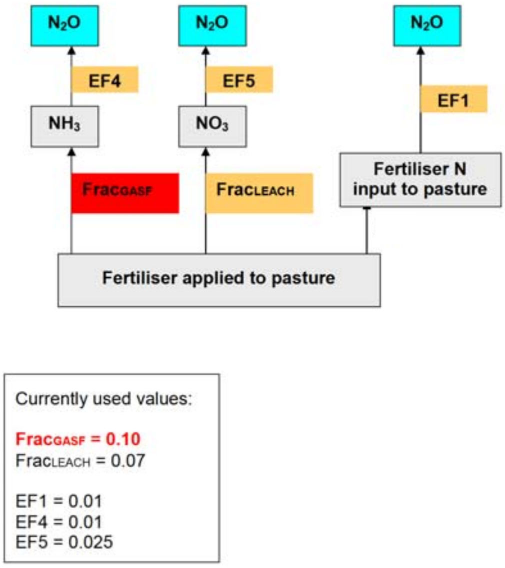


Figure 2. Flow chart depicting direct and indirect sources of $N_2O$ from fertiliser usage in New Zealand agriculture.

### 1.2 <u>Approach</u>:

A literature survey was undertaken of all published NZ studies relating to $Frac_{GASM}$ and $Frac_{GASF}$ as well as relevant published peer-reviewed pasture-based studies carried out overseas. We also consulted with NZ-based colleagues in other Universities and CRIs to obtain any other unpublished information of relevance to $Frac_{GASM}$ and $Frac_{GASF}$ (eg theses, reports etc). These data were scrutinised as to their quality and relevance and then summarised in tabular format. Assessments of means, ranges and standard deviations were calculated and these resulting values were further summarised and discussed. We conclude with some recommendations for further work that could be undertaken to validate for typical New Zealand conditions, our suggested revised $Frac_{GASM}$ and $Frac_{GASF}$ values.

## Section 2. The ammonia volatilisation process in pastoral agriculture

As mentioned earlier, the production and emission of ammonia from excreted nitrogen is the principal component of $Frac_{GASM}$ in the NZ situation. This 'ammonia volatilisation' is essentially a physico-chemical phenomenon and occurs independently of the other main Ngas-producing mechanisms: nitrification and biological denitrification (Sherlock & Goh, 1984; 1985a; 1985b). In the context of grazed pastures, ammonia volatilisation begins almost immediately following the voiding of ruminant urine, reaches a peak within one or two days and then declines quite rapidly over the following 5 to 10 days. The proportion of the voided urine-N that is volatilised as $NH_{3(g)}$ during that time can be substantial (see section 4.1). Both the instantaneous rate of $NH_3$ volatilisation and the total amount volatilised are affected by a number of factors. Principal amongst these are: the presence of 'ammoniacal-N' (or NHx)[5] at the soil surface itself, the pH of the soil solution containing that ammoniacal-N, the soil surface temperature and the wind-speed (Sherlock et al., 1995). Of somewhat lesser importance is the cation exchange capacity of the soil and its related pH buffering capacity.

### 2.1 <u>$NH_3$ volatilisation from urine in grazed pastures</u>

In the grazed pasture context, ammoniacal-N is generated at the soil surface in abundant quantities shortly following ruminant urination. It is formed when the major nitrogen-containing species in urine, namely urea, $CO(NH_2)_2$, is catalytically hydrolysed by the ubiquitous soil enzyme, urease. This hydrolysis (equation 1) generates the bases ammonia, $NH_{3(aq)}$, and bicarbonate, $HCO_3^-{}_{(aq)}$, both of which serve to drive the pH of the soil solution at the soil surface to values often > pH 9.

$$CO(NH_2)_{2(aq)} + 2\,H_2O \xrightarrow{\text{urease}} NH_4^+{}_{(aq)} + NH_{3(aq)} + HCO_3^-{}_{(aq)} \qquad \text{[Equ. 1]}$$

#### *2.1.1 Influence of pH*

At such high pHs, the proportion of the dissolved ammoniacal-N present as volatilisable $NH_{3(aq)}$, is increased markedly. Indeed at pH 9.2 at 20°C, the relative proportions of $NH_4^+{}_{(aq)}$ and $NH_{3(aq)}$ are 50/50 (Sherlock & Goh, 1984). With each pH unit

[5] 'Ammoniacal-N' is the term used here to describe the sum of the mineral-N dissolved in the soil solution as both ammonium ($NH_4^+{}_{(aq)}$) and ammonia ($NH_{3(aq)}$) together with ammonium ($NH_4^+$) ions held more strongly on cation exchange sites within the soil colloids. 'Ammoniacal-N' is sometimes abbreviated to 'NHx'.

drop below that value, the proportion of the total ‘NHx’ present as $NH_{3(aq)}$ drops by a factor of ~ 10. Thus at pH 8.2, $NH_{3(aq)}$ forms just 10 % of the total NHx pool while at pH 7.2 only ~ 1 % of the NHx is present as volatilisable $NH_{3(aq)}$. In a urine-induced ‘volatilisation event’ the surface soil pH typically undergoes an initial rapid increase to pH ~ 9 and then a decline to around pH 7 over the next 7 – 10 days. It has been argued that this decline in pH is the major factor which ultimately limits (self-limits) the extent of ammoniacal-N loss from the urine patch (Sherlock and Goh, 1985a).

### *2.1.2 Influence of temperature*

Before the dissolved $NH_{3(aq)}$ can volatilise, and thereby contribute towards $Frac_{GASM}$, it must undergo a phase change to generate $NH_{3(g)}$. Like most gases, $NH_3$ is more water soluble at low temperatures than at higher temperatures. For $NH_3$ this temperature dependent solubility is particularly marked and strongly influences the instantaneous rate of $NH_{3(g)}$ volatilisation from a soil surface. The equilibrium constant between $NH_4^+{}_{(aq)}$ and $NH_{3(aq)}$ is also strongly influenced by temperature. Using known thermodynamic measurements of this equilibrium constant and the Henry’s Law solubility constant for $NH_{3(g)}$, it can be shown that for every 10°C change in temperature, the relative proportions of the $NH_{3(g)}$ and NHx present in a system change by a factor of about three (Sherlock & Goh, 1985a). Thus temperature has a major influence on the generation of $NH_{3(g)}$ and its subsequent volatilisation.

### *2.1.3 Influence of wind speed*

But just because volatilisable $NH_{3(g)}$ may be present at, or close to, the soil surface, it does not necessarily mean that it will contribute to $Frac_{GASM}$. Its final release to the atmosphere is dictated by the $NH_{3(g)}$ concentration gradient that exists across the soil-atmosphere interface. In situations where significant $NH_{3(g)}$ volatilisation is known to occur (e.g. fresh ruminant urine patches) the concentration of $NH_{3(g)}$ at the soil surface is typically many times that present in the bulk atmosphere. However, this concentration gradient is also strongly affected by wind speed. Strong winds favour the maintenance of a strong concentration gradient and hence volatilisation, while very low winds lead to lower rates of $NH_{3(g)}$ volatilisation (Sherlock et al., 1985a). But strong winds also serve to rapidly deplete the reservoir of volatilisable $NH_{3(g)}$ at, or close to, the soil surface and this contributes (along with the reduction in surface soil pH; see section 2.1.1) to the rapid decline in $NH_{3(g)}$ volatilisation that is typically observed in a urine-induced volatilisation event (Sherlock et al., 1985a). Once that reservoir of volatilisable $NH_{3(g)}$ is depleted, wind speed becomes largely irrelevant because $NH_{3(g)}$ volatilisation will have ceased.

### *2.1.4 Influence of CEC and Soil Type*

The influence of, and interaction between, most of these factors is shown below (Figure 3). Included there is the somewhat ambiguous influence of soil colloids in retaining more strongly at least some of the $NH_4^+{}_{(aq)}$ present in the soil solution. In theory, soils with a high cation exchange capacity (CEC) should have higher proportions of their NHx retained on the negatively charged soil colloids rendering it less available for volatilisation. However, the competition for exchange sites between $NH_4^+$ and potassium ($K^+$) ions, which are abundant in urine, complicates this simplistic description and makes generalisations concerning the influence of specific soil types difficult, especially for urine-affected soils.

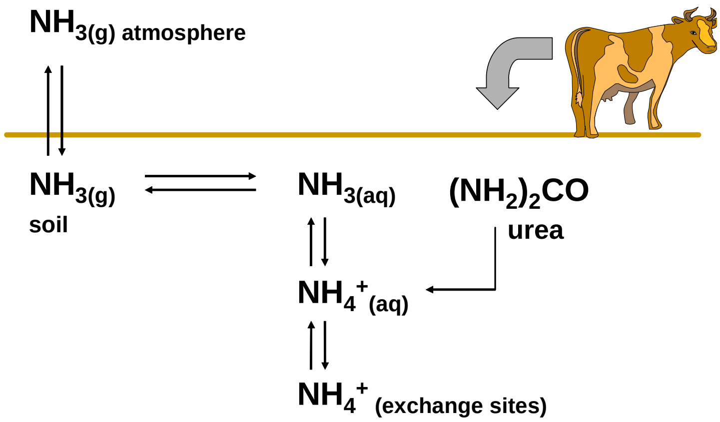


Figure 3. Simplified depiction of the physico-chemical factors driving ammonia volatilisation from urine patches in grazed NZ pastures.

## 2.2 <u>$NH_3$ volatilisation from dung excreted onto grazed pastures</u>

In contrast to the descriptions above relating to the transformation of urine-N leading to very significant production and release of $NH_{3(g)}$, excreted dung produces little $NH_{3(g)}$. This is largely a consequence of the failure of dung to develop the high pH conditions needed to de-protonate $NH_4^+$ to yield volatilisable $NH_3$. Dung contains very little, if any, urea, so cannot generate the high pH environment that accompanies urea hydrolysis. Instead, the nitrogen contained in dung is largely recalcitrant 'organic-N'. Mineralisation of this organic-N to ammoniacal-N does occur, but the rate of that transformation is much slower than the N-transformation rates in urine patches and it is not accompanied by significant elevations in pH. Also dung, unlike urine does not tend to come into intimate contact with the soil. For example, bovine dung typically forms 'pats' and acts as an almost completely separate domain. These 'pats' tend to dry rapidly and the crust that forms acts to impede gas exchange. So the overall contribution of dung deposition to $Frac_{GASM}$ is relatively minor compared to urine (see section 4.1).

## 2.3 $NH_3$ volatilisation from surface applied N-containing fertilisers

Direct ammonia volatilisation from fertilisers which contributes towards $Frac_{GASF}$, is only an issue for fertilisers that already contain ammoniacal-N, or fertilisers that produce ammoniacal-N by reaction with soil enzymes e.g. urea. Ammonia volatilisation is not a phenomenon that occurs from fertilisers whose nitrogen content is present exclusively as nitrate, $NO_3^-$. Nevertheless, any nitrogen-containing fertiliser which increases the N-content of the herbage being grazed by herbivores will tend to increase the total amount of N those animals excrete (Nex) and also enhance the proportion of that Nex that is excreted in the urine (Whitehead, 1986; Ledgard, 2001). And since $NH_{3(g)}$ volatilisation from urine-N is considerably greater than that from dung-N, the result may be a net increase in $NH_{3(g)}$ volatilisation from the N-excreted and an increase in $Frac_{GASM}$. Here we consider just the potential for immediate $NH_{3(g)}$ volatilisation from surface applied N-fertilisers which contribute towards $Frac_{GASF}$.

### *2.3.1 $NH_3$ volatilisation from urea fertiliser*

Between 1990 and 2005 there was a 6-fold increase in nitrogen fertiliser usage in NZ from 51,787 to 308,406 tonnes N. Currently, the majority of this fertiliser (~ 80%) is granulated urea, with the largest proportion being surface-applied to dairy pasture soils (W. Catto, pers. com., 2008). As will be apparent from section 2.1, that urea fertiliser should (and does) undergo essentially the same transformations as the urea component of urine, and will suffer some $NH_{3(g)}$ volatilisation. And as already mentioned, any $NH_{3(g)}$ released from urea fertiliser contributes to factor $Frac_{GASF}$ in NZ's inventory. Volatilisation of $NH_{3(g)}$ from surface-applied urea fertiliser can be greatly reduced if soon after application, the pasture is irrigated so that the fertiliser is dissolved and physically moved beneath the soil surface (Black et al 1987a). This markedly reduces the NHx concentration at the soil surface and also the extent of any subsequent pH increase. Physical incorporation of granulated urea fertiliser in cropping systems at planting has a similar effect to irrigation by almost completely eliminating $NH_{3(g)}$ volatilisation. But where irrigation or physical incorporation is not possible, $NH_{3(g)}$ volatilisation emissions from urea can be substantial (see section 6.1).

### *2.3.2 $NH_3$ volatilisation from DAP and MAP fertilisers*

Diammonium phosphate (DAP) and monoammonium phosphate (MAP) are ammoniacal fertilisers that are used to a lesser extent in NZ than urea. In principle both of these fertilisers could suffer from $NH_{3(g)}$ volatilisation when surface applied to pastoral soils. In most situations only DAP suffers some $NH_{3(g)}$ loss (Black et al, 1985b). The $NH_{3(g)}$ volatilisation from DAP is almost always less than that suffered from a comparable application of urea and occurs as a consequence of the hydrolysis equilibrium undergone by the hydrogen phosphate anion, $HPO_4^{2-}{}_{(aq)}$. This hydrolysis equilibrium is depicted below (Equation 2).

$$HPO_4^{2-}{}_{(aq)} \quad + \quad H_2O \quad \longleftrightarrow \quad H_2PO_4^{-}{}_{(aq)} \quad + \quad OH^{-}{}_{(aq)} \qquad \text{[Equ.2]}$$

The position of this equilibrium in soil solution following DAP application causes a small but significant elevation in surface soil pH to *ca* pH = 8 which is enough to induce limited de-protonation of $NH_4^{+}{}_{(aq)}$ to $NH_{3(aq)}$ and promote some volatilisation (Black et al 1985b). In contrast the dihydrogen phosphate ion, $H_2PO_4^{-}{}_{(aq)}$, present in MAP does not undergo significant pH altering hydrolysis and any $NH_{3(g)}$ volatilisation from this fertiliser is minimal, when surface applied to typical, non-calcareous, pasture soils.

### *2.3.3 $NH_3$ volatilisation from Ammonium Sulphate and Ammonium Nitrate fertiliser*

Both ammonium sulphate (AS) and ammonium nitrate (AN) are very comparable to MAP in terms of their ability to undergo $NH_{3(g)}$ volatilisation. Like the $H_2PO_4^{-}{}_{(aq)}$ ion present in MAP, the sulphate ion, $SO_4^{2-}{}_{(aq)}$, in AS and the nitrate ion, $NO_3^{-}{}_{(aq)}$, in AN, undergo little hydrolysis and do not elevate the soil solution pH to any extent. Thus AS, AN and MAP are only likely to generate $NH_{3(g)}$ when applied to soils (e.g. calcareous soils) that themselves have a naturally high pH (pH > 7.5). Most agricultural soils in NZ are not in this category.

The relative $NH_{3(g)}$ emissions from the N-fertilisers discussed above were studied by Whitehead & Raistrick (1990). Those workers showed a very clear relationship existed between the extent of cumulative $NH_{3(g)}$-N emissions 8 days following fertiliser application and the pH attained within the fertilized soil 24 hours following fertiliser application. For the non-calcareous soils studied, the relative $NH_{3(g)}$ emissions declined in the order: urea > DAP > AS=AN=MAP.

## 2.4 $NH_3$ volatilisation measurement methodology

Of all common gases, $NH_3$ has the distinction of being the most water soluble. This property often confounds the accurate measurement of $NH_{3(g)}$ emissions from soils due to its (re-)dissolution in moisture films within the measuring apparatus. And as discussed earlier, $NH_{3(g)}$ volatilisation is particularly sensitive to temperature and some measurement techniques employed in the past did not adequately address this. So in our later review of the magnitudes of $NH_{3(g)}$ volatilisation emissions (Sections 4, 5 & 6) we make efforts to identify the type of measurement technique employed. There are a number of excellent recent reviews dealing with the pros and cons of methods to measure ammonia volatilisation. A readily accessible review is available through the FAO website[6]. We summarise below the main attributes of the principal measurement techniques used to quantify $NH_{3(g)}$ volatilisation by researchers.

### *2.4.1 N-balance methods*

N-balance methods rely on accurately quantifying all of the applied-N in the soil-plant system following the expected completion of the 'volatilisation event'. Ammonia emissions are calculated as the difference between the known amount of N-added and the amount of N ultimately quantified within the soil and plants. This technique assumes that any losses other than by $NH_{3(g)}$ volatilisation (e.g. denitrification, leaching etc) are inconsequential. This is clearly not always the case and such measurements need to be interpreted cautiously. Another problem encountered using this technique is that any rapid immobilisation of applied mineral-N into the organic-N fraction within the soil is almost impossible to discern without the use of a $^{15}N$ tracer in the applied-N.

### *2.4.2 Static chambers*

The static chambers (or enclosures) employed in $NH_{3(g)}$ volatilisation studies are often short cylinders of sufficient basal diameter to cover the actively volatilising surface (e.g. urine patch or dung pat). The volatilised $NH_{3(g)}$ is typically trapped in dilute aqueous acid held in a separate container placed within the chamber above the soil surface. This trap is changed

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[6] http://www.fao.org/docrep/004/y2780e/y2780e03.htm#P0_0 (accessed June 6, 2008)

periodically and its $NH_4^+{}_{(aq)}$ content can be determined by standard chemical means. With any chamber method, care is needed to minimise the extent of any experimental artefacts created by the chamber itself. In the case of $NH_3$, any condensation that collects on the interior surface of the chamber acts as an alternative trap (or sink) for the volatilised $NH_3$ as does any condensation on the plant leaves or soil. In addition, without active air movement the rate of volatilisation is limited by the rate of diffusion of the volatilised $NH_{3(g)}$ to the acid trap. Care must also be taken to shade the chamber from direct sunlight or insulate it to ensure that it doesn't cause heating of the enclosed air or soil. But of course a darkened chamber will not permit normal photosynthetic activity and any departure from "real" outside temperatures will have a marked effect on the rate of volatilisation (see section 2.1.2). Consequently for accurate assessments of the dynamics or extent of $NH_{3(g)}$ volatilisation, static chambers are not ideal. However, they can still be useful when comparing the relative 'volatilisation potentials' of different N-treatments or different management strategies under pseudo field conditions. They are also very cheap to construct and use. Another variant of the static chamber method employs passive diffusional $NH_{3(g)}$ samplers placed inside and outside of a chamber that is ventilated at a constant rate (Svensson, 1994).

### *2.4.3 Non-static (Aspirated) chambers and wind-tunnels*

Many of the negative features of static chambers are overcome by actively drawing outside air through the chamber headspace (aspiration) and passing this $NH_3$–laden air through an external acid trap. If the airflow is sufficient, then any temperature anomalies that can occur with static chambers are very substantially reduced and thus this permits the use of non-shaded transparent chambers. Hence normal photosynthetic activity of the enclosed herbage during daylight hours is maintained. In situations where the aspirated chambers are located within a larger fertilised, dung or urine affected area, consideration needs to be given to the $NH_{3(g)}$ already present in the air entering the chamber. Removing that $NH_{3(g)}$ by including an anterior acid trap would tend to enhance the $NH_{3(g)}$ volatilisation from the enclosed area by increasing the $NH_{3(g)}$ concentration gradient and by reducing the overall atmospheric pressure within the chamber headspace. But not removing the $NH_{3(g)}$ from the air entering the chamber would make correct flux assessments problematical. Consequently aspirated chambers may not be well suited to measuring $NH_{3(g)}$ emissions from extended source areas. However, these reservations are not as relevant where the $NH_{3(g)}$ source is small in area and can be fully accommodated within the chamber itself e.g. a "urine patch" or “dung pat”. Aspirated chambers are more expensive to set up and operate than non-aspirated chambers, but are likely to provide a more accurate estimate of the actually $NH_{3(g)}$ emissions.

A variant of the aspirated chamber that has been employed quite effectively by overseas (esp. UK) researchers is the “wind tunnel”. This method attempts to minimize the modifying influence of chambers by using fans to better approximate a typical ambient wind-speed during the time of the measurement. An accurate knowledge of the airflow through the wind tunnel is coupled with separate anterior and posterior sub-sampling of that airflow (usually through acid traps). This allows the $NH_{3(g)}$ flux to be determined. Any problems arising from rainfall events during the cover period are addressed by moving the tunnel periodically to a different, but similarly treated, location. Wind tunnels are the most expensive chamber variant, but arguably deliver the most realistic estimates of $NH_{3(g)}$ volatilisation emissions.

#### *2.4.4 Micrometeorological methods*

Experimental artefacts arising from the use of chambers are largely eliminated by employing one of a number of micrometeorological methods. These methods rely on the measurement of gas concentration gradients, wind speeds and other micrometeorological phenomena to calculate surface $NH_{3(g)}$ fluxes from a much larger (field scale) area than can be accommodated within any practical chamber or wind tunnel. These methods include: the Energy Balance, Eddy Correlation and Aerodynamic procedures that have been used by researchers for many years for measuring the exchange of a range of soil-derived gases (e.g. $CO_2$ and $H_2O$). These procedures typically require large areas with uniform upwind distances (fetch) of several hundred metres. They are well suited to large, uniform, flat fertilised fields.

A micrometeorological mass balance procedure that can be carried out over much smaller areas, and is particularly suited to measuring $NH_{3(g)}$ volatilisation, is the “Integrated Horizontal Flux” (IHF) method. This method typically requires a circular treated plot within a larger un-treated area; the circular plot being 20 to 30 metres in radius. A mast is located in the centre of the treated plot and devices are placed at various heights on that mast to measure the product of wind speed and $NH_{3(g)}$ concentration. These measurements can be made separately using acid traps and anemometers (e.g. Black et al., 1989) or together using a passive sampler that responds linearly to the prevailing wind speed (Leuning et al., 1985; Sherlock et al., 1989). The outcome is a series of measurements of the horizontal $NH_{3(g)}$ flux at specific heights above the centre of the volatilising plot which can be converted to a vertical flux using the formula:

$$F = (1/X) \int_0^Z \overline{u(C_g - C_b)}\, dz \qquad \text{[Equ. 3]}$$

where: $u$ denotes wind speed, $C_g$ and $C_b$ are the $NH_{3(g)}$ concentrations at the same height at the centre of the volatilising plot and upwind of the volatilising plot, $z$ is the height above the soil surface and $X$ is the radius of the circular plot. Measurement periods are typically between 2 to 4 hours in length early in a 'volatilisation event' when fluxes are high, but sometimes extend to once daily when fluxes are low (Sherlock et al., 2002). Integrating these vertical fluxes against time yields the total $NH_{3(g)}$ emission from the soil surface during the combined measurement periods. Knowing the total amount of N applied to the circular plot enables determination of the $Frac_{GASM}$ or $Frac_{GASF}$ as appropriate.

As mentioned already, the advantage of this type of micrometeorological method over chamber methods is that the volatilisation process is not affected by the experimental artefacts that may compromise chamber-based measurements. The disadvantages of this type of approach are the relatively high equipment and labour costs, and the limited scope for replication. A simplified version of this Integrated Horizontal Flux (IHF) approach has been developed that requires just a single measurement at a specific height ($Z_{inst}$) above the centre of the plot (Wilson et al., 1983; Black et al., 1985a). Another variant uses passive absorption devices (Ferm tubes), that are placed on masts around the circumference of the treated plot (Sherlock et al, 2002) and changed regularly.

#### *2.4.5 Concluding comments*

None of the methods currently available to measure $NH_{3(g)}$ emissions from grazed pasture is ideal. Each method has its advantages and disadvantages. Micrometeorological methods (especially the IHF approach) are best suited to whole system studies and are not compromised by the experimental artefacts which can affect chamber measurements. However micrometeorological methods cannot easily distinguish the $NH_{3(g)}$ emissions source e.g. urine versus dung. Only chambers and wind-tunnels appear to have that capability. In the tabulated review data that follows (sections 4, 5 & 6) we list the methodology employed since this helps in understanding the range of values reported and in formulating our conclusions.

## Section 3. Overview of the NOx producing mechanisms in soils

'NOx' is the term used to denote the sum of nitric oxide, $NO_{(g)}$, and nitrogen dioxide, $NO_{2(g)}$, present in system. In Earth's troposphere $NO_{(g)}$ and $NO_{2(g)}$ readily interconvert, usually via a pseudo-equilibrium involving ozone, $O_{3(g)}$, as depicted in Equation 4 below:

$$NO_{(g)} + O_{3(g)} \longleftrightarrow NO_{2(g)} + O_{2(g)} \qquad \text{[Equ. 4]}$$

The measurement of these two N-containing gases is often performed using the same instrument (see later) which is tuned to detect either $NO_{2(g)}$ by itself, or NOx after its $NO_{(g)}$ component has been converted to $NO_{2(g)}$. $NO_{(g)}$ itself is then determined by difference i.e. NOx – $NO_2$. Because of these factors, atmospheric scientists find it convenient to refer to the presence of both gases together; hence 'NOx'.

### 3.1 Biological production of $NO_{(g)}$ in soils

In soils, $NO_{(g)}$ is an obligatory intermediate in the denitrification process and is formed also as a by-product of the nitrification process as shown below:

#### *3.1.1 The denitrification process* (Knowles, 1982)

$$NO_3^- \xrightarrow{\text{nitrate reductase}} NO_2^- \xrightarrow{\text{nitrite reductase}} NO \xrightarrow{\text{NO-reductase}} N_2O \xrightarrow{N_2O\text{-reductase}} N_2 \qquad \text{[Equ. 5]}$$

#### *3.1.2 The nitrification process* (Knowles, 1982)

$$\begin{tikzcd} & & NO \arrow[dr] & N_2O & \\ NH_4^+ \arrow[r] & NH_2OH \arrow[r] & (HNO) \arrow[u] \arrow[r] & NO_2^- \arrow[u] \arrow[r] & NO_3^- \end{tikzcd} \qquad \text{[Equ. 6]}$$

A simplified conceptual model of these processes is the so-called "hole in the pipe model" diagrammed below (Figure 4). The emissions of $NO_{(g)}$ (and $N_2O_{(g)}$) are regulated by the size of the 'holes" in the pipe through which these gases can "escape". In contrast to $NO_{(g)}$, there is little evidence for $NO_{2(g)}$ being formed within, or released directly from, soils. If it was formed in soils it would likely dissolve readily within the soil moisture and undergo a redox reaction to generate nitrate, $NO_3^-{}_{(aq)}$, and nitrite, $NO_2^-{}_{(aq)}$. [Equation 7].

$$2\,NO_{2(aq)} + H_2O \longrightarrow 2H^+_{(aq)} + NO_3^-{}_{(aq)} + NO_2^-{}_{(aq)} \qquad \text{[Equ. 7]}$$

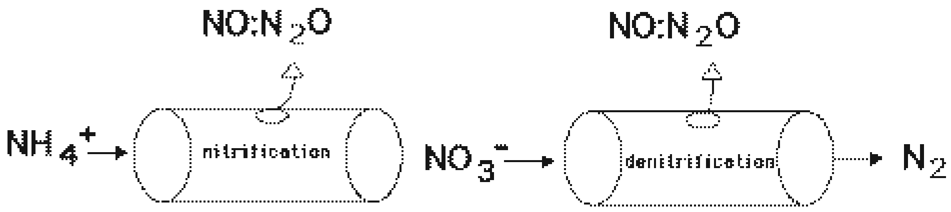


Fig.4: The "Hole in the Pipe" conceptual model indicates the flows of inorganic nitrogen through the microbial processes of nitrification and denitrification. Nitrogen oxides escape through "leaks" in the pipe. (Adapted from Firestone and Davidson, 1989).

Thus, NO can be formed under both anaerobic conditions via denitrification and aerobic conditions via nitrification. It is also formed by a recently discovered variant of these processes known as "nitrifier-denitrification" which is performed by ammonia oxidizers (Kuai and Verstraete, 1998).

Whatever the mechanism of its production, $NO_{(g)}$ readily converts in the lower troposphere to the more reactive $NO_{2(g)}$ [Equ. 4] and then to $NO_2^-$ and $NO_3^-$ [Equ. 7]. These products may then be deposited on a land surface downwind to become possible indirect sources of $N_2O$. The amounts of $NO_{(g)}$ released from soils are typically only a small fraction of the amount of N applied (see section 7), and make only a minor contribution to $Frac_{GASM}$ and $Frac_{GASF}$. Nevertheless, NO (as NOx) is part of NZ's agricultural GHG inventory and its contribution needs to be reviewed.

The conditions which favour the production and release of $NO_{(g)}$ by these biologically mediated processes are the same conditions which affect most biological process in soils, namely: aeration status, moisture content, pH, temperature, oxidisable-C supply (denitrification only) and amount of applied-N. Detailed reviews of nitrification, denitrification and nitrifier-denitrification are available elsewhere (Knowles, 1982; Skiba et al., 1993; Wrage & Velthrop, 2001).

### 3.2 Abiotic production of $NO_{(g)}$ in soils

As well as being produced by biologically-mediated processes, production of $NO_{(g)}$ by abiotic processes has also been shown. Arguably the most important of these abiotic processes is the spontaneous and rapid decomposition of nitrous acid ($HNO_2$) at low pH (pH < 4) (van Cleemput and Samater 1996) as shown in equation 8 below:

$$3\ HNO_{2(aq)} \longrightarrow HNO_{3(aq)} + 2\ NO_{(g)} + H_2O \qquad [Equ.8]$$

The $HNO_{2(aq)}$ itself may be formed in conditions where nitrite, $NO_2^-{}_{(aq)}$, is generated and where it can be protonated (equation 9).

$$H^+_{(aq)} \quad + \quad NO_2^-{}_{(aq)} \longrightarrow HNO_{2(aq)} \qquad \text{[Equ. 9]}$$

Venterea and Rolston (2000) have reported that in sterile soils, $NO_{(g)}$ production is highly correlated with $HNO_{2(aq)}$ concentration. Clough et al. (2003) have suggested that conditions favourable to $HNO_{2(aq)}$ generation may exist at the margins of ruminant urine patches where high $NH_{3(aq)}$ concentrations can lead to the accumulation of $NO_2^-{}_{(aq)}$ and its diffusion to zones of low pH where it can undergo protonation to $HNO_{2(aq)}$. A research programme focussing specifically on $NO_{(g)}$ production in urine patches is nearing completion at Lincoln University and the unpublished results from that programme are reported later (see section 7).

Other abiotic mechanisms leading to $NO_{(g)}$ (and $N_2O$) emissions arise from reactions of $HNO_2$ with phenolic and other functional group constituents of soil organic matter (Stevenson and Swaby 1964; Stevenson et al. 1970; Stevenson 1994; Thoran and Mikita 2000). In recent work by Trebs (2001) in Brazilian pasture soils, it was estimated that 50% of the NO production originated from abiotic processes.

## 3.3 NOx measurement methodology

The procedures used to measure NOx fluxes from soils are similar in concept to those used to measure $NH_{3(g)}$ and include static and aspirated chambers and micrometeorological methods. Like soil $N_2O_{(g)}$ fluxes, NOx fluxes are typically very small, and so chambers are most often used. But unlike $N_2O_{(g)}$, $NO_{(g)}$ and $NO_{2(g)}$ are highly reactive and so NOx fluxes are almost invariably determined *in-situ* in the field using sensitive chemiluminescence detectors. Early versions of these detectors required ozone generators to create electronically excited $NO_2$ via the reaction given earlier (equ.4) (Galbally & Roy, 1978). More modern instruments utilise other chemistry to excite $NO_{2(g)}$ to a state which undergoes the luminescence for detection by a sensitive photomultiplier tube. Nitric oxide, $NO_{(g)}$, is detected by first being oxidised chemically to $NO_{2(g)}$. The measured amount of $NO_{2(g)}$ is then equal to $NO_{(g)}$ + $NO_{2(g)}$ (i.e. NOx). By measuring air samples without the oxidation conversion, $NO_{2(g)}$ only is determined. Thus, the proportion of $NO_{(g)}$ in the combined NOx is derived by difference.

## Section 4. Review of International data on ammonia volatilisation in pastoral agriculture

Whether we have succeeded in capturing all relevant international data on ammonia volatilisation from pastoral agriculture is arguable. What we did succeed in doing was setting aside all the voluminous $NH_3$ volatilisation data available which deals with flooded soils, cattle feedlots, manure spreading, slurry measurements and most measurements carried out under controlled conditions in the laboratory. These we deemed not relevant to the principal objective of reviewing $Frac_{GASM}$. We also set aside those studies which relied on mass balances or nitrogen budgets to indirectly estimate N-loss through $NH_3$ volatilisation. Nevertheless, that left at least 22 high quality original publications reporting over 184 separate datasets which either directly report the $NH_3$ volatilisation contribution to $Frac_{GASM}$ or which enable that contribution to be estimated.

Studies of ammonia volatilisation in pastoral agriculture tend to fall into one of three categories: disaggregated studies of emissions from either (i) urine or (ii) dung that are almost always carried out using aspirated chambers or wind-tunnels, and (iii) "whole system" measurements which aim to quantify total $NH_3$ emissions from voided excreta. These "whole system" measurements are almost exclusively made using the IHF method described earlier (section 2.4.4). These different approaches are reflected in how we have structured our report. It also makes the inevitable process of calculating and reporting weighted means and ranges somewhat easier and more transparent for the reader.

Prior to the mid-1980s most of the more reputable research into excreta-derived or fertiliser-derived $NH_3$-N emissions was performed using aspirated chambers placed on simulated urine patches, dung pats or recently fertilised soil. As noted earlier (section 2.4.3), and as noted by other researchers, chambers potentially generate a number of artefacts which can interfere with and alter the $NH_3$-N loss process. For example, in their review of $NH_3$ volatilisation from dairy farming in temperate areas, Bussink and Oenema (1998) comment with respect to $NH_3$ volatilisation: "The range in losses seems to be somewhat larger in studies using enclosure techniques than in studies using meteorological techniques". This needs to be borne in mind when assessing the data presented and drawing appropriate conclusions.

## 4.1 Ammonia emissions from urine and dung

During and prior to the 1980s, a number of Australian researchers were active in investigating $NH_3$ volatilisation from urine patches. Reports from that period include those from Barlow (1972), McGarity and Rajaratnum (1973) and Vallis et al. (1982), all of which employed variants of aspirated chambers. But unlike the others, the apparatus employed by Vallis et al. (1982) was designed to simulate ambient wind speed and so combined some of the attributes of an aspirated chamber with attributes more associated with later wind-tunnels (e.g. Ryden et al. 1987). Vallis et al. (1982) measured $NH_3$-N emissions from urine patches in subtropical pasture in south east Queensland. In three separate un-replicated studies, emissions from simulated urine patches were 18.8 %, 14.4 % and 28.4 % from urine applications in winter, early summer and late summer respectively (mean = 20.5 %).

Several years later, Ryden et al. (1987) employed wind-tunnels to measure $NH_3$-N emission factors for urine and dung separately in a series of four experiments on ryegrass plots carried out at Hurley in Berkshire, UK. The mean $NH_3$-N emissions obtained following dairy cow urine applications to separate pasture plots were quite similar to those measured by Vallis et al. (1982), namely 16.0 % (range 8.8 - 24.7 %) of the urine-N applied. But these emissions were over 10-times those sustained from cattle dung (1.2 %) which was measured independently. This major difference between the $NH_3$-N emissions from urine and dung has been noted by many researchers both prior to, and subsequent to, the work of Ryden et al. (1987). For instance, Ledgard (2001) in his review of nitrogen cycling in low input legume-based pastoral agriculture estimated mean $NH_3$-N emissions of 20 % from a range of studies of the N excreted as urine and only 4 % from the N excreted as dung. He further comments that these values, especially the dung volatilisation values, were likely to be overestimates due to the chamber techniques employed in the studies reviewed.

Whitehead and Bristow (1990) used the same wind-tunnel system to measure $NH_{3(g)}$ emissions from urine, taken from a cow that was fed grass silage and sugar beet pulp. To identify the subsequent N-transformations, they labelled the urine with $N^{15}$-urea. After correcting for a portion of the applied-N that was immediately lost in drainage, recovery of this $^{15}N$ label in the volatilised $NH_3$ amounted to 17.8 % 10 days after application. And in related studies over several years, Lockyer and Whitehead (1990) employed these wind-tunnels to measure $NH_{3(g)}$ volatilisation from cattle urine applied to pasture under a range of seasonal and experimental conditions (Table 4.1). The mean cumulative $NH_{3(g)}$-N emissions across a series of twelve experiments over five years was 13.4 % (range: 3.7 - 26.9 %; standard deviation: 7.7 %). Average soil (and air temperatures) in the four days following urine application were highly correlated (r = 0.91) to the total $NH_3$-N emitted in the 15 days following urine application.

In a comprehensive series of seventeen experiments carried out at Wageningen in Holland which again employed wind-tunnels, Vertregt and Rutgers (1991) measured average $NH_{3(g)}$ emissions of 10.0 % (range 3.5 - 16.6 %; standard deviation 3.4 %) from synthetic urine-N applied at rates of approximately 600 kg N/ha. While these results are consistent with those of Lockyer and Whitehead (1990) they did not show the relationship with temperature found by those workers.

. Following the studies summarised above, there appears to be a relative dearth of wind-tunnel or chamber-based urine or dung-derived $NH_{3(g)}$ measurements until the recent report by Saarijarvi et al. (2006). These workers employed Svensson's 'JTI' chamber technique which is claimed to combine the attributes of a chamber with those of a micrometeorological procedure (see section 2.4.2 and Svensson 1994). Saarijarvi et al., (2006) reported on a series of experiments conducted during the summer months on a timothy-meadow fescue (*Phleum pratense- Festuca pratensis*) pasture in Finland where the mean soil temperature at 10 cm depth was an appreciable 14.6ºC. $NH_3$-N emissions from urine patches and dung pats were measured separately. Emissions from the urine patches following 3 separate applications were 18.4 %, 17.8 % and 9.5 % of the urine-N (average = 15.2 %) while emissions from the dung pats averaged just 1.3 % (range 1.2 - 1.4 %) of the dung-N. These results were remarkably similar to those of Ryden et al. (1987) reported earlier. Furthermore, irrigation treatments imposed during one of the experiments clearly showed that $NH_3$-N losses from urine patches could be significantly reduced by 46 – 75 %.

The mean value for all of the 41 wind-tunnel and chamber-based international studies on $NH_{3(g)}$ emissions from urine-N applied to pasture reviewed above is: 12.9 % (range: 2.4 - 28.4 %; standard deviation: 6.3 %). In contrast, the mean value for the four wind-tunnel based studies on dung, have found $NH_{3(g)}$ emissions of just 1.5 % (range: 1.2 - 2.0 %; standard deviation: 0.4 %).

**Table 4.1** Direct measurements of ammonia volatilisation from herbivore urine applied to pasture: International data

| Country | N source | Mean % Urine-N volatilised | Variability (SD) | N | Range | Reference | Methodology |
|---|---|---|---|---|---|---|---|
| Australia | Sheep urine | 6.5 | - | 1 | - | McGarity & Rajaratnam, 1973 | aspirated chamber |
| Australia | Cattle urine | 20.5 | 7.2 | 3 | 14.4 - 28.4 | Vallis et al., 1982 | aspirated chamber |
| England | Dairy cow urine | 16.0 | 7.6 | 4 | 8.8 - 24.7 | Ryden et al., 1987 | wind-tunnel |
| England | Cow urine +15-N | 17.8 | - | 1 | - | Whitehead & Bristow, 1990 | wind-tunnel |
| England | Dairy cow urine | 13.4 | 7.7 | 12 | 3.7 - 26.9 | Lockyer & Whitehead, 1990 | wind-tunnel |
| Netherlands | Synthetic urine | 10.0 | 3.4 | 17 | 3.5 -16.6 | Vertregt & Rutgers, 1991 | wind-tunnel |
| Finland | Dairy cow urine | 15.2 | 5.0 | 3 | 9.5 – 18.4 | Saarijarvi et al., 2006 | chamber (JTI method) |
| | **Overall** | **12.9 [b]** | **6.3** | **41** | **%CV [a] = 49%** | | |

**Table 4.2** Direct measurements of ammonia volatilisation from herbivore dung applied to pasture: International data

| Country | N source | Mean % Dung-N volatilised | Variability (SD) | N | Range | Reference | Methodology |
|---|---|---|---|---|---|---|---|
| England | Cow dung | 1.2 | - | 1 | - | Ryden et al., 1987 | wind-tunnel |
| England | Sheep dung | 2.0 | - | 1 | | Ryden et al., 1987 | wind-tunnel |
| Finland | Dairy cow dung | 1.3 | | 2 | 1.2 – 1.4 | Saarijarvi et al., 2006 | chamber (JTI method) |
| | **Overall** | **1.5** | **0.4** | **4** | **%CV [a] = 26%** | | |

[a] **%CV = (Standard deviation ÷ Mean) x 100 %**

[b] **weighted mean of all 41 studies**

## 4.2 Ammonia emissions from "whole system" grazing

The first "whole system" micrometeorological determination of $NH_{3(g)}$ volatilisation from grazed pasture was carried out using an "energy balance" approach by Denmead, Simpson and Freney in Queensland, Australia (Denmead et al., 1974). These researchers determined that 26 % of the urine-N voided by the 200 sheep grazing the pasture was emitted as $NH_{3(g)}$. Much later, Jarvis et al. (1989) employed the simpler IHF micrometeorological method (section 2.4.4) in a series of $NH_3$ loss studies on pastures rotationally grazed by cattle spanning the months of May through October in the years 1986–1987. In those studies, carried out at Hurley in Berkshire UK., these researchers measured $NH_3$ emissions during and after seven 1-week grazings by yearling steers from three different pasture managements: ryegrass only swards receiving either 420 or 210 kg fertiliser-N/annum (420N and 210N), and a grass-clover sward receiving no additional fertiliser-N (GC). Their $NH_3$ emission results were reported in a number of formats including: (i) kg $NH_3$-N/ha/yr, (ii) kg $NH_3$-N/animal/day, (iii) % of fertiliser or fixed N input emitted as $NH_3$-N and (iv) % of dietary N available for consumption emitted as $NH_3$-N. Use of the IHF method precluded the disaggregation of these total emissions into urine-derived emissions and those originating from dung. Their mean kg $NH_3$-N/animal/day values for the 420N, 210N and GC treatments were 0.0185, 0.0085 and 0.0055 respectively. Using these values, and assuming an annual Nex value of 53.8 kgN/animal/yr (UK Inventory, 1990) we estimate the mean $NH_3$-N emissions sustained (i.e. percentage of Nex emitted as $NH_3$-N) were: 12.5 %, 5.8 % and 3.7 % respectively from these three pasture managements (Table 4.3).

In a follow-up study, Jarvis et al. (1991) report a similar series of $NH_3$ loss studies on pastures rotationally grazed by sheep. These spanned the months of May through October in the years 1988–1989. Four different pasture managements were employed: ryegrass only swards receiving either 420 or zero kg fertiliser-N/ha/yr (420N or 0 N); a pure clover sward (Cl); and a mixed ryegrass/clover sward (GC). Their reported mean daily $NH_3$-N emissions per animal were again used to estimate the proportion of excreted-N released as $NH_3$-N. Their mean values for the 420N, 0 N, Cl and GC treatments were: $1.235 \times 10^{-3}$, $0.915 \times 10^{-3}$, $1.900 \times 10^{-3}$ and $0.193 \times 10^{-3}$ kg $NH_3$-N/sheep/day respectively. Expressed as a percentage of an assumed Nex value of 5.24 kg N/sheep/yr (UK National Inventory 1990) these $NH_3$-N emissions correspond to only 8.6%, 6.4%, 13.2% and 1.3% respectively for the four different pasture management systems (Table 4.3). These values are very similar to those sustained from similar cattle-grazed systems reported above.

Prior to the work of Jarvis et al. (1989, 1991) reported above, Ryden et al. (1987) employed the IHF method in a similar series of experiments on paddocks of ryegrass fertilized with 420 kg N/ha/yr and on unfertilised ryegrass/white clover mixed swards. Both systems were rotationally grazed by beef cattle; the fertilized ryegrass was grazed five times while the unfertilized grass-clover pasture was grazed twice. This work was also carried out at Hurley in Berkshire, UK. As well as using the IHF method, these workers also employed wind-tunnels to measure emission factors for urine and dung separately (see section 4.1 above). $NH_3$-N emissions from the 5 grazings of the fertilised ryegrass averaged 14.7 % (range: 7.1–27.7) of the average Nex. In contrast, the emission from the N-excreted on the mixed ryegrass-clover sward averaged only 1.8 % of Nex. These values are similar to those obtained subsequently by Jarvis et al. (1989) that we re-calculated above. It is noteworthy that the mean $NH_3$-N emission these researchers obtained following dairy urine and beef cattle dung applications to separate pasture plots beneath wind-tunnels were: 16.0 % and 1.2 % respectively. Using these two values, and assuming a 60 %:40 % distribution of the nitrogen excreted between the urine and dung respectively (Ledgard, 2001) a net value of 10.1 % of the excreted-N would be emitted as $NH_3$-N. This value is very similar to the 9.2 % average value (mean of 12.5 & 5.8 %) obtained independently and subsequently by Jarvis et al. (1989).

The observations above are further supported by the very extensive work of Bussink (1992, 1994). The first publication reports work carried out in 1987 and 1988, while the second publication reports further work carried out at the same location in Flevopolder, Netherlands between 1989 and 1990. All measurements employed the IHF method and studied the $NH_{3(g)}$ volatilisation losses from Holstein Frisian dairy cows rotationally grazed on ryegrass (*Lolium perenne* L.) pasture that received annual fertiliser inputs of 250, 400 or 550 kgN/ha as calcium ammonium nitrate (CAN). Because CAN does not itself volatilise $NH_{3(g)}$ (section 2.3.3), all the $NH_{3(g)}$ emissions must have originated directly from the excreta itself. The proportion of Nex excreted as urine-N ranged from 68 % to 78 %. The results for 24 separate grazing cycles are reported in the first publication (Bussink, 1992) while the later publication (Bussink, 1994) reports the results of a further 29 cycles. Excreta-derived emissions of $NH_3$-N in 1987 and 1988 were equivalent to 8.5 % and 7.7 % respectively of 'Nex' from the swards receiving annual dressings of 550 kgN/ha. And the $NH_3$-N emission from the sward receiving 250 kgN/ha in 1988 was equivalent to just 3.1 % of Nex (Table 4.3). During the two grazing cycles measured in 1989, $NH_3$-N emissions averaged 5.4 %, 13.9 % and 14.4 % of Nex for the

250, 400 and 550 kgN/ha pasture plots respectively. In 1990 $NH_3$-N emissions for the plots fertilised with 250, 400 and 550 kgN/ha, amounted to 3.3 %, 6.9 % and 6.9 % respectively of the N-excreted by the cows during grazing (Table 4.3).

A total of 70 separate beef and dairy cow grazing events on fertilised pasture are shown in Table 4.3. $NH_3$ emissions were measured for each of these events using the IHF micrometeorological method. Of those 70 events, 47 were on perennial ryegrass pasture which received at least 400 kgN/ha/yr of fertiliser-N. The weighted mean value of the $NH_3$-N emissions from those 47 studies is 9.6% of the excreta-N. The other 23 grazing events were on pasture receiving 210-250 kgN/ha/yr. A weighted mean value for the $NH_3$-N emissions from those studies is just 4.2 % of the excreta-N. This is only slightly greater than the weighted mean (ie 3.3 %) for the 9 studies involving beef cattle or dairy cows grazing grass/clover pastures that had received no supplementary fertiliser.

## 4.3 <u>Discussion</u>

As noted in the introduction (section 1.1) and again later (section 7.2), NOx emissions make only a very small contribution to active N-gas emission from grazing. The bulk of those emissions are as $NH_{3(g)}$. All of the international work reviewed above points to the fraction of the N deposited on pasture during grazing (Nex) subsequently released as $NH_3$-N being much less than the $Frac_{GASM}$ values that countries such as the United Kingdom (UK) employ in their own national $N_2O$ emissions inventories[7]. The UK uses a value of 0.2 for $Frac_{GASM}$ in their $N_2O$ inventory but it is clear from the data above, that a value much less this might seem more appropriate. In reconciling this apparent anomaly we need to recognise that emissions from pastures during grazing in the UK forms only a relatively minor portion of the total $NH_3$–N emissions from excreted-N that is integrated under $Frac_{GASM}$.

Misselbrook et al. (2000) estimate that of the 52.3 kt $NH_3$-N emitted per annum from cattle (beef and dairy) in the UK, just 6.6 kt (13 %) is emitted during grazing. The bulk is emitted during housing of the animals and the subsequent land spreading of their manure. An even more extreme situation pertains for pig farming in the UK. Of the 12.0 kt of $NH_3$-N emitted by that sector each year, just 0.4 kt (3.3 %) is emitted while the pigs are outdoors (Misselbrook et al., 2000). The UNECE ammonia expert panel in its 1998 summary of

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[7] GBR-2008-2006-v1.5.xls. Table 4.D. Sectoral Background Data for Agriculture Agricultural Soils .

Europe's ammonia emission factors reports that of the 100 kg N per year excreted by a typical European dairy cow, just 40 kg is deposited directly onto pasture during grazing, and just 3.9 kg (i.e. 8 %) of that deposited N is emitted as $NH_3$-N (van der Hoek, 1998). The remaining 60 kg of Nex are collected and stored and ultimately spread as manure back onto the pasture. Prior to and during that spreading, 25 % of its N content is released as $NH_3$-N. When the Nex from other European animal classes (sheep pigs, poultry etc) is disaggregated in this way, the net outcome for $Frac_{GASM}$ corresponds closely to the current IPPC default (0.2). In contrast in NZ, 97 % of the N excreted across all livestock classes is voided directly onto pasture (Figure 1).

So in the UK and other European countries, the proportion of Nex voided directly onto pastures is much lower that in NZ, but $NH_3$-N emissions from other "Animal Waste Management Systems" (AWMS) are correspondingly much greater. Together these emissions amount to ~ 0.2 (i.e. ~ 20 %) of Nex; hence the use of this value when reporting $Frac_{GASM}$ in their inventories. In New Zealand the contribution of "Animal Waste Management Systems" other than direct deposition of excreted-N onto pasture during grazing is very minor (see Figure 1), and can be largely disregarded for inventory purposes. Consequently the focus of attention for quantifying $Frac_{GASM}$ for New Zealand's $N_2O$ inventory must fall on measurements of $NH_{3(g)}$ emissions from excreta deposited directly onto NZ pastures. Such measurements are reviewed in the following section.

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**Table 4.3** Direct measurements of ammonia volatilisation from "whole system" grazing using the IHF[a] method: International data

| Country | Year of Study | Pasture type | Animal type | Fertiliser (kgN/ha/yr) | Number of grazings (N) | Mean % Excreted-N volatilised | Variability (SD) | Range | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Queensland (Aus) | 1972 | Grass/clover | Sheep | 0 | 1 | 26.0 [d] | - | - | Denmead et al., 1974 |
| England | 1986 ? | Perennial Ryegrass | Beef cattle | 420 | 5 | 14.7 | 7.7 | 7.1 – 27.7 | Ryden et al., 1987 |
| England | 1986? | Grass/Clover | Beef cattle | 0 | 2 | 1.8 | - | 1.3 – 2.3 | Ryden et al., 1987 |
| England | 1986-87 | Perennial Ryegrass | Yearling steers | 420 | 7 | 12.5 [b] | NA | NA | Jarvis et al., 1989 |
| England | 1986-87 | Perennial Ryegrass | Yearling steers | 210 | 7 | 5.8 [b] | NA | NA | Jarvis et al., 1989 |
| England | 1986-87 | Grass/Clover | Yearling steers | 0 | 7 | 3.7 [b] | NA | NA | Jarvis et al., 1989 |
| England | 1988-89 | Perennial Ryegrass | Sheep | 420 | 16 | 8.6 [c] | NA | NA | Jarvis et al., 1991 |
| England | 1988-89 | Perennial Ryegrass | Sheep | 0 | 13 | 6.4 [c] | NA | NA | Jarvis et al., 1991 |
| England | 1988-89 | Clover | Sheep | 0 | 13 | 13.2 [c] | NA | NA | Jarvis et al., 1991 |
| England | 1988-89 | Grass/Clover | Sheep | 0 | 17 | 1.3 [c] | NA | NA | Jarvis et al., 1991 |
| Holland | 1987 | Perennial Ryegrass | Dairy cows | 550 | 8 | 8.5 | 3.9 | 5.2 – 14.8 | Bussink, 1992 |
| Holland | 1988 | Perennial Ryegrass | Dairy cows | 250 | 7 | 3.1 | 1.7 | 1.6 – 5.7 | Bussink, 1992 |
| Holland | 1988 | Perennial Ryegrass | Dairy cows | 550 | 9 | 7.7 | 4.1 | 1.2 – 12.9 | Bussink, 1992 |
| Holland | 1989 | Perennial Ryegrass | Dairy cows | 250 | 2 | 5.3 | - | 2.1 – 7.1 | Bussink, 1994 |
| Holland | 1989 | Perennial Ryegrass | Dairy cows | 400 | 2 | 13.9 | - | 10.2 - 16.7 | Bussink, 1994 |
| Holland | 1989 | Perennial Ryegrass | Dairy cows | 550 | 2 | 14.4 | - | 9.8 – 18.0 | Bussink, 1994 |
| Holland | 1990 | Perennial Ryegrass | Dairy cows | 250 | 7 | 3.3 | 2.6 | 0.0 – 7.4 | Bussink, 1994 |
| Holland | 1990 | Perennial Ryegrass | Dairy cows | 400 | 7 | 6.9 | 5.5 | 2.5 – 17.8 | Bussink, 1994 |
| Holland | 1990 | Perennial Ryegrass | Dairy cows | 550 | 7 | 6.9 | 4.0 | 2.1 – 15.5 | Bussink, 1994 |

[a] IHF = Integrated Horizontal Flux method (section 2.4.4)

[b] assumes an N-excretion rate (Nex) of 53.8kgN/steer/year (UK National Inventory, 1990)

[c] assumes an N-excretion rate (Nex) of 5.24kgN/sheep/year (UK National Inventory, 1990)

[d] used a different micrometeorological (Energy Balance) method

NA = not available

# Section 5. Review of New Zealand data on ammonia volatilisation in pastoral agriculture

## 5.1 <u>Ammonia emissions from urine and dung</u>

Studies of ammonia volatilisation from excreted-N in New Zealand appear to have begun in the late 1940s by Doak. In this often quoted and still highly relevant paper, (Doak, 1952) used an aspirated chamber method in the field to measure the $NH_{3(g)}$ emissions from sheep urine patches. The mean emission from three measurements was 12.1 % of the applied urine-N. Subsequent work by Ball et al (1979), Carran et al. (1982) and Ball and Keeney (1983), (reported in Ball and Ryden, 1984) all used a variant of the aspirated chamber approach, and yielded $NH_{3(g)}$ emission values from urine of between 5 and 66 % (Table 5.1). In that work, which was carried out in both Manawatu and Southland, greatest emissions coincided with the warm and dry conditions of summer.

Sherlock & Goh (1984) used a continuously aspirated chamber technique to measure $NH_{3(g)}$ emissions from sheep urine applied to pasture in Canterbury. Their measurements ranged from 12.2 to 24.6 % of the applied urine-N and, as reported by Ball and Ryden (1984), the greatest emissions coincided with the warm summer period.

Ball's experimental system was subsequently employed by Sugimoto et al. (1992) to determine the $NH_{3(g)}$ emissions from cow dung pats. Those workers found that unlike the $NH_{3(g)}$ emissions from urine, $NH_{3(g)}$ emissions from dung were much smaller but also more protracted. Emissions from six separate measurements spanning two seasons ranged from 2.8 to 8.1 % of the dung-N (mean 5.6 %). The highest emissions occurred from "pats" which the researchers themselves noted probably contained unrealistically high levels of dung (6 kg fresh per $0.1m^{-2}$, equivalent to 2000kg N $ha^{-1}$). The mean $NH_{3(g)}$ emissions from the four, more realistic rates of application, averaged 4.5 % of the dung-N which, although four times that reported earlier for UK conditions (Table 4.2), was nevertheless much lower than that from urine (Tables 4.1 and 5.1). These appear to be the only measurements of $NH_{3(g)}$ emission from dung that have been carried out in NZ (Table 5.2).

The recent use of nitrification and urease inhibitors in pastoral agriculture in New Zealand, has led to a renewed interest in their possible effects on $NH_{3(g)}$ emission from excreted-N. Concern has been expressed that the use of DCD, a nitrification inhibitor, on pastures could slow the nitrification of $NH_4^+{}_{(aq)}$ sufficiently for $NH_{3(g)}$ emissions to increase. Di and Cameron (2004) explored this possibility in a field experiment using aspirated chambers similar to those used by Sherlock and Goh (1984). Emissions from urine alone applied at 1000 kg N $ha^{-1}$ amounted to just 3.5 % of the applied-N (Table 5.1), while the application of DCD to urine patches actually reduced subsequent $NH_{3(g)}$ emissions to 1.7 %, although the difference was not statistically significant (Table 5.2). These findings were supported more recently by Jagrati Singh at Palmerston North who explored the effects of several of these products, not only on $NH_{3(g)}$ emissions, but also on $N_2O$ emissions from urine affected soil. In that work, which was carried out under controlled conditions on soil cores in a glasshouse, $NH_{3(g)}$ emissions ranged from 0.95 to 8.9 % of the applied urine-N (Singh et al., 2008a & 2008b). And like the findings of Di & Cameron (2004), Singh et al. (2008 a & b) showed that DCD had no significant effect on $NH_{3(g)}$ emissions, although the urease inhibitor, nBTPT (section 6.3), did significantly reduce emissions from 8.9 to 6.9 % of the applied urine-N (Tables 5.1 & 5.2). Menneer et al. (2008) also recently carried out an investigation of the fate of urine-N applied under field conditions to a pumice soil at Taupo. Amongst other things these researchers measured the $NH_{3(g)}$ emission from cow urine applied at 775 kgN/ha) using the aspirated chamber technique employed by Black et al. (1984). In the 20 days following urine application, 14 % of the urine-N was emitted as $NH_3$-N. These researchers were also able to demonstrate that neither DCD nor 4MP[8] applied along with the urine had any influence on the magnitude of subsequent $NH_{3(g)}$ emissions. But they were able to show that the urease inhibitor nBTPT markedly reduced $NH_{3(g)}$ emissions to just 5 % of the applied urine-N; a reduction of 64 % (Tables 5.1 & 5.2).

## 5.2 Ammonia emissions from "whole system" grazing

Unlike the European situation where "whole system" grazing has been studied intensively using the IHF method (Section 2.4.4 & Table 4.3) there appears to have been only one comparable attempt in New Zealand. Ledgard et al. (1999) employed passive $NH_{3(g)}$ samplers (as described by Leuning et al., 1985), to quantify $NH_{3(g)}$ volatilisation emissions from a series of dairy farmlets in the Waikato. That intensive three year study involved three N fertiliser regimes and two different stocking rates. Because a zero N-fertiliser treatment was included, these researchers were able to distinguish $NH_{3(g)}$ emissions derived from excreted-N from the emissions derived from the fertiliser (urea) used. Their initial paper

[8] 4MP = 4-methylpyrazole, another nitrification inhibitor.

(Ledgard et al. 1996) provided annual excretal-N rates for this study. After taking account of excreta N loss to lanes and cowsheds, it can be determined that the $NH_{3(g)}$ emissions from the zero-N farmlets averaged just 4.0 % of the N excreted onto the pasture over the three years monitored (Table 5.3).

The only other significant occasions where this IHF approach has been made in NZ to measure $NH_{3(g)}$ volatilisation from non-fertiliser-N applications were those of Sherlock & van der Weerden (1992) and Sherlock et al. (2002). However as one study involved synthetic urine applied as a single "mega-patch" and the other involved pig slurry, neither is particularly relevant to quantifying NZ's $Frac_{GASM}$ and the results are not reported here.

**Table 5.1** Direct measurements of ammonia volatilisation from herbivore urine applied to pasture: New Zealand data

| Location | N source | Rate(s) of Application (kg N $ha^{-1}$) | Mean % Urine-N volatilised | Variability (SD) | N | Range | Reference | Methodology |
|---|---|---|---|---|---|---|---|---|
| Manawatu | Cow urine | 150 | 12.1 | NA | 3 | NA | Doak, 1952 | aspirated chamber |
| Manawatu | Cattle urine | 300 – 600 | 16.5 | 2.1 | 2 | 15 - 18 | Ball et al., 1979 | aspirated chamber |
| Southland | Dairy cow urine | 300 | 26.5 | 13.4 | 2 | 17 - 36 | Carran et al., 1982 | aspirated chamber |
| Manawatu | Cattle urine | 300 – 600 | 29.0 | 32.5 | 3 | 5 - 66 | Ball & Ryden, 1984 | aspirated chamber |
| Canterbury | Dairy cow urine | 500 | 19.7 | 6.6 | 3 | 12.2 – 24.6 | Sherlock & Goh, 1984 | aspirated chamber |
| Canterbury | Dairy cow urine | 1000 | 3.5 | - | 1 | - | Di & Cameron, 2004 | aspirated chamber |
| Manawatu | Dairy cow urine | 144 - 570 | 2.4 | 1.7 | 3 | 0.95 – 4.2 | Singh et al., 2008a | aspirated chamber * |
| Manawatu | Dairy cow urine | 476 | 8.9 | - | 1 | - | Singh et al., 2008b | aspirated chamber * |
| Taupo | Dairy cow urine | **775** | **14.0** | **-** | **1** | **-** | Menneer et al.., 2008 | aspirated chamber |
| | | **Overall** | **15.9**[b] | **15.3** | **19** | **%CV [a] = 96%** | | |

[a] **%CV = (Standard deviation ÷ Mean) x 100 %**

[b] **weighted mean of all 18 studies**

*** experiments performed on soil cores in a greenhouse**

**Table 5.2** Direct measurements of ammonia volatilisation from pasture treated with cattle dung or with herbivore urine together with a nitrification inhibitor (DCD) or urease inhibitor (nBTPT): New Zealand data.

| Location | N source | Rate(s) of Application (kg N $ha^{-1}$) | Mean % Urine-N volatilised | Variability (SD) | N | Range | Reference | Methodology |
|---|---|---|---|---|---|---|---|---|
| Canterbury | Dairy cow urine + DCD | 1000 | 1.7 | - | 1 | - | Di & Cameron, 2004 | aspirated chamber |
| Manawatu | Dairy cow urine + DCD | 144 - 570 | 2.6 | 1.6 | 3 | 1.1 – 4.4 | Singh et al., 2008a | aspirated chamber * |
| Manawatu | Dairy cow urine + nBTPT | 476 | 6.9 | - | 1 | - | Singh et al., 2008b | aspirated chamber * |
| Taupo | Dairy cow urine + DCD | 775 | 14 | - | 1 | - | Menneer et al., 2008 | aspirated chamber |
| Taupo | Dairy cow urine + nBTPT | 775 | 5 | - | 1 | - | Menneer at al. 2008 | aspirated chamber |
| Taupo | Dairy cow urine + 4MP | 775 | 17 | - | 1 | - | Menneer at al. 2008 | aspirated chamber |
| Manawatu | Cattle dung | 650 | 3.1 | 0.4 | 2 | 2.8 – 3.4 | Sugimoto et al. 1992 | aspirated chamber |
| Manawatu | Cattle dung | 1300 | 5.9 | 0.2 | 2 | 6.0 – 5.8 | Sugimoto et al. 1992 | aspirated chamber |
| Manawatu | Cattle dung | 2000 | 7.7 | 0.5 | 2 | 8.1 – 7.4 | Sugimoto et al. 1992 | aspirated chamber |

*** experiments performed on soil cores in a greenhouse**

**Table 5.3** Direct measurements of ammonia volatilisation from "whole system" grazing using the IHF[a] method: NZ data

| Location | N source | Rate(s) of Application (kg N $ha^{-1}$) | Mean % Urine-N volatilised | Variability (SD) | N | Range | Reference | Methodology |
|---|---|---|---|---|---|---|---|---|
| Waikato | Dairy cow urine | 395 | 4.0 | 0.3 | 3 | 3.8 – 4.3 | Ledgard et al 1996 & 1999 | IHF method |

## 5.3 Discussion

As has been noted previously (Section 4.3 and Figure 1), 97% of the N excreted by NZ's farmed livestock is currently excreted directly onto pasture. However, it is noteworthy that the increasing use of wintering-off pads, particularly in high rainfall areas of the South Island, will likely result in a gradual downwards shift in this value.

As already mentioned (Section 1.1) mitigation of $NH_3$ emissions from applied manure-N is subject to regulation in many parts of Europe. This is not the case in NZ where trans-boundary (trans-national) air pollutant effects are minimal. Until recently, research on excreta-N in NZ has largely focussed on N-use efficiency. Any environmental concerns were largely confined to the leaching of excreted-N as nitrate. Consequently there have been relatively few measurements of $NH_{3(g)}$ volatilisation from animal excreta in NZ compared to other countries. Nevertheless, the limited amount of NZ data available tells the same story as the more extensive international data acquired under similar conditions.

Firstly, direct $NH_3$-N emissions from urine applied to pasture soils measured in NZ using aspirated chambers averaged 15.9 % (Table 5.1); only slightly more than the 12.9 % (Table 4.1) average obtained mainly using wind tunnels in overseas studies. The somewhat larger values measured in NZ may be real or they may be due to artefacts associated with the measurement techniques employed; wind tunnels likely being more reliable than aspirated chambers. Secondly, the limited NZ data available for $NH_3$-N emissions from dung applied at realistic rates on pasture averaged 4.5 % (Table 5.2). While somewhat higher than the wind tunnel derived results obtained on pastures overseas (1.5 %) (Table 4.2) they are like the overseas values, appreciably lower than the $NH_{3(g)}$ emissions from urine. Thirdly, when non-chamber IHF methods are employed to measure $NH_{3(g)}$ from total N-excreted, the single reliable NZ study undertaken gives very similar results to the much larger database of similar overseas studies. The 4.0 % mean value obtained by Ledgard et al (1996 & 1999) (Table 5.3), agrees very closely with the values for similar European grazing systems i.e. 3.3 to 4.2 % (Section 4.2, Table 4.3 & Section 8.1, Table 8.1). This last observation especially, indicates strongly that overseas data reported in the international literature can be used to assist in the re-evaluation of a country-specific $Frac_{GASM}$ for New Zealand.

# Section 6. Review of International and New Zealand data on ammonia volatilisation from fertiliser-N in grazed pastures

## 6.1 Ammonia emissions from broadcast urea

There have been many overseas studies of $NH_{3(g)}$ emissions from fertiliser. Most deal with cropping systems of various sorts and a high proportion involve fertiliser types that are not widely used in New Zealand. We tried to limit this section of the review therefore, to just those studies involving fertiliser applied to pasture. And since urea accounts for ~ 80 % of the fertiliser purchases in NZ (W. Catto pers. com., 2008) with the rest being mainly DAP, we also tried to confine our review to just those two fertilisers. But this was not a simple task. There is an enormous literature dealing with $NH_{3(g)}$ volatilisation from nitrogenous fertilisers. Most of it deals with agricultural production systems of little relevance to NZ's $N_2O$ inventory (e.g. rice production, intensive cropping etc). In trying to identify just those field-based studies dealing mainly with urea, surface-applied to pasture soil, we have had to be selective, and in being selective we have almost certainly missed some studies of relevance. Nevertheless, we have identified 60 field-based studies carried out under temperate climatic conditions which are relevant and which appear to present a consistent picture (Table 6.1). We also identified a number of reviews of ammonia volatilisation by others of relevance to NZ's $N_2O$ inventory (e.g. Harrison & Webb, 2001; van der Weerden & Jarvis, 1997; Misselbrook et al., 2000).

Some of the earliest relevant research identified was that conducted by Scott Black and his colleagues at Lincoln University in NZ in the 1980s; the work being reported in a series of papers (Black et al., 1984; 1985a; 1985b; 1987a; 1987b; 1989). Of most relevance to $Frac_{GASF}$ amongst that work was their study of the effect of rate of urea application on the extent of subsequent $NH_{3(g)}$-N emission. These workers showed that $NH_{3(g)}$ emissions increased from an average of 10.8 % of the urea-N applied at 30 kgN/ha to 33 % of the urea-N applied at (albeit unrealistically high) rates of 300 kgN/ha. While that work has both local and international significance, arguably the much more extensive work of Chadwick et al. (2005) in the UK is just as relevant to any revision of NZ's $Frac_{GASF}$. That work, conducted across a range of grassland sites in 2003-2004 utilised wind tunnels to quantify the $NH_{3(g)}$ emissions following urea, and other fertiliser applications to grassland soils. The rates of application used were overly high by NZ standards (100 kg N/ha) but one trial included a range of application rates down to 30kg N/ha. In Figure 5 we plot that data, along with other data from studies reported in the international literature. The data points for the UK studies of Chadwick et al. (2005) carried out at urea application rates of 100 kg N/ha are specifically identified and their quite wide spread gives a good visual indication of the extent of the variability encountered due to differences in soil type, meteorological (e.g. rainfall) and seasonal effects. But when all these data are viewed collectively, a reasonably consistent picture appears which confirms the earlier findings of Black et al. (1985b): namely that as rates of urea-N applications increase, the percentage of that applied-N that is volatilised as $NH_{3(g)}$ also increases. Black et al. (1985b) observed that this 'rate of application effect' is probably due to the influence that individual urea granules exert on elevating the pH of the soil surface beneath, and immediately surrounding, the site where each granule falls. At higher rates of urea application (> 60 kg urea-N/ha), the urea diffusing from individual granules merges and results in higher and more prolonged increases in soil surface pH than is experienced at lower (~ 30 kg urea-N/ha) rates of application. At low rates of urea-N application, the overlapping of urea diffusing from adjacent granules would take place only infrequently, so a much smaller portion of the soil surface would have a pH high enough to sustain $NH_{3(g)}$ volatilisation.

Of the 79 individual measurements reviewed (Table 6.1), 60 were carried out under field conditions and 19 of those were carried out on individual urea-N applications of 45 kg N/ha or less. Application rates of urea-N would very rarely exceed that value under typical pastoral farming conditions in NZ (W. Catto pers. Com. 2008). It is noteworthy that the mean percentage $NH_{3(g)}$ emissions from those 19 studies was 10.8 % (SD ~ 2.9) which is only slightly greater than the value for $Frac_{GASF}$ that is currently used in NZ's $N_2O$ inventory. But a comparison such as this is premature without first taking into account the contribution made to $Frac_{GASF}$ by the other non-urea N-fertilisers used in NZ and emissions as $NOx_{(g)}$ (section 7).

**Table 6.1** Direct measurements of ammonia volatilisation from broadcast granulated urea fertiliser

| Location | Rate(s) of Application (kg N $ha^{-1}$) | Mean % Urine-N volatilised | Variability (SD) | N | Range | Reference | Methodology |
|---|---|---|---|---|---|---|---|
| Canterbury NZ | 15 | 7.0 | - | 1 | - | Black et al., 1985b | aspirated chamber |
| Waikato NZ | 23 | 11.2 | 3.8 | 3 | 7.5 – 15.0 | Ledgard et al., 1999 | IHF method |
| Canterbury NZ | 25 | 7.5 | - | 1 | - | Di & Cameron, 2004 | aspirated chamber |
| Canterbury NZ | 30 | 10.8 | 2.8 | 7 | 7.3 -14.0 | Black et al. 1984; 1985b; 1987 | aspirated chamber |
| UK | 30 | 12.0 | - | 1 | - | Chadwick et al., 2005 | Wind tunnel |
| Waikato NZ | 45 | 11.6 | 3.2 | 6 | 7.5 – 15.2 | Ledgard et al., 1999 | IHF method |
| Canterbury NZ | 60 | 20.0 | - | 1 | - | Black et al., 1985b | aspirated chamber |
| UK | 60 | 20.0 | - | 1 | - | Chadwick et al., 2005 | Wind tunnel |
| UK | 70 | 14.4 | - | 1 | - | Ryden et al., 1987 | Wind tunnel |
| UK | 70 | 16.1 | 5.7 | 2 | 12.1 – 20.1 | Van der Weerden & Jarvis, 1997 | Wind tunnel |
| Netherlands | 80 | 19.0 | - | 1 | - | Velthof et al., 1990 | Wind tunnel |
| Netherlands | 90 | 7.0 * | - | 1 | - | Velthof et al., 1990 | Wind tunnel |
| Denmark | 90 | 17.8 | - | 1 | - | Sommer & Jenson, 1994 | Wind tunnel |
| Argentina | 90 | 18.9 | - | 1 | - | Barbieri & Echeverria, 2003 | Semi-open static |
| UK | 90 | 37.2 | 12.4 | 2 | 28.4 – 46.0 | Van der Weerden & Jarvis, 1997 | Wind tunnel |
| UK | 90 | 20.0 | - | 1 | - | Chadwick et al., 2005 | Wind tunnel |
| USA | 100 | 20.7 | 11.0 | 16 | 5.76 – 38.90 | Watson et al., 1994 | Controlled env. study |
| Canterbury NZ | 100 | 24.8 | 5.0 | 2 | 21.2 – 28.3 | Black et al., 1985a; 1989 | IHF method |
| Canterbury NZ | 100 | 22.5 | 4.1 | 5 | 16.6 – 27.8 | Black et al., 1985a; 1985b;1987;1989 | aspirated chamber |
| UK | 100 | 26.7 | 12.9 | 15 | 10 – 58.0 | Chadwick et al., 2005 | Wind tunnel |
| USA | 120 | 26.0 | - | 1 | - | Gameh et al., 1990 | Controlled env. study |
| Netherlands | 120 | 32.0 | - | 1 | - | Velthof et al., 1990 | Wind tunnel |
| UK | 120 | 30.3 | 10.8 | 2 | 22.6 – 37.9 | Van der Weerden & Jarvis, 1997 | Wind tunnel |
| UK | 150 | 23.0 | - | 1 | - | Chadwick et al., 2005 | Wind tunnel |
| Waikato NZ | 150 | 4.2 # | - | - | - | Zaman et al., 2008 | Intermittent aspiration |
| Argentina | 180 | 26.7 | - | 1 | - | Barbieri & Echeverria, 2003 | Semi-open static |
| Canterbury NZ | 200 | 33.0 | - | 1 | - | Black et al., 1985b | aspirated chamber |
| Canterbury NZ | 300 | 33.2 | - | 1 | - | Black et al., 1987 | aspirated chamber |
| USA | 300 | 37.8 | 3.2 | 2 | 35.5 – 40.0 | Knight et al., 2007 | Controlled env. study |

* result from a very wet period
# high rainfall the day following urea application, dissolved and moved the fertilizer below the surface producing this anomalously low result.

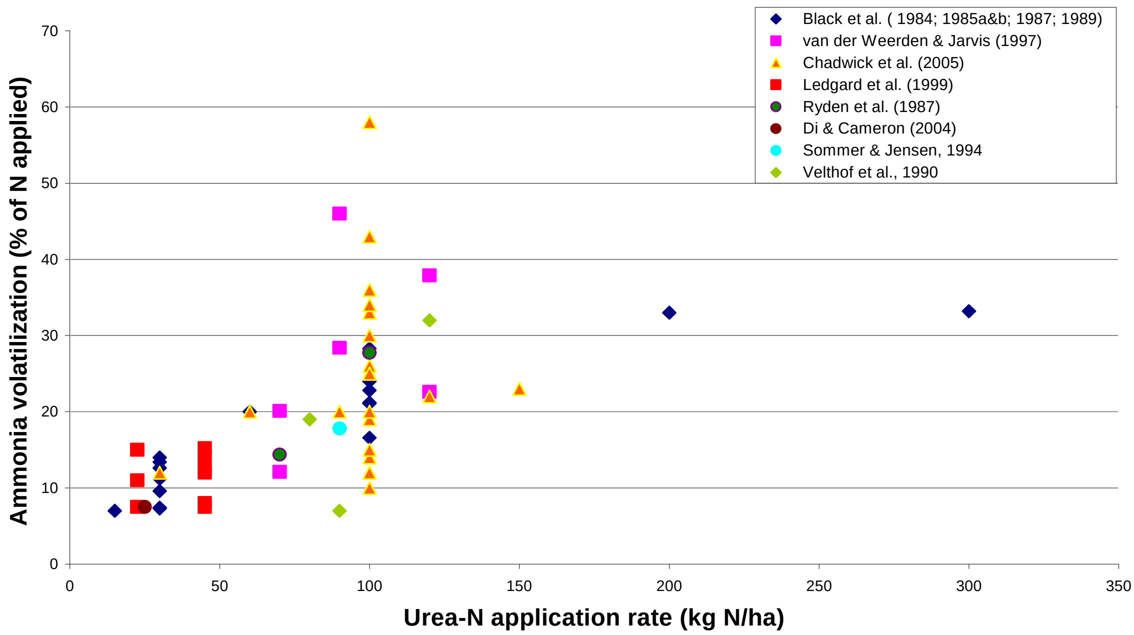


**Figure 5. Field measurements of ammonia emissions from 54 studies of urea fertiliser surface-applied at various rates to grassland soil**

## 6.2 Ammonia emissions from other nitrogenous fertilisers

After urea, the second most important nitrogenous fertiliser used in New Zealand is diammonium phosphate (DAP) and collectively these two fertilisers account for almost all of the N-fertiliser used in New Zealand (W. Catto, pers.com). Relatively few studies have attempted to quantify $NH_{3(g)}$ emissions from both of these fertilisers simultaneously under field conditions (Sommer & Jensen, 1994). But it is only through such studies that emissions from DAP are easily scaled with respect to those from urea, and reveal any rate dependant relationship of the sort identified for urea (section 6.1).

The work undertaken by Scott Black and his colleagues at Lincoln University in the mid 1980s appears to be the first in NZ dealing with $NH_{3(g)}$ emissions from fertilisers other than urea. Those researchers carried out a series of five studies measuring emissions from urea, DAP, ammonium sulphate (AS) and calcium ammonium nitrate (CAN) applied at rates of 30 kg N/ha across a range of seasons (Black et al., 1985b). Emissions of the applied-N averaged: urea 11.9 %, DAP 5.3 %, AS 1.0 % and CAN 0.8 %. So in those studies carried out on a Templeton silt loam soil in Canterbury, the $NH_{3(g)}$ emissions from DAP were *ca* 0.45 of those from an equivalent surface application of urea.

But how universal are those observations ? Are the $NH_{3(g)}$ emissions sustained from DAP always substantially less than those sustained from urea ? The work of Whitehead and Raistrick (1990) indicates that in most situations the answer is yes. As was noted previously (section 2.3.2), surface soil pH is a major factor influencing $NH_{3(g)}$ volatilisation. In their lab-based study, Whitehead and Raistrick (1990) showed clearly that there is a close relationship between the extent of volatilisation, expressed as a percentage of the applied ammonium-N or urea-N, and the pH attained after 24 hours by the corresponding mixtures of soil and fertiliser. In that study, non-calcareous soils with pHs between 5.5 and 7.1 always showed considerably lower $NH_{3(g)}$ emissions from DAP than from urea, in ratios (~ 0.30) not inconsistent with those found by Black et al. (1985b). The only exception was for a very calcareous soil (75 % free $CaCO_3$) which suffered higher $NH_{3(g)}$ emissions from DAP than from urea (Table 6.2). Those authors attributed that peculiar behaviour to the formation of $CaHPO_4$, octacalcium phosphate and apatite. Essentially the formation of these very insoluble calcium phosphate salts helps to solubilise $CaCO_{3(s)}$ and release the pH raising carbonate ion, $CO_3^{2-}{}_{(aq)}$, into the soil solution. A higher soil pH favours the formation of volatilisable $NH_{3(aq)}$ in the soil solution and enhances $NH_{3(g)}$ loss.

Sommer and Jensen (1994) conducted similar experiments but with wind tunnels under field conditions in Denmark. They applied various N-fertilisers at rates of between 80 – 120 kgN/ha to a sandy, non-calcareous soil growing either ryegrass (*Lolium multiflorum* L.) pasture or winter wheat (*Triticum aestivum* L.) and measured the resulting $NH_{3(g)}$ emissions over the following 15 – 20 days. In their studies, emissions of $NH_{3(g)}$ from DAP were consistently 25 – 50 % lower than from urea. And with the exception of the single study carried out on a calcareous soil, all of the other 12 comparative measurements reviewed consistently show $NH_{3(g)}$ emissions from DAP are less than those sustained from urea (Table 6.2). On average the $NH_{3(g)}$ emissions from DAP were 43 % (SD 17 %) of those sustained from urea applied at the same rate.

## 6.3 Influence of Urease Inhibitors

Urea-based fertilisers which include urease inhibitors are now commercially available. Principal amongst these products are those which include N-(n-butyl) thiophosphoric triamide (nBTPT), a very effective urease inhibitor. Urea fertilisers containing nBTPT, known commercially as 'Agrotain', are now available in NZ [9] . The inclusion of a small amount of nBTPT in these formulations retards the rate of urea hydrolysis. One of the consequences of this is a significant reduction in the proportion of the applied-N that is emitted as $NH_{3(g)}$ (Singh et al. 2008c).

The first (unpublished) experiments in NZ to clearly demonstrate this effect were carried out in Canterbury by Scott Black and his colleagues at Lincoln University in the mid 1980s. Two urease inhibitors were sourced and studied. Phenyl phosphorodiamidate (PPD) was available commercially, but nBTPT wasn't. However, a small quantity (~ 1g) of nBTPT was supplied by one of the principal nitrogen fertiliser researchers of that time: the late Prof Jack Bremner from Iowa State University. Black and his colleagues formulated those urease inhibitors into hand-made urea granules of uniform size and applied them, along with hand-made unamended urea granules to a Templeton silt loam pasture soil. The results are summarised in Table 6.3. Both inhibitors proved very effective in reducing $NH_{3(g)}$ volatilisation, but of the two inhibitors nBTPT was the more effective.

The single urea manufacturer in NZ at that time (Petrochem) did not have the resources to pursue the development of an alternative, nBTPT-impregnated, product. However overseas companies continued the necessary development and certification work required and products now containing nBTPT, suitable for use on grazed pastures are available worldwide. There is no doubt that the incorporation of nBTPT does retard and reduce $NH_{3(g)}$ volatilisation losses from granulated urea. The very extensive series of field trials undertaken by Chadwick et al. (2005) in the UK showed nBTPT incorporated into urea at rates of 0.05 – 0.1 % reduced $NH_{3(g)}$ emissions by an average of 70 % (range 41-100 %) compared with unamended urea. More recently, research undertaken in NZ by Singh et al. (2008b) has confirmed that the nBTPT-containing commercial urea fertilisers; SustaiN Yellow and SustaiN Green, both emitted just 2.8 % of their N content as $NH_{3(g)}$. This represents a 40 % reduction in $NH_{3(g)}$ emission compared with ordinary urea applied at a rate of 100 kgN/ha.

## 6.4 Discussion

The reviewed data for broadcast urea fertiliser are consistent with a 'rate of application effect' whereby the proportion of the applied-N emitted as $NH_{3(g)}$ increases as the rate of urea application increases. Emissions are lowest (~ 11 %) at rates of urea-N typically applied by NZ pastoral farmers (i.e. ≤ 45 kgN/ha) but reach ~ 30 % at rates of 300 kgN/ha. The data for DAP are more sparse, but there too a 'rate of application effect' appears to exist. Like urea, emissions are lowest (~ 5%) at rates of DAP typically applied by NZ farmers. $Frac_{GASF}$ for NZ is dominated by the $NH_{3(g)}$ emissions from both of these fertilisers. A weighted mean for their total contribution to $Frac_{GASF}$ can be estimated using the following conservative assumptions:

- Of the fertiliser used in NZ, 80 % is urea applied at ≤ 45 kgN/ha per application.
- The proportion of that applied urea-N emitted as $NH_{3(g)}$-N (i.e. its 'emission factor') is 10.8 %.
- The remaining 20 % of the fertiliser used in NZ is predominantly DAP whose emission factor is 4.6 % (i.e. 43 % of the corresponding urea emission factor).

The resulting weighted mean value of 0.096 (i.e. 9.6 %) is very similar to the value of 0.1; NZ's currently used default value for $Frac_{GASF}$ . But that weighted mean value does not take into account the use of urea incorporating urease inhibitors or the contribution from fertiliser-derived NOx. Fertiliser-derived NOx will be addressed in the following section.

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[9] For example: SustaiN Yellow, SustaiN Green and SustaiN FPA available through Summit Quinphos all contain nBTPT

**Table 6.2** Simultaneous direct measurements of ammonia volatilisation from broadcast diammonium phosphate and urea fertilisers

| Location | Fertiliser | Rate(s) of Application (kg N $ha^{-1}$) | Mean % Urine-N volatilised | Variability (SD) | N | Range | Reference | Methodology |
|---|---|---|---|---|---|---|---|---|
| Canterbury NZ | urea | 30 | 11.9 | 2.9 | 5 | 7.4-15.0 | Black et al 1985b | aspirated chamber |
| Canterbury NZ | DAP | 30 | 5.3 | 2.6 | 5 | 2.2-8.2 | Black et al. 1985b | aspirated chamber |
| | | | | | | | | |
| UK | urea | 100 | 28.3 | 8.7 | 3 | 21.0-38.0 | Whitehead & Raistrick 1990 | Controlled env. study |
| UK | DAP | 100 | 8.0 | 2.6 | 3 | 5.0-9.5 | Whitehead & Raistrick 1990 | Controlled env. study |
| | | | | | | | | |
| UK | Urea | 100 * | 41.0 | | 1 | - | Whitehead & Raistrick 1990 | Controlled env. study |
| UK | DAP | 100 * | 51.0 | - | 1 | - | Whitehead & Raistrick 1990 | Controlled env. study |
| | | | | | | | | |
| Denmark | Urea | 80-120 | 25.0 | 5.4 | 4 | 17.8-29.8 | Sommer & Jensen, 1994 | Wind tunnel |
| Denmark | DAP | 80-120 | 14.4 | 4.5 | 5 | 9.9-19.9 | Sommer & Jensen, 1994 | Wind tunnel |
| | | | | | | | | |

*** fertilisers added to calcareous soil (75% free $CaCO_3$)**

**Table 6.3.** Cumulative ammonia losses (% of N-applied) 20 days after broadcast application of urea (100 kgN/ha) impregnated with various amounts of the urease inhibitors: PPD and nBTPT [#].

**--------- Granule composition – Inhibitor / urea (% by weight) --------**

| | **0** | **0.01** | **0.1** | **1.0** |
|---|---|---|---|---|
| **No inhibitor** | 19.0 | - | - | - |
| **nBTPT** | - | 8.3 | 4.6 | 2.8 |
| **PPD** | - | - | 13.9 | 5.2 |

[#] Unpublished results of work by Black et al., Canterbury NZ, 1985.

# Section 7. Review of International and NZ data on NOx emissions from pastoral agriculture

## 7.1 NOx emissions from animal excreta and fertilized pasture

Interest in NOx emissions from soils received a major boost in 1978 following the publication of a paper in the journal 'Nature' by Galbally & Roy (1978). Those researchers used a sensitive chemiluminescence procedure to make the first ever direct field measurements of $NO_{(g)}$ emissions from soils; their work focussing on grazed and ungrazed pasture soils in Australia. Emission rates averaged 1.6 ng NO-N $m^{-2}$ $s^{-1}$ for ungrazed and 3.5 ng NO-N $m^{-2}$ $s^{-1}$ for grazed pastures (equivalent to annual emission rates of 0.5 and 1.1 kg NO-N $ha^{-1}$ $yr^{-1}$ respectively). That research, and much of the subsequent research by others, has been focussed mainly at "bottom-up" efforts to develop and refine Earth's global NOx emission inventory. Relatively few studies have attempted to quantify specifically the NOx emissions following urine and/or dung depositions on pasture. The results of the few studies which have are summarised in Table 7.1. Also summarised there are some of the more relevant field-derived data from studies of NOx emissions from fertiliser-N applied to pasture.

## 7.2 Discussion

Of most relevance to this current review is the recent research carried out by Shabana Khan as part of her PhD programme at Lincoln University (Khan, unpublished 2008). Shabana carried out two field experiments; one under summertime (warm and dry) and another under wintertime (cool and wet), conditions. She was able to show, using an aspirated chamber technique with chemiluminescence detection, that winter-time NOx emissions from urine patches in Canterbury were barely measurable. In contrast, summertime NOx emissions[10] were readily measurable but amounted to only 0.09 – 0.29 % of the urine-N applied at 1000 and 500 kg N/ha respectively in the 80 day period following urine application (Table 7.1). In contrast to $NH_{3(g)}$ volatilisation, percentage emissions as NOx did not increase with application rate; indeed percentage emissions from the higher urine-N application treatment (1000 kg urine-N/ha) were actually less than those sustained from the 500 kg urine-N/ha application.

[10] Of the 'NOx' emissions measured by Khan, almost all was as nitric oxide (NO). Almost no nitrogen dioxide ($NO_2$) was emitted.

Assuming the summertime and wintertime values obtained represent the likely extremes for NOx emissions from urine patches throughout NZ, and assuming also that NOx emissions from dung are similar to those from urine, then the contribution of NOx-N to $Frac_{GASM}$ would amount to only ~ 0.1 % (or 0.001). This is a tiny contribution to $Frac_{GASM}$, being 2 orders of magnitude less than the much greater contribution due to $NH_{3(g)}$ volatilisation (i.e 10 % or ~ 0.1) (Section 8.1).

Surprisingly, we could find no references to field studies involving the measurement of NOx emissions following the application of urea fertiliser to pasture. One recent study of NOx emissions from urea by Meijide et al. (2007) involved a maize crop. In that study, NOx emissions amounted to just 0.13 % of the applied urea-N over the 150 days following urea application at 175 kg urea-N/ha. A few studies involving fertiliser-N applied to pasture have involved ammonium nitrate, $NH_4NO_3$ (Harrison et al. 1995; Williams et al. 1998). The weighted mean NOx-N emissions across the 18 $NH_4NO_3$ studies reported in Table 7.1 are 0.27 % of the applied fertiliser-N. In the absence of reliable information for NOx emissions from urea applied to pasture we are almost obliged to assume a similar value for the contribution of NOx-N to NZ's $Frac_{GASF}$ . Making that assumption, we tentatively conclude that the NOx–N emissions from fertiliser use in NZ probably amount to just 3 % of the much more important $NH_{3(g)}$ emissions. Together with the proposed contributions of $NH_{3(g)}$ from urea and DAP applied at less than 45 kgN/ha (0.096, section 6.4), the overall value for $Frac_{GASF}$ (0.096 + 0.003 = 0.099) conforms closely to NZ's currently employed value of 0.1.

**Table 7.1** Direct measurements of NOx emissions from herbivore urine, excreta or N fertiliser applied to pasture: International & New Zealand data

| Location | Season | Duration (Days) | N Source | Rate(s) of Application (kg N $ha^{-1}$) | Mean % Applied-N emitted | Variability (SD) | N | Range | Reference | Methodology |
|---|---|---|---|---|---|---|---|---|---|---|
| Canterbury NZ | Summer | 80 | Cow urine | 1000 | 0.087 | 0.027 | 3 | 0.06-0.11 | Khan, 2008 unpublished | aspirated chamber |
| Canterbury NZ | Summer | 80 | Cow urine | 500 | 0.285 | 0.060 | 3 | 0.22-0.33 | Khan, 2008 unpublished | aspirated chamber |
| Canterbury NZ | Winter | 42 | Cow urine | 1000 | 0.0008 | 0.0001 | 3 | 5 - 7 (x $10^{-4}$) | Khan, 2008 unpublished | aspirated chamber |
| Canterbury NZ | Winter | 42 | Cow urine | 500 | 0.0006 | 0.00007 | 3 | - | Khan, 2008 unpublished | aspirated chamber |
| UK | Summer | 13 | Cow urine | 447 | 0.032 | - | 1 | - | Colbourn et al., 1987 | aspirated chamber |
| Australia | Summer | 28 | Sheep urine | 205 | 0.00087 | - | 1 | - | Bronson et al., 1999 | aspirated chamber |
| Japan | Autumn & Winter | 175 | Pig urine + excreta | 601 | 0.45 | - | 1 | - | Watanabe et al., 1997 | aspirated chamber |
| Japan | Autumn & Winter | 175 | Cattle urine + Cattle excreta | 1161 | 0.48 | - | 1 | - | Watanabe et al., 1997 | aspirated chamber |
| Spain | Winter | 150 | urea | 175 | 0.130 | 0.03 | 3 | ? | Meijide et al., 2007 | aspirated chamber |
| Spain | Winter | 150 | Pig slurry | 175 | 0.068 | 0.03 | 3 | ? | Meijide et al., 2007 | aspirated chamber |
| UK | Spring | 25 | $NH_4NO_3$ | 48 | 0.39 | ? | 4 | ? | Harrison et al., 1995 | aspirated chamber |
| UK | Spring | 25 | $NH_4NO_3$ | 96 | 0.36 | ? | 4 | ? | Harrison et al., 1995 | aspirated chamber |
| UK | Spring | 25 | $NH_4NO_3$ | 192 | 0.39 | ? | 4 | ? | Harrison et al., 1995 | aspirated chamber |
| UK | Autumn | 24 | $NH_4NO_3$ | 120 | 0.06 | ? | 6 | ? | Williams et al., 1998 | aspirated chamber |

# Section 8. General Discussion, Conclusions and recommendations

## 8.1 Frac$_{GASM}$

As clearly shown in sections 4 and 5, overseas data reported in the international literature can be used to assist in the re-evaluation of a country-specific Frac$_{GASM}$ for New Zealand. Using mean international $NH_3$-N emission data obtained by chamber and wind tunnel measurements (Tables 4.1, 4.2 & 8.1), and assuming a urine-N: dung-N split of 68 %: 32 % [11], the proportion of excreted-N emitted as $NH_3$-N can be estimated as 9.3 (SD ~ 4.5) %. This value transposed into a New Zealand context would equate to a Frac$_{GASM}$ value of 0.093 (or 0.094 if the very minor contribution due to NOx is included) [12]. Recall the current value used in NZ's inventory is 0.2.

If we now perform the same calculation on the much more limited number of chamber measurements of urine and dung in NZ (section 5.1, Tables 5.1, 5.2 & 8.1) the proportion of excreted-N emitted as $NH_3$-N can be estimated as 12.3 %. This value transposed into a New Zealand context would equate to a Frac$_{GASM}$ value of 0.123 (or 0.124 when the very minor contribution due to NOx emissions is included). On the basis of these two values alone (0.094 and 0.124) a downwards revision of NZ's Frac$_{GASM}$ from 0.2 to 0.1 would seem appropriate and justifiable.

**Recommendation 1:**
**A New Zealand specific value of 0.1 for Frac$_{GASM}$ be considered for adoption.**

But a case might be made for an even larger reduction in NZ's Frac$_{GASM}$ value if instead of focussing just on chamber and wind tunnel measurements, a greater emphasis is placed on the international "whole system" (IHF) measurements described in section 4.2 (Tables 4.3 & 8.1). Within that suite of data, the highest average net $NH_3$-N emissions occurred from the 47 studies of cattle grazing on perennial ryegrass pasture that received at least 400 kgN/ha/yr of fertiliser-N[13]. The weighted mean value of the $NH_3$-N emissions from those 47 grazing events is 9.6 % of the excreta-N. This is remarkably similar to the two values derived independently above (i.e. 9.3 & 12.3 %). But at lower rates of fertilization of between 210 and 250 kgN/ha/yr,

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[11] This ratio is assumed to be the same as that delivered by OVERSEER for herbivore excreta in NZ as reported by Kelliher et al. (2005).
[12] Assuming that the NOx emission factor for excreta-N is ~ 0.001 (section 7.2).
[13] The fertilizer-N was either non-volatile, or the fertilizer emissions were taken into account separately.

23 grazing events gave a weighted mean value for the $NH_3$-N emissions of just 4.2 % of the excreta-N. And from the 9 studies involving beef cattle or dairy cows grazing unfertilised grass/clover pastures the slightly lower weighted mean of 3.3 % was obtained. As pointed out already (Section 5.3) these last two values bracket the only similar study carried out on unfertilised ryegrass-clover pasture in NZ (4.0 %). So from these "whole system" IHF studies that don't employ chambers it could be argued that a NZ specific value of ~ 0.04 for $Frac_{GASM}$ might be more appropriate than the value (0.1) based on chamber and wind tunnel data alone. But such a recommendation is premature at this time since the number of local non-chamber based studies of $NH_{3(g)}$ emissions from grazed pastures are limited to those few reported by Ledgard et al. (1999). More non-chamber studies to refine $Frac_{GASM}$ are clearly warranted.

**Recommendation 2:**
**Research be supported for "whole system" non-chamber measurements of grazed pasture systems to further refine the New Zealand specific value for $Frac_{GASM}$.**

To help give scale to these recommendations we consider the direct effects on NZ's anthropogenic GHG inventory of altering $Frac_{GASM}$ as indicated above. Changing $Frac_{GASM}$ from 0.2 to 0.1 reduces NZ's 2006 $N_2O$ inventory by *ca* 6 % from 41.075 to 38.620 Gg $N_2O$[14]. This difference of 2.455 Gg $N_2O$ equates to 761.05 Gg $CO_2$-equivalents. Should future research justify a reduction of $Frac_{GASM}$ to ~ 0.04, the 2006 inventory would reduce by 3.928 Gg $N_2O$ which equates to 1,218 Gg $CO_2$-equivalents.

## 8.2 $Frac_{GASF}$

There remains a dearth of reliable information concerning NOx emissions following urea or DAP application to pastures. We were obliged therefore to look to measurements involving other fertiliser types (e.g. $NH_4NO_3$) or urea applied to non-pasture crops. Our best estimate for the contribution of NOx to $Frac_{GASF}$ in NZ is ≤ 0.003 (Tables 7.1 & 8.1). This tiny contribution is overshadowed by the much larger $NH_{3(g)}$ emissions from both urea and DAP. A weighted mean value for the $NH_{3(g)}$ emissions sustained from these two fertilisers applied at rates typically applied to NZ pasture (≤ 45 kgN/ha) was 9.6 % of the applied fertiliser-N (Section 6.4). These two components of $Frac_{GASF}$ sum to 0.099 (i.e. 0.096 + 0.003) which is essentially identical to the value NZ currently uses (0.1). Currently NZ uses

[14] EXCEL spreadsheet "Ag-2008 submission nir table builder.XLS" supplied by S. Petrie (MfE) July 2008.

a default value of 0.1 for $Frac_{GASF}$. We believe now there is sufficient justification to make the following recommendation:

**Recommendation 3:**

**A New Zealand specific value of 0.1 for $Frac_{GASF}$ be considered for adoption.**

An issue of relevance to $Frac_{GASF}$ that was mentioned earlier (Section 2.3.1) is the potential that exists to markedly reduce $NH_{3(g)}$ emissions following fertiliser application if the fertiliser is irrigated into the soil soon after application, or indeed if the farmer applies the fertiliser just prior to a significant rainfall event (Black et al., 1987a). Some situations (e.g. irrigated dairying in Canterbury) lend themselves better to this possible practice than others. However, it is unlikely, given the relatively small agronomic N-losses that occur normally, whether many farmers would bother deliberately implementing this strategy just to reduce $NH_{3(g)}$ emissions. Nevertheless the possibility for rain or irrigation to reduce $NH_{3(g)}$ emissions is well recognised and must occur, if only by chance, from time to time.

As well as irrigation, another mitigation tool which reduces $NH_{3(g)}$ volatilisation is urea impregnated, or coated, with urease inhibitor (Section 6.3 & Table 6.3). Farmers may justify the use of these fertilisers if they result in greater N uptake and dry matter (DM) production but are unlikely to use them just to mitigate $NH_{3(g)}$ emissions. Nevertheless, both timely irrigation and the use of urease inhibitors are tools which have the potential to reduce $Frac_{GASF}$ and thereby, in principle, reduce indirect $N_2O$ emissions from NZ agriculture.

To give scale to the effects such strategies might have on NZ's $N_2O$ inventory we present two, albeit rather optimistic, scenarios which themselves neglect any possible secondary detrimental (pollution swapping) effects e.g. the stimulation of direct $N_2O$ emissions induced by excessive irrigation of the soil:

**Scenario 1**: Farmers employ irrigation immediately following urea (or DAP) fertiliser application, and fertiliser application is timed to coincide with significant rainfall. It is assumed that these strategies are employed to the extent that half of the N-fertiliser used in NZ sustains just 10 % of its 'normal' emissions. The resulting overall reduction in $Frac_{GASF}$ from 0.1 to 0.055, would reduce NZ's $N_2O$ inventory by 0.234 Gg $N_2O$ or 72 Gg $CO_2$-equivalents.

**Scenario 2**: The use of urea treated with urease inhibitors gains ~ 50 % of market share for all urea fertiliser used in NZ and the $NH_{3(g)}$ emissions from such fertilisers are reduced by 40 % (Section 6.3). The resulting overall reduction in $Frac_{GASF}$ from 0.1 to 0.08, would reduce NZ's $N_2O$ inventory by 0.104 Gg $N_2O$ or 32 Gg $CO_2$-equivalents.

**Recommendation 4:**

**Research be supported to explore the efficacy of urease inhibitors to reduce $NH_{3(g)}$ emissions from urea fertiliser in New Zealand, with a view of further refining NZ's $Frac_{GASF}$ value.**

**Table 8.1** Summary of Emission Factors reviewed in previous sections

| Location | N-Source | Notes | Gas emitted | Mean % N emission | N | CV * (%) | Type of Study | Section (this review) |
|---|---|---|---|---|---|---|---|---|
| International | Urine | - | $NH_3$ | 12.9 | 41 | 49 | Wind tunnel and chamber | 4.1 |
| International | Dung | - | $NH_3$ | 1.5 | 4 | 26 | Wind tunnel and chamber | 4.1 |
| International | Cattle excreta | ~ 400kgN fert./yr | $NH_3$ | 9.6 | 47 | NA | "whole system" grazing (IHF) | 4.2 |
| International | Cattle excreta | ~ 200kgN fert./yr | $NH_3$ | 4.2 | 23 | NA | "whole system" grazing (IHF) | 4.2 |
| International | Cattle excreta | Grazed grass-clover | $NH_3$ | 3.3 | 9 | NA | "whole system" grazing (IHF) | 4.2 |
| England | Sheep excreta | Grazed grass-clover | $NH_3$ | 1.3 | 17 | NA | "whole system" grazing (IHF) | 4.2 |
| New Zealand | Cattle urine | 150-1000 kgN/ha | $NH_3$ | 15.9 | 19 | 96 | Aspirated chamber | 5.1 |
| New Zealand | Cattle dung | 650-1300 kgN/ha | $NH_3$ | 4.5 | 4 | 4 | Aspirated chamber | 5.1 |
| New Zealand | Cattle excreta | Grazed grass-clover | $NH_3$ | 4.0 | 3 | 7.5 | "whole system" grazing (IHF) | 5.2 |
| International & NZ | Urea | ≤ 45 kg urea-N/ha | $NH_3$ | 10.8 | 19 | 27 | Wind tunnel, chamber & IHF | 6.1 |
| International & NZ | DAP | ≤ 45 kg urea-N/ha | $NH_3$ | 4.6 | 13 | NA | Lab, chamber & wind tunnel | 6.4 |
| NZ | Urine | 500-1000ha | NOx | 0.1 | 12 | 143 | Aspirated chamber | 7.2 |
| International | Urea & $NH_4NO_3$ | 48-192 kgN/ha | NOx | 0.3 | 21 | 160 | Aspirated chamber | 7.2 |

*** %CV = (Standard deviation ÷ Mean) x 100 %**

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