

Greenhouse gas emissions from ammonium-based nitrogen fertilisers and lime

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Contents

| | | |
|-------|--|----|
| 1. | Executive Summary | 1 |
| 2. | Introduction | 3 |
| 3. | N fertiliser and lime use in New Zealand | 6 |
| 3.1 | Nitrogen fertilisers | 6 |
| 3.2 | Agricultural Lime | 8 |
| 4. | Nitrous oxide emissions factors (EF_1) for ammonium-based N fertilisers | 9 |
| 4.1 | Processes responsible for N_2O emissions | 9 |
| 4.2 | Influence of form of N fertiliser on N_2O emission factors | 11 |
| 4.3 | Potential improvements to GHG inventory reporting | 15 |
| 5. | Ammonia emission factors ($Frac_{GASF}$) for ammonium-based N fertilisers | 15 |
| 5.1 | Processes responsible for NH_3 volatilisation | 15 |
| 5.2 | Influence of N fertiliser form on $Frac_{GASF}$ | 16 |
| 5.2.1 | DAP | 16 |
| 5.2.2 | AS | 17 |
| 5.2.3 | Influence of soil pH on DAP and AS $Frac_{GASF}$ values | 19 |
| 5.3 | Potential improvements to GHG inventory reporting | 20 |
| 6. | Carbon dioxide EF_{LIME} and $EF_{DOLomite}$ values for agricultural lime and dolomite | 20 |
| 6.1 | Processes responsible for CO_2 emissions | 20 |
| 6.2 | Derivation of country-specific emission factors and activity data | 22 |
| 6.3 | Potential improvements to GHG inventory reporting | 22 |
| 7. | Conclusions | 23 |
| 8. | Acknowledgements | 24 |
| 9. | References | 25 |
| 10. | Appendix 1 | 31 |

1. Executive Summary

This report provides a review of the international literature on the nitrous oxide (N_2O) and ammonia (NH_3) emission factors for the two most common non-urea N fertilisers applied to New Zealand soils: ammonium phosphate (AP) and ammonium sulphate (AS). Our review also includes research and discussion on carbon dioxide (CO_2) emission factors for limestone and dolomite.

Greenhouse gas (GHG) emissions from non-urea fertiliser and lime application to agricultural soils are currently estimated by multiplying the amount of product applied to land (i.e. activity data) by emission factors for each product. The N_2O and NH_3 emission factors for non-urea fertiliser and CO_2 emission factors for lime and dolomite currently employed in the New Zealand GHG inventory, including a description of how these are used for calculating GHG emissions, are shown below:

EF₁ for non-urea N fertiliser

New Zealand uses the Intergovernmental Panel for Climate Change (IPCC) default emission factor (EF_1) of 1% of applied N for non-urea fertiliser. For comparative purposes, New Zealand has adopted a country-specific EF_1 value for urea fertiliser (EF_{1-UREA}) of 0.59%. To estimate N_2O -N emissions (t N_2O -N /year) from N fertiliser, the amount of fertiliser nitrogen (N) is multiplied by the appropriate EF value. This emission is converted to tonnes of N_2O /year by multiplying N_2O -N /year by 44/28, for the molecular weights of two N atoms and one molecule of N_2O are 28 and 44 g/mol, respectively. Greenhouse gas emissions are typically reported using the unit 'carbon dioxide equivalents' (t CO_2e), as this accounts for the different global warming potentials (GWP) of different GHGs. For N_2O , the GWP is 298 times greater than CO_2 , based on a 100-year horizon. Therefore, to convert t N_2O /year to t CO_2e /year, emissions are multiplied by 298. Nitrous oxide emitted from fertiliser is an example of a 'direct' N_2O emission.

Frac_{GASF} for N fertiliser

The proportion of synthetic fertiliser N volatilised as ammonia (NH_3) and nitric oxides (NO_x) is described as $Frac_{GASF}$, kg N volatilised per kg of N applied. New Zealand has adopted the country-specific $Frac_{GASF}$ value of 10% of N applied. Ammonia and nitric oxide volatilisation is an example of an 'indirect' N_2O emission source, as these gases are deposited onto soil downwind as an N input, where soil microbial activity results in further N_2O emissions. Nitrous oxide emissions are calculated by multiplying the amount of N volatilised by the emission factor EF_4 .

CO₂ emission factors for lime and dolomite

Annual CO₂ emissions from limestone (CaCO₃) or dolomite (CaMg(CO₃)₂) applications have emission factor (EF) units of tonnes carbon (C) per tonne of CaCO₃ or CaMg(CO₃)₂ applied per year. The EF values are 0.12 for limestone and 0.13 for dolomite and are equivalent to the carbonate-C contents of these materials (12% for CaCO₃, 13% for CaMg(CO₃)₂). The CO₂-C emissions are calculated by multiplying the amount of lime or dolomite by the appropriate EF value. To convert into CO₂ emissions, the CO₂-C emissions are multiplied by 44/12, for the molecular weights of C and CO₂ are 12 and 44 g/mol, respectively. The EF for lime and dolomite will be hereafter referred to as EF_{LIME} and EF_{DOLOMITE}, respectively.

Nitrous oxide emissions factors (EF₁) for AS and AP fertilisers

We identified 16 N₂O emission factor studies on AS or AP fertilisers applied to soils in temperate climates, providing 30 N₂O EF₁ values. Of these, 29 values related to AS while only one EF₁ value was found for AP fertiliser (as diammonium phosphate (DAP)). Based on the collated data, the mean N₂O EF₁ value for AS was 0.35%. Our dataset contained 17 values where both AS and urea were applied to soils. The mean EF₁ value for AS and urea was 0.38% and 0.57%, respectively. The single DAP study produced an EF₁ value of 1%, which was similar to the EF₁ value determined for a corresponding urea treatment (1.1%). We were unable to find any mono-ammonium phosphate (MAP) fertiliser studies that met the scope of the review.

Ammonia volatilisation (Frac_{GASF}) for AS and AP fertiliser

We identified 15 field studies, including four from New Zealand, providing 58 Frac_{GASF} values, where 17 related to DAP and 41 related to AS. Collated data suggested a mean Frac_{GASF} value of 9.7% and 7.1% of N applied for AS and DAP, respectively. However, NH₃ volatilisation is strongly influenced by soil pH, with NH₃ losses from DAP and urea increasing with increasing pH. Losses from AS, on the other hand, appear to be greater from alkaline soils. These mean Frac_{GASF} values calculated for AS and DAP have been influenced by the wide range of soil pH conditions, with many studies on AS conducted at soil pH between 7 and 9. New Zealand's agricultural soils are generally acidic to neutral. Under these conditions, New Zealand studies suggest that NH₃ volatilisation is minor (typically less than 3% of applied N) from AS fertiliser, while losses from DAP are approximately 50% of that from urea. As for N₂O, we were unable to locate any field studies that reported Frac_{GASF} values for MAP fertiliser.

Carbon dioxide emission factors for lime (EF_{LIME}) and dolomite (EF_{DOLOMITE})

Two studies proposed country-specific EF_{LIME} values for lime. Proposed mean EF_{LIME} values were 0.039 and 0.059 t C/t lime for, respectively, Korean upland soils and the US, compared with the IPCC default value of 0.12. Carbon dioxide emissions from lime and

dolomite application to soil are likely to be lower than the maximum potential loss, which assumes 100% of the C in lime and dolomite is dissociated and emitted as CO₂. The lower loss is primarily due to the initial reaction of CO₂ to bicarbonate during dissolution of lime, which offsets a proportion of the CO₂ released.

While not strictly focusing on emission factors, it is important to include a comment on the activity data used for estimating CO₂ emissions from lime and dolomite. The current default methodology assumes lime and dolomite are 100% pure (i.e. the quarried lime and dolomite products are 100% CaCO₃ or 100% CaMg(CO₃)₂, respectively). However, it is known that these quarried products have lower purities. For instance, lime sold by Ravensdown has a purity of between 69 and 97%. Accounting for lime and dolomite purity would improve the accuracy of New Zealand's GHG inventory reporting.

Potential improvements to GHG inventory calculations in relation to NH₄⁺-based fertiliser, lime and dolomite

1. There may be justification for determining a country-specific EF₁ value for NH₄⁺-based fertilisers, as the collated data suggests EF₁ values are similar for NH₄⁺-based and urea N fertilisers. However, the current evidence for this is greater for AS (n=17) than for DAP (n=1).
2. Under New Zealand's acidic to neutral soil pH conditions, the data would suggest NH₃ volatilisation is minor from AS fertiliser, while losses from DAP are approximately 50% of that from urea. There is justification for determining country-specific Frac_{GASF} values for AS and DAP fertilisers.
3. Adoption of country-specific activity data accounting for the purity of lime and dolomite could be investigated. This should include an assessment of how to meet IPCC's monitoring, reporting and verification requirements in relation to lime and dolomite purity.

2. Introduction

Agriculture is responsible for 48% of the total greenhouse gas (GHG) emission from New Zealand, and for 95% of nitrous oxide (N₂O). An inventory of national GHG emissions is reported annually to the United Nations Framework Convention on Climate Change (UNFCCC). To calculate these emissions New Zealand uses its agricultural inventory model (AIM). AIM currently estimates GHG emissions from non-urea N fertiliser and lime application to agricultural soils by multiplying the amount of product applied to land (i.e. activity data) by emission factors for each product (MfE, 2019). An example is shown for non-urea N fertiliser in Figure 1.

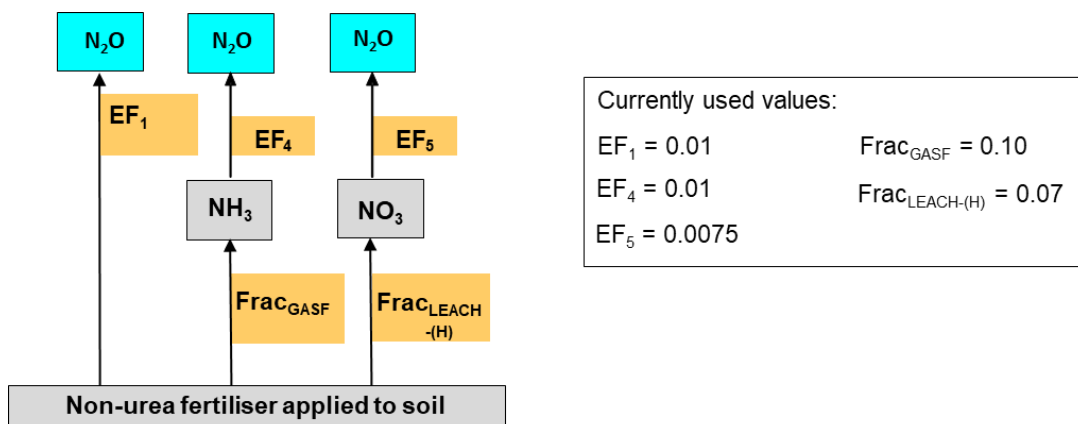


Fig. 1: Flow chart of the national N₂O inventory methodology showing emissions from non-urea N fertiliser applied to land in NZ.

For direct N₂O emissions from non-urea fertiliser, New Zealand has adopted the Intergovernmental Panel on Climate Change (IPCC) default emission factor (EF_1) of 1% of N applied (IPCC, 2006; Fig. 1). To estimate N₂O-N emissions (t N₂O-N /year) from N fertiliser, the amount of fertiliser nitrogen (N) is multiplied by the appropriate EF value. This emission is converted to tonnes of N₂O/year by multiplying N₂O-N /year by 44/28, for the molecular weights of two N atoms and one molecule of N₂O are 28 and 44 g/mol, respectively. Greenhouse gas emissions are typically reported using the unit ‘carbon dioxide equivalents’ (t CO₂e), as this accounts for the different global warming potentials (GWP) of different GHGs. For N₂O, the GWP is 298 times greater than CO₂, based on a 100-year horizon. Therefore, to convert t N₂O/year to t CO₂e/year, emissions are multiplied by 298. Nitrous oxide emitted from fertiliser is an example of a ‘direct’ N₂O emission.

Indirect N₂O emissions are derived from gaseous emissions of ammonia (NH₃) and NO_x as well as from N leaching, where N₂O from deposited NH₃ and NO_x is calculated using emission factor EF_4 while N₂O emissions from surface water bodies following N leaching is calculated by emission factor EF_5 (Fig. 1). For gaseous emissions of ammonia (NH₃) and NO_x from synthetic N fertilisers ($Frac_{GASF}$), New Zealand has adopted the country-specific value of 10% of N applied, or 0.10 kg N emitted per kg N applied (Fig. 1; MfE, 2019), based on a review conducted by Sherlock et al (2008). This value is applied to both urea and non-urea fertiliser.

For carbon dioxide (CO₂) emissions from lime and dolomite, New Zealand has adopted the IPCC default emission factors of 0.12 for limestone and 0.13 for dolomite, which are equivalent to the carbonate-C contents of these materials (12% for CaCO₃, 13% for CaMg(CO₃)₂) (IPCC, 2006). The CO₂-C emissions are calculated by multiplying the

amount of lime or dolomite by the appropriate EF value. To convert into CO₂ emissions, the CO₂-C emissions are multiplied by 44/12, for the molecular weights of C and CO₂ are 12 and 44 g/mol, respectively.

The Fertiliser Association of New Zealand (FANZ) commissioned this review to improve their understanding of N₂O and NH₃ emissions from ammonium-based N fertilisers and CO₂ emissions from lime and dolomite.

This review provides (i) an overview of the use of N fertilisers and lime in New Zealand, (ii) a review of the international literature on the N₂O and NH₃ emission factors for the two most common non-urea N fertilisers applied to New Zealand soils: ammonium phosphate (AP) and ammonium sulphate (AS), (iii) a review of the international literature on CO₂ emissions from lime and dolomite, and (iv) summary conclusions from these reviews. While NO_x emissions are a component of the Frac_{GASF} emission factor (IPCC, 2006), an earlier review by Sherlock et al. (2008) suggested that NO_x represents *ca* 3% of total Frac_{GASF} [NH₃ + NO_x] emissions from N fertiliser (i.e. 3% of 10% = 0.3% of N applied). On this basis, NO_x was not included in the current review.

The brief for this review was as follows:

1. Conduct a search of published national and international literature
2. Review the searched literature, including estimates of emission factors relating to the following:
 - a. N₂O and NH₃ emission factors for standard ammonium sulphate (AS) and ammonium phosphate (AP) fertilisers
 - b. CO₂ emissions for agricultural lime and dolomite

The review was restricted to GHG losses following surface application to agricultural soil, and excluded fertilisers and lime incorporated into soil. The review was also restricted to field studies conducted in temperate climates, as these are most relevant to New Zealand agriculture. For the review, a literature search of overseas and New Zealand publications was undertaken for both AS and AP fertilisers and lime field studies conducted on pastoral, cropping and horticultural land uses. Key data was gathered from published papers and summarised in a spreadsheet. Where sufficient data was available, we have presented mean emission factors for N₂O, NH₃ and CO₂ and analysed the effect of key variables on emission factors.

3. N fertiliser and lime use in New Zealand

3.1 Nitrogen fertilisers

A wide variety of ammonium-containing and -forming compounds are used as N fertilisers in crop and pasture production, e.g. ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$), ammonium nitrate NH_4NO_3 , urea $(\text{NH}_2)_2\text{CO}$, mono-ammonium phosphate (MAP, $\text{NH}_4\text{H}_2\text{PO}_4$) and diammonium phosphate (DAP, $(\text{NH}_4)_2\text{HPO}_4$). All these materials may be applied as dry salts or as liquid fertilisers formed by dissolving or suspending the salts in water. The reaction with soil is the same regardless of whether these fertilisers are applied dry or in liquid form (Nelson, 1982).

The use of N fertilisers on New Zealand pastoral land plays a significant role in replacing N transferred off-farm in animal products. The two main ammonium-based N fertilisers applied to New Zealand soils are:

- 1) Ammonium sulphate (AS), commonly referred to as Sulphate of Ammonia (SOP). This fertiliser contains 20% N.
- 2) Ammonium phosphate fertiliser, which comes in two forms:
 - a) Monoammonium Phosphate (MAP), containing 11% N and 23% P, or
 - b) Diammonium Phosphate (DAP), containing 18% N and 20% P.

The main difference between MAP and DAP relates to the proportion of N relative to P. In New Zealand, DAP is the most commonly used ammonium phosphate fertiliser with around 80% usage compared to MAP of 20%, with the latter mainly confined to the horticultural sector (Ants Roberts, Ravensdown, pers. comm.).

The usage of AS and DAP fertilisers in New Zealand compared to urea can be gauged by examining the statistics on tonnage used in primary industries (Table 1; Statistics NZ, 2017). There has been a 100% increase in the use of AS and a 4% increase in DAP, respectively, between 2002 and 2017. During this 15-year period the use of urea has increased 90%. Data on MAP fertiliser usage was not available from Statistics NZ.

Table 1: Comparison of urea, AS and DAP fertiliser tonnage used in 2002, 2012 and 2017 (% of total amount in brackets). Note: 'Urea' includes standard urea and urease inhibitor-treated urea. Data sourced from Statistics NZ (2017).

| N fertiliser | 2002 | 2012 | 2017 |
|-----------------------|----------------|----------------|----------------|
| Urea | 314,354 (58) | 501,303 (77) | 597,492 (68) |
| Ammonium sulphate | 43,546 (8) | 43,166 (7) | 86,652 (22) |
| DAP | 182,958 (34) | 107,337 (16) | 190,701 (10) |
| Total (tonnes) | 540,858 | 651,806 | 874,845 |

Table 2 outlines the sectors of New Zealand's primary industries where these N fertiliser products were most used in 2012. Dairy farming used the largest amounts of urea and AS fertiliser, whereas DAP was used more by dry stock farmers. Pastoral farmers used between 82-86% of all N fertiliser forms.

Table 2: Breakdown of primary industry sectors where nitrogen fertiliser was used in 2012 (% of total usage). Data sourced from Statistics NZ (2017).

| Land use | Urea | Ammonium sulphate (AS) | Diammonium phosphate (DAP) |
|----------------------|-------------|-------------------------------|-----------------------------------|
| Dairy cattle farming | 71.8 | 67.9 | 38.2 |
| Dry Stock farming | 14.2 | 18.5 | 43.3 |
| Arable | 10.5 | 9.5 | 10.6 |
| Horticulture | 2.2 | 2.9 | 4.8 |
| Other* | 1.3 | 1.1 | 3.1 |

* The main component of "Other" is forestry.

The manufacture, transport and land application of N fertilisers contribute to GHG emissions. However, national reporting of GHG emissions from the agricultural sector is restricted to the emissions following land application. Calculation of emissions for national reporting relies on two key factors: activity data and emission factors. Activity data relates to the amount of N fertiliser used per annum, while emission factors relate to the percentage of N fertiliser emitted as N₂O or NH₃. Emissions from manufacturing and

transport are accounted for within the energy sector of the national GHG inventory (MfE, 2019). The emission factor for N₂O (EF₁) and NH₃ (Frac_{GASF}) are defined below and will be referred to throughout this review.

EF₁ for non-urea N fertiliser

New Zealand uses the IPCC default emission factor (EF₁) of 1% of applied N for non-urea fertiliser. EF₁ refers to the amount of N₂O emitted from the various inorganic and organic N applications to soils. Under the IPCC guidelines, this emission factor also applies to N₂O emissions from crop residue and mineralisation of soil organic matter in mineral soils due to land-use change or management. New Zealand has, however, developed a country-specific EF₁ value for urea fertiliser (EF_{1-UREA}), as this is the dominant form of N fertiliser applied to New Zealand soils. The country-specific EF_{1-UREA} value for urea fertiliser is 0.59% (MfE, 2019), based on an analysis of field studies (van der Weerden et al. 2016a).

Frac_{GASF} for N fertiliser

The amount of N volatilised as ammonia (NH₃) and nitric oxides (NO_x) is described as Frac_{GASF}, which is defined as the fraction of synthetic fertiliser N that volatilises as NH₃ and NO_x and is expressed as kg N volatilised per kg of N applied. For gaseous emissions (NH₃ and NO_x; Frac_{GASF}) from synthetic fertilisers that lead to indirect N₂O emissions, New Zealand has adopted the country-specific value of 10% of N applied (MfE, 2019), based on a review conducted by Sherlock et al. (2008). This value is applied to both urea and non-urea N fertiliser.

3.2 Agricultural Lime

New Zealand's grass/legume-based pastoral system gradually increases soil acidity due to several plant and soil processes, including mineralisation of organic matter, N transformations within urine patches and dissolution of most N fertilisers (e.g. AS) and elemental S fertiliser (Morton, 2019). Soil acidity can increase the risk of aluminium (Al) and manganese (Mn) toxicity while also reducing plant available N, phosphorus (P) and molybdenum (Mo) supply (Wheeler and O'Connor, 1998). Lime is alkaline and its application thus neutralises this acidity, reversing the process of acidification. Liming can also promote mineralisation of soil organic matter by enhancing changes in the bacterial population and activity as a result of a high pH environment (Ahmad et al. 2014). The rate of acidification and hence the amount of lime required for neutralising this acid will depend primarily on pasture productivity, with highly productive pastures (e.g. 15-18 tonnes dry matter/year) requiring up to 2.0-2.5 tonnes/ha every 5 years (Morton, 2019).

Limestone is a sedimentary rock consisting of calcium carbonate (CaCO_3) from the remnants of shells and marine fossils laid down in layers. Dolomite ($\text{CaMg}(\text{CO}_3)_2$) is another liming material (23% calcium (Ca) and 11% magnesium (Mg)) that is applied to agricultural soils, particularly if there is a need to supply Mg as well as increase soil pH. While lime quarries are plentiful throughout New Zealand there is only one deposit of dolomite, located in the Golden Bay region at the top of the South Island. In 1999, almost 2 million tonnes of limestone were quarried for agricultural use (referred to as AgLime) compared to around 100,000 tonnes for dolomite (Christie et al. 1999). However, a later survey of New Zealand's mineral status has suggested that AgLime usage has declined from 2.02 million tonnes in 2009 to 1.42 million tonnes by 2013 (USGS, 2016).

As for N fertilisers, the manufacture, transport and land application of lime contributes to GHG emissions. In the national GHG inventory, emissions following land application are reported as part of the agricultural sector. Emissions from manufacturing and transport are accounted for within the energy sector of the national GHG inventory (MfE, 2019). Calculation of CO_2 emissions from lime and dolomite applications relies on two key factors: the amount of limestone or dolomite applied to soils per annum and emission factors i.e. the percentage of C in the limestone or dolomite emitted as CO_2 .

New Zealand has adopted the Tier 1 default emission factors for lime and dolomite (IPCC, 2006). These emission factors are defined below and will be referred to throughout this review.

CO_2 emission factors for lime and dolomite

Annual CO_2 emissions from lime or dolomite application have emission factor (EF) units of tonnes C per tonne of limestone or dolomite applied per year. These EF values are 0.12 for limestone and 0.13 for dolomite and are equivalent to the carbonate-C contents of the materials (12% for CaCO_3 , 13% for $\text{CaMg}(\text{CO}_3)_2$) (IPCC, 2006). The EF values for lime and dolomite will be hereafter referred to as EF_{LIME} and $\text{EF}_{\text{DOLOMITE}}$, respectively.

4. Nitrous oxide emissions factors (EF_1) for ammonium-based N fertilisers

4.1 Processes responsible for N_2O emissions

Several soil and climatic variables influence N_2O production and emissions from N fertiliser applied to soil. The complexity of the interactions between variables often restricts our ability to adequately predict N_2O fluxes and associated emission factors. Nitrification and denitrification are accepted as being the dominant processes responsible for N_2O

production, although nitrifier-denitrification, co-denitrification and chemo-denitrification can also lead to N₂O formation given a suitable microbial community and environmental conditions (Hallin et al. 2018; Selbie et al. 2015). A range of proximal and distal regulating factors (Fig. 2) affect these processes and thus N₂O emissions, some of them to a greater extent than others.

Nitrous oxide emissions from N fertilisers are strongly influenced by the combined effects of soil types and annual climatic fluctuations on a regional scale, potentially masking the individual effects of plant or crop type and N fertiliser form (Henault et al. 1998). Large increases in N₂O emissions occur when soil water content exceeds 65-80% water filled pore space (WFPS) (Velthof and Oenema, 1995; McTaggart et al. 2002). Water filled pore space is defined as the proportion of the soil's total porosity that is filled with water, where a saturated soil is equivalent to 100% WFPS while a soil at field capacity is equivalent to approximately 60-70% WFPS. McTaggart et al. (2002) conducted a laboratory study on N₂O emissions from different fertiliser forms applied to soils with contrasting textures and soil water contents. These workers found that the magnitude of emissions was strongly influenced by soil water content, which was in turn governed by soil physical properties such as clay content. The New Zealand dataset used for generating a country-specific EF₁ value for urea fertiliser (van der Weerden et al. 2016a) also included information on rainfall and soil water content data. A preliminary assessment of this data, conducted for this review, would suggest that urea EF₁ is positively related to the amount of rainfall and soil water content measured in the first month following fertiliser application (unpubl. data). Further work would be required to confirm this effect.

The effect of N rate on N₂O EF values is currently uncertain. Several N fertiliser studies have shown that increasing N application rates leads to either increasing, constant or decreasing N₂O emission factors (Kim et al. 2013; Rashti et al. 2015). A review of N₂O emission factors from N fertiliser applied to vegetable production soils showed that when N rates were greater than 250 kg N/ha, 59% of the variation in seasonal EF values was explained by soil water content, soil pH and air temperature (Rashti et al. 2015). These researchers did not specify the fertiliser form in their study, preventing any assessment of emissions from, for example, AS and AP fertilisers.

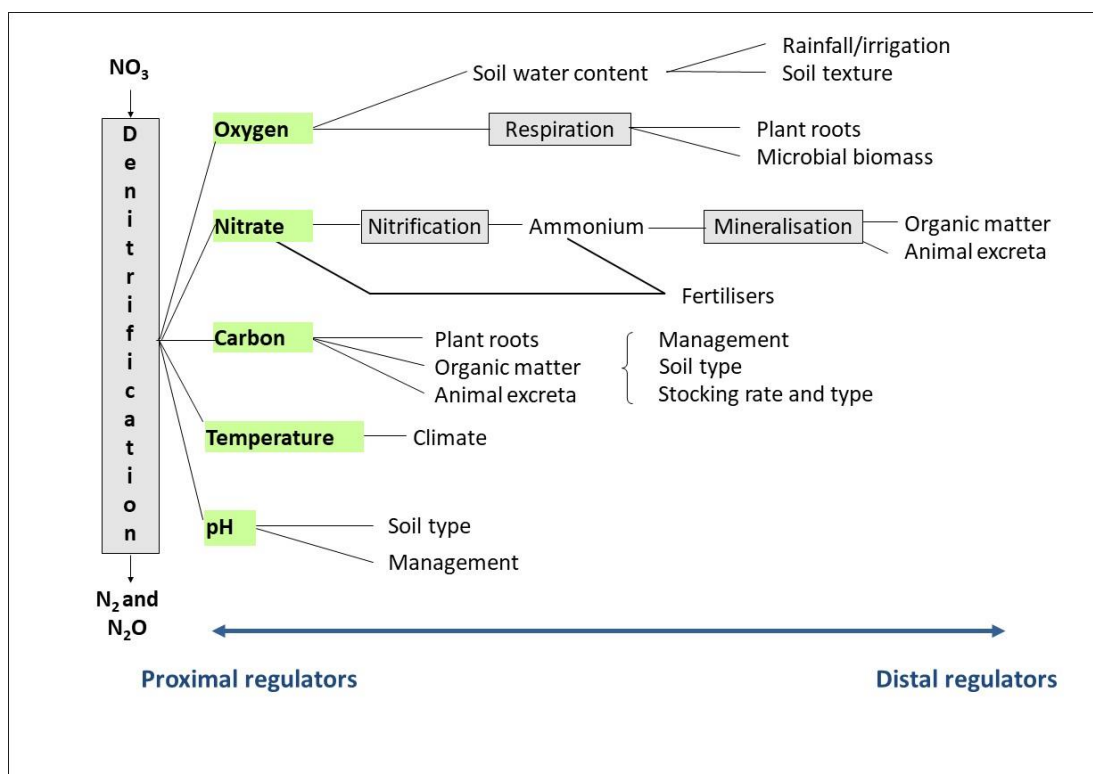


Fig. 2: Schematic diagram of proximal (green boxes) and distal factors affecting N_2O emissions via denitrification from agricultural soils. Boxes represent biological processes (source: de Klein et al. 2001).

4.2 Influence of form of N fertiliser on N_2O emission factors

Our review of published field studies on N_2O emission factors following surface application of AS or AP to pasture or crops growing in temperate climates identified 16 studies providing 30 N_2O EF values (Table A1; Appendix 1). Of this dataset, 29 EF_1 values related to AS while only one EF_1 value related to DAP. The mean N_2O EF_1 value for ammonium sulphate is 0.35% ($n=29$), while the sole DAP study, conducted in New Zealand, suggested an EF_1 value of 1.00% (Table 3). We were unable to find any MAP fertiliser studies that met the scope of the review.

A comparison of emission factors for AS fertiliser with those reported for urea may assist with interpretation of the collated data. Of the 29 AS emission factors, 17 were measured from field studies that included corresponding urea treatments. When our dataset was limited to these 17 values, the mean EF for AS is 0.38% ($n=17$), which is similar to the overall mean of 0.35% for AS ($n=29$). The corresponding mean EF for urea is greater, at 0.57%, although there was no significant difference in the mean EF_1 values for AS and urea ($P = 0.48$, $n=17$). There was also no relationship between AS and urea fertiliser EF_1 values ($R^2 = 0.04$; Fig. 3).

Table 3: Mean and range of N₂O emission factors (EF₁) for AS and DAP fertiliser.

| N fertiliser form | EF ₁ (%) | |
|-------------------|---------------------|-------------|
| | Mean | range |
| Ammonium Sulphate | 0.35 (n=29) | 0.04 – 1.30 |
| DAP | 1.00 (n=1) | N/A |

N/A = not applicable

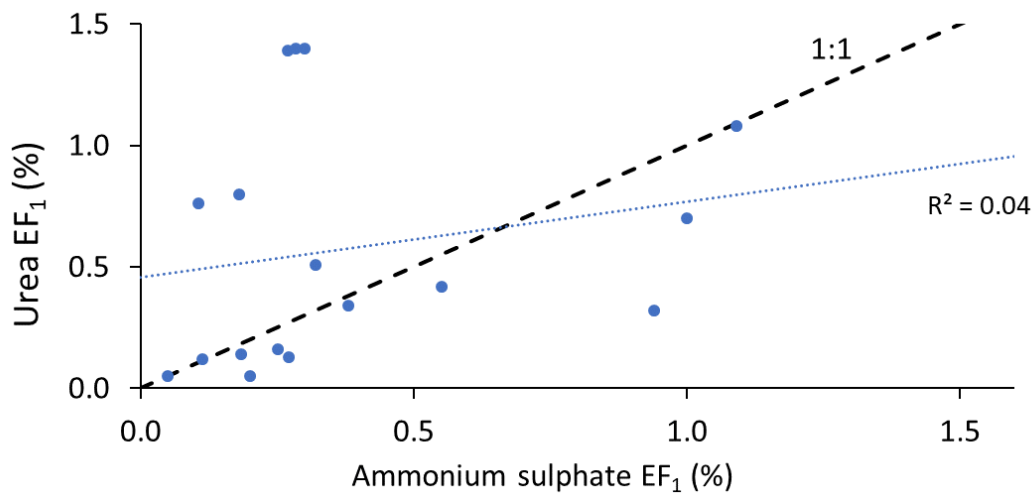


Fig. 3: Comparison of N₂O emission factor (EF₁) values for ammonium sulphate and urea fertiliser. Data restricted to field studies where both fertiliser forms were included (n=17). Dotted line refers to linear regression between AS and urea EF₁; dashed line refers to 1:1 fit.

The single DAP study produced an EF₁ value of 1%, which was similar to the EF₁ value determined for the corresponding urea treatment (1.1%). This study was conducted in New Zealand on a free draining silt loam soil, where soil water content was relatively high at between 80-95% WFPS during the first 3 weeks following fertiliser application (Zaman et al. 2008). Nitrous oxide emissions from DAP and urea were greatest over this period, declining with decreasing soil water content (Zaman et al. 2008). Given soil moisture is a key driver of N₂O emissions, these EF₁ values could be regarded as being at the upper end of EF₁ values and therefore are unlikely to reflect typical losses from New Zealand pastoral systems. We have already established that the country-specific EF₁ value for urea is 0.59% of the N applied.

Crop type information was available for 27 of the 29 AS values. Of these, 17 were derived from pasture studies while the remaining 10 were measured from various crop types including barley, wheat, rapeseed, maize and melons. The mean EF₁ for pasture-applied AS was 0.29 (Table 4). In contrast, for a wide range of crops the mean EF for AS was 0.50. It is important to consider the large overlap in values between crops and pasture, as indicated by the 95% confidence intervals. The two New Zealand values for AS fertiliser come from a single grassland study conducted in the Manawatu region (Bhandral et al. 2007; Table 5). These researchers determined the interactive effects of soil compaction and form of N sources (cattle urine, AS, potassium nitrate and urea fertilisers applied at a rate of 600 kg N/ha) on N₂O emissions from a sandy loam grassland soil. The EF₁ values for AS and urea were similar at about 1.1% for compacted soils. Losses from AS and urea were also similar from non-compacted soils, at about 0.2 – 0.3% of the applied N. In contrast, the nitrate-based fertiliser produced EF₁ values that were ca 10 times larger (Table 5).

Table 4: N₂O emission factors (EF₁) reported for AS fertiliser, determined from crop and pastoral field studies.

| Crop type | Number of values | EF₁ (%) | 95% confidence interval^A |
|------------------|-------------------------|---------------------------|--|
| Crops (all) | 10 | 0.50 | 0.18 – 1.22 |
| Pasture | 17 | 0.29 | 0.04 – 1.05 |
| Canada | 3 | 0.17 | ND ^B |
| China | 2 | 0.21 | ND |
| Netherlands | 6 | 0.31 | ND |
| New Zealand | 2 | 0.67 | ND |
| Scotland | 4 | 0.22 | ND |

^A95% confidence interval estimated as the 2.5th and 97.5th percentile of the range of values

^BND = not determined, due to insufficient data.

Table 5: Nitrous oxide emission factors from N fertiliser and urine applied at an equivalent rate of 600 kg N/ha to compacted and non-compacted grassland in Manawatu. Data derived from Bhandral et al. (2007), where the control treatment received only water.

| N source | Emission factor (% of N applied lost as N ₂ O) | |
|-------------------|---|-------------|
| | Compacted | Uncompacted |
| Ammonium sulphate | 1.09 | 0.25 |
| Urea | 1.08 | 0.17 |
| Potassium Nitrate | 9.85 | 0.54 |
| Urine | 1.09 | 0.30 |

While the rate of N fertiliser application in the Bhandral et al. (2007) study (600 kg N/ha) was significantly greater than typically applied to New Zealand soils (ca 30-50 kg N/ha per dressing), the results showed that fertiliser form (urea vs NH₄⁺-based vs NO₃⁻-based fertiliser) can influence N₂O emissions and associated emission factors. Other researchers have also observed differences in N₂O emissions due to fertiliser form. For example, Smith et al. (1997) noted that under cool wet conditions favouring denitrification, nitrate fertilisers produce higher emissions, whereas under warmer, drier conditions in summer emissions from urea or NH₄⁺-based fertilisers were higher. Kuikman et al. (2006) analysed N₂O measurements taken across the Netherlands and concluded that N₂O emissions were greater from NO₃⁻-based fertilisers than from NH₄⁺-based fertilisers and urea due to the former providing a more readily available mineral N pool for denitrification. Smith et al. (2012) reported on a UK-wide series of field experiments comparing N fertiliser forms, where there was evidence of lower emissions from urea. This may have also been partly due to losses of NH₃ following rapid urea hydrolysis, which can reduce the net amount of N remaining in the soil as a potential source of N₂O (van der Weerden et al. 2016b).

New Zealand currently employs the IPCC 2006 guidelines default value of 1% (IPCC, 2006) for non-urea N fertiliser (MfE, 2019). Most of the non-urea fertiliser used in New Zealand is NH₄⁺-based (Stats NZ, 2017). Overseas studies have reported lower EF₁ values for urea and NH₄⁺-based fertilisers compared to the IPCC 2006 guidelines default value of 1%. For example, Misselbrook et al. (2014) reported on a series of UK experiments, where the mean EF₁ for urea and ammonium nitrate fertiliser, applied at rates of between 40 and 80 kg N ha⁻¹, were 0.47% and 0.80%, respectively. The Netherlands has adopted an EF₁ value of 0.5% for urea and NH₄⁺-based fertilisers applied

to mineral soils (Kuikman et al., 2006; Velthof and Mosquera, 2011). Based on the EF₁ value of 1% currently used in the New Zealand GHG inventory, the GHG emission from non-urea fertiliser is equivalent to 5.4 t CO₂e per tonne of fertiliser-N. If New Zealand was to adopt the country-specific urea fertiliser emission factor (EF_{1UREA}) of 0.59%, calculated GHG emissions from non-urea fertiliser would decline to 3.5 t CO₂e per tonne of fertiliser-N.

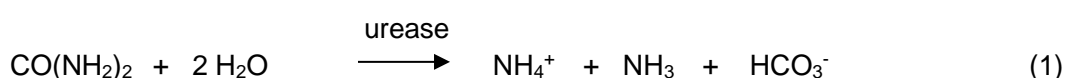
4.3 Potential improvements to GHG inventory reporting

New Zealand has adopted a country-specific urea EF₁ value of 0.59% based on robust and extensive field experimentation (van der Weerden et al. 2016b). There may be justification for also determining a country-specific EF₁ value for non-urea NH₄⁺-based fertilisers. A comparison of 17 studies where both AS and urea were included suggested no significant difference in emission factors between these two fertiliser forms. The current default EF₁ value of 1% for AS fertiliser may, therefore, be over-estimating N₂O emissions from this fertiliser form. Furthermore, a single New Zealand study that produced DAP and urea fertiliser emission factors of 1.0 and 1.1%, respectively, suggests that an annual average EF₁ value of 1% for DAP may also be over-estimating annual average N₂O emissions from this fertiliser form, given urea's lower country-specific value. However, with only a single comparison of N₂O emissions from DAP and urea, further evidence is required to confirm this suggestion.

5. Ammonia emission factors (Frac_{GASF}) for ammonium-based N fertilisers

5.1 Processes responsible for NH₃ volatilisation

The two main sources of NH₃ volatilisation from New Zealand agriculture are urine deposited onto pastoral soils during grazing and urea fertiliser applied to pasture and crops. In both cases, urea (which is contained within urine) is rapidly hydrolysed by the urease enzyme to form ammonia, NH₃, and bicarbonate, HCO₃⁻ (Equation 1), leading to an elevated soil pH often greater than pH 9. Under these pH conditions, the proportion of the dissolved ammoniacal-N present as volatilisable NH₃ is increased markedly. This is due to an elevation of pH by 1 unit potentially increasing the proportion of total ammoniacal-N present as NH₃ by a factor of ca 10 (Sherlock et al. 2008).



The loss of NH₃ will be greatest either (i) from soils with a pH greater than 7 or (ii) when a fertiliser form (urea or NH₄⁺-based) produces a high pH following application to a soil

(Black et al. 1985). Nitrate-based fertilisers do not directly lead to NH₃ volatilisation, although, for grazed systems, this fertiliser form will indirectly lead to enhanced NH₃ volatilisation from urine patches by increasing pasture biomass and N intake by grazing livestock, in turn resulting in greater N excretion onto soils (Sherlock et al. 2008).

5.2 Influence of N fertiliser form on Frac_{GASF}

We identified 15 field studies, including four from New Zealand, providing 58 Frac_{GASF} values, where 17 related to DAP and 41 related to AS (Table A2, Appendix 1). As for N₂O, we were unable to locate any field studies relating to MAP fertiliser. Data collated from the reviewed literature suggested a mean Frac_{GASF} value of 9.7% and 7.1% for AS (n=41) and DAP (n=17), respectively (Table 6).

Table 6: Means and ranges of NH₃ Frac_{GASF} values (%) for AS and DAP fertilisers.

| N fertiliser form | Frac _{GASF} (% of N applied) | |
|-------------------|---------------------------------------|------------|
| | mean | range |
| DAP | 7.1 (n=17) | 1.4 – 19.4 |
| Ammonium Sulphate | 9.7 (n=41) | 0.2 – 58.2 |

5.2.1 DAP

Sherlock et al. (2008) provided a detailed description of the processes leading to NH₃ volatilisation from DAP fertiliser. Briefly, both DAP and MAP can volatilise NH₃ when applied to soils. However, in most situations NH₃ loss from DAP is greater than from MAP because of the hydrolysis of the hydrogen phosphate anion, HPO₄²⁻, to the dihydrogen phosphate ion H₂PO₄⁻ which increases the amount of OH⁻ in the soil, thus increasing pH. While our review was unable to find any field studies relating to MAP fertiliser, NH₃ volatilisation from this fertiliser form is considered to be negligible when applied to non-calcareous soils due to MAP containing the dihydrogen phosphate ion, H₂PO₄⁻. Hydrolysis of this ion is likely to be minimal, which avoids any significant increase in soil pH (Sherlock et al. 2008).

The hydrolysis of DAP causes a small but significant increase in surface soil pH to ca pH 8, sufficient to promote some NH₃ volatilisation (Black et al. 1985). Losses of NH₃ from urea fertiliser applied to acidic to neutral soils are greater than

from DAP, primarily due to the greater increase in soil pH following urea hydrolysis. However, Whitehead and Raistrick (1990) observed NH₃ emissions from DAP increased with increasing pH, whereas NH₃ emissions from urea were less dependent on the initial soil pH. This latter effect was attributed to urea hydrolysis increasing the pH immediately around the fertiliser granule to ca pH 8.5-9.2 (Black et al. 1989; Fenn, 1988) irrespective of the initial pH.

Most field trials measuring NH₃ volatilisation from DAP also included urea fertiliser as a treatment, allowing a comparison of Frac_{GASF} values between these two fertiliser forms. There were 16 Frac_{GASF} values associated with these experiments, with a mean Frac_{GASF} value for DAP of 6.5% and a mean for urea of 13.3% (n=16). Soil pH for these field studies ranged from ca pH 4 to 6; under these conditions we found a significant correlation between DAP and urea Frac_{GASF} values (R² = 0.79; P < 0.001; n=16; Fig. 4), with NH₃ losses from DAP consistently lower than from urea.

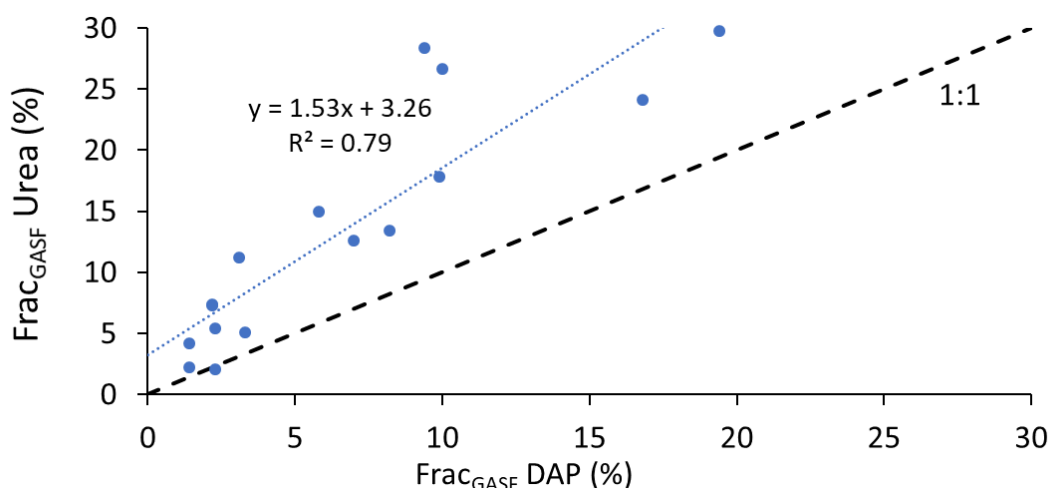


Fig. 4: Comparison of NH₃ Frac_{GASF} values (%) for DAP and urea (n=16). Data is restricted to field studies where both fertiliser forms were included. Dotted line refers to linear regression between DAP and urea Frac_{GASF}; dashed line refers to 1:1 fit.

5.2.2 AS

The NH₃ volatilisation process from AS fertiliser is similar to that from MAP fertiliser, due to the sulphate ion, SO₄²⁻, in AS behaving similarly to the H₂PO₄⁻ ion present in MAP (Sherlock et al. 2008). This sulphate ion undergoes minor hydrolysis, which results in a minor increase in soil pH. For instance, Black et al. (1985) observed NH₃ losses of between 0.2 and 2.1% of N applied at 30 kg N/ha as AS to a New Zealand pasture on a Templeton silt loam with a pH of 6.1. These researchers suggested the low losses were due to the (relatively) low surface soil

pH and the fact that SO_4^{2-} does not hydrolyse to produce a basic solution. Using the same soil, again with an initial pH of 6.1, these researchers applied AS at a rate of 100 kg N/ha to a bare soil and measured negligible NH_3 losses (0.6% of applied N). In contrast, urea applied at the same N rate resulted in 21% of N lost as NH_3 (Black et al. 1989).

As for the DAP studies, the majority of AS field trials identified in our review also included urea fertiliser as a treatment (n= 33 out of 41), allowing a comparison of urea and AS $\text{Frac}_{\text{GASF}}$ values. The mean $\text{Frac}_{\text{GASF}}$ value for AS was 8.3% (n=33) while the corresponding mean $\text{Frac}_{\text{GASF}}$ value for urea was greater, at 14.1% (n=33). There was a poor relationship between $\text{Frac}_{\text{GASF}}$ values for AS and urea ($R^2 = 0.05$; $P = 0.20$; n=33; Fig.5), which can be partly explained by the large range in soil pH conditions in these field studies. Indeed, an analysis of the pooled DAP, AS and urea fertiliser data illustrates the effect of soil pH on NH_3 emissions, with the majority of AS data with high $\text{Frac}_{\text{GASF}}$ values measured from field sites with soil pH ≥ 8 (Fig. 6). Ammonia volatilisation from AS can be greater than from urea when applied to calcareous soils (Vermoesen et al. 1992). It was earlier noted that NH_3 emissions from DAP increased with increasing pH (Whitehead and Raistrick, 1990); these workers made the same conclusion with respect to AS fertiliser. Because soil pH has a large influence on NH_3 emissions from AS, Harrison and Webb (2001), suggested $\text{Frac}_{\text{GASF}}$ values of 2% and 18% for soils with pH <7 and >7, respectively. Given New Zealand soils are typically acidic or neutral, NH_3 losses from AS fertiliser will most likely be lower than from urea fertiliser.

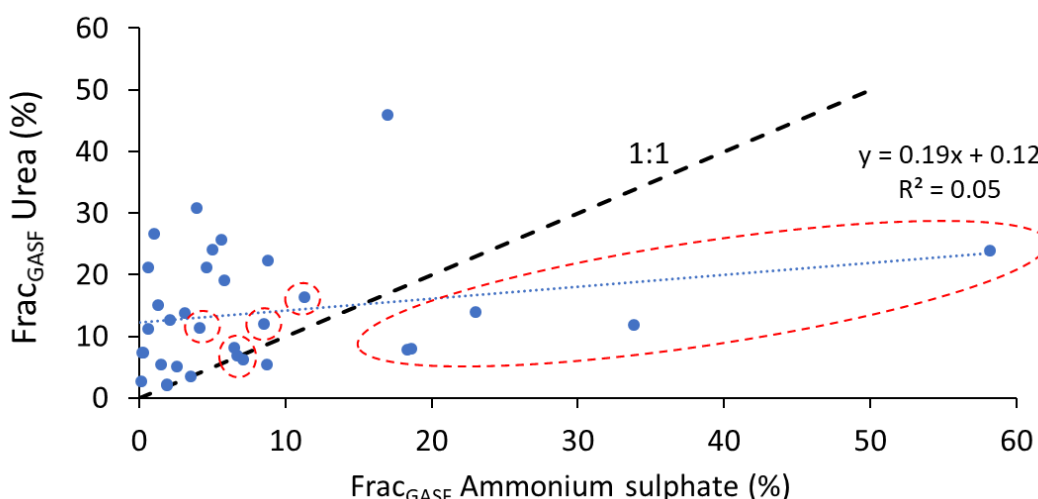


Fig. 5: Comparison of NH_3 $\text{Frac}_{\text{GASF}}$ values (%) for AS and urea (n=33). Data is restricted to field studies where both fertiliser forms were included. Circled data obtained from sites where soil pH ranged from 8 to 9.3. Dotted line refers to linear regression between AS and urea $\text{Frac}_{\text{GASF}}$; dashed line refers to 1:1 fit.

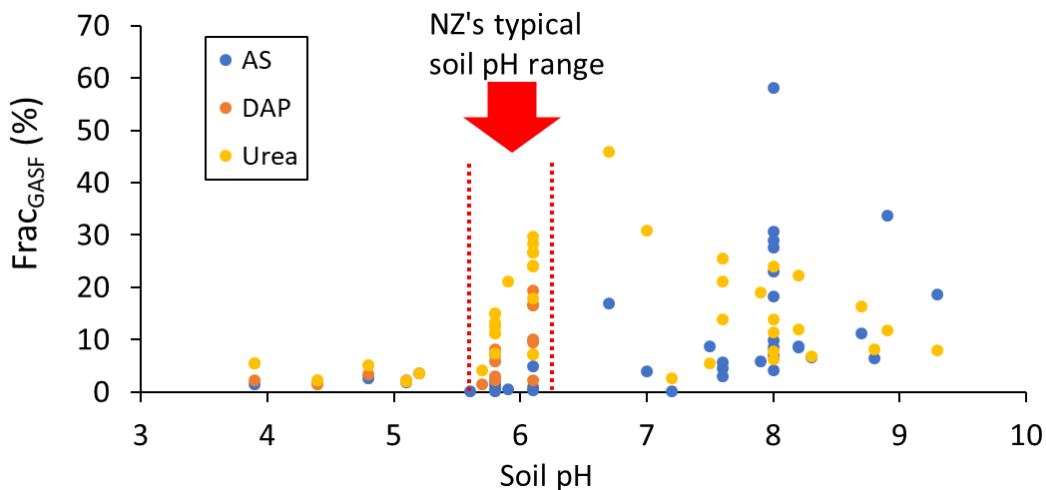


Fig. 6: Comparison of initial soil pH and NH₃ volatilisation (Frac_{GAS_F}, %) for DAP, AS and urea fertilisers.

5.2.3 Influence of soil pH on DAP and AS Frac_{GAS_F} values

As noted earlier, NH₃ emissions from AS can be greater from urea at high soil pH. Alkaline soils also elevate NH₃ emissions from DAP (Whitehead and Raistrick, 1990), however our dataset does not contain DAP values above soil pH 6.1, thus limiting any assessment of the effect of soil pH on emissions from this fertiliser form. Regardless, the effect of soil pH on NH₃ emissions from AS and DAP was included in the European Union NH₃ emissions inventory guidebook by adopting a ‘pH multiplier’ for soils above pH 7 (Anon., 2003). To illustrate, soils below pH 7 were assigned a Frac_{GAS_F} value of 2.5% for both AS and DAP; for soils above pH 7 this value was increased 10-fold to 25%.

Because New Zealand agricultural soils are typically between 5.6 and 6.2 (Sparling and Schipper, 2004), with 5.8 and 6.0 considered to be optimum for pastoral production (Morton, 2019), the data in Figure 6 suggests the range of Frac_{GAS_F} values for DAP relevant to New Zealand soil pH conditions lie between 0 and ca 20%. The range is lower for AS fertiliser at this pH range, at between 0 and 5%.

Bouwman et al. (2002) reported a mean NH₃ loss of 21%, 11% and 16% of N applied for urea, AP and AS, respectively, based on an analysis of global data. However, the number of studies for each fertiliser form varied greatly, ranging from 74 urea studies to 3 AP studies. The high NH₃ volatilisation losses associated with AS reported by Bouwman et al. (2002) may be due to the soil pH at the time of the study, given the majority of AS data in our review was measured from soils with initial pH ranging from 7 to 9 (Fig. 6).

Black et al. (1984) used an enclosure method to measure the daily volatilisation losses of ammonia from urea, DAP and AS broadcast onto pasture in spring at a rate of 30 kg N/ha. These workers measured NH₃ losses in the absence or presence of sheep urine applied one week before the fertiliser. Ammonia losses from urea, DAP and AS applied to non-urine-treated soils were, respectively, 7.3, 2.2 and 0.3% of the N applied. For urine-treated soil, NH₃ losses were 26.7, 10.0 and 1.0% of the N applied as urea, DAP and AS, respectively. Black et al. (1984) concluded that the daily pattern of NH₃ loss was related to soil pH changes. A similar trend was observed by the same research group when urea, DAP and AS were applied to pasture at different times of the year (Black et al. 1985). Ammonia volatilisation from urea, DAP and AS ranged between, respectively, 7.4 - 15.0%, 2.2 - 7.0% and 0.2 - 2.1% of N applied. The studies conducted by Black et al. (1984; 1985) illustrate the relatively small losses of NH₃ from AS, while losses from DAP were approximately half of those measured from urea. When restricting data to near-neutral soils, researchers have observed that relative NH₃ emissions decline in the following order: urea > DAP > AS = Ammonium Sulphate Nitrate = Ammonium Nitrate = MAP (Black et al. 1985; Whitehead & Raistrick, 1990; Sommer and Jensen, 1993; del Moro et al. 2017).

5.3 Potential improvements to GHG inventory reporting

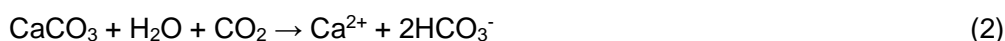
There is sufficient evidence to suggest DAP and AS fertilisers have lower $Frac_{GASF}$ values than urea (Fig. 6), which currently has a country-specific value of 10% (MfE, 2019). Under New Zealand's soil pH conditions, NH₃ losses are minor from AS fertiliser (*ca* ≤ 2%), while losses from DAP are approximately 50% of those from urea (Black et al. 1984, 1985, 1989).

6. Carbon dioxide EF_{LIME} and $EF_{DOLOMITE}$ values for agricultural lime and dolomite

6.1 Processes responsible for CO₂ emissions

The IPCC Tier 1 default emission factors for limestone and dolomite are 0.12 and 0.13 t C per t crushed rock, respectively (IPCC, 2006). It is acknowledged by the IPCC that these values represent the maximum amount of CO₂ that could be emitted, assuming 100% of the C in lime and dolomite dissociated to CO₂. Research by West and McBride (2005) has shown that emissions can be much lower than this theoretical maximum. Based on this research, the IPCC guidelines include an emission factor uncertainty of -50%. The

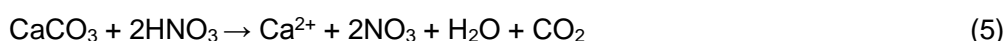
rationale for the lower emissions reported by West & McBride (2005) are summarised below. The chemical processes following the application of lime to soil are as follows:



The reaction shows that two moles of bicarbonate are produced for every mole of CO_2 removed from the atmosphere i.e. a net release of one mole of carbonate per mole of CaCO_3 applied. In contrast, the theoretical maximum assumes a net release of two moles of bicarbonate for every mole of CaCO_3 applied. The resulting bicarbonate may either remain in the soil or be leached through the soil profile. Bicarbonate remaining in the soil is expected to react with available H^+ to form carbonic acid (H_2CO_3) (equation 3), following acidification of the soil. This H_2CO_3 forms an equilibrium with CO_2 and water (equation 4). As noted earlier, soil acidification can occur due to mineralisation of organic matter or N transformation processes that occur within soil affected by urine or fertiliser applications.



In the presence of nitrogen fertiliser, CaCO_3 will react with nitric acid (HNO_3), which is formed from NO_3^- and H^+ ions. When calcium carbonate reacts with HNO_3 , CO_2 is released as follows:



Therefore, when lime or dolomite is applied to acidic soils where NO_3 is present, the dissolution of CaCO_3 only results in a net release of one mole of CO_2 per mole of CaCO_3 applied.

West and McBride (2005) also examined soil leaching and river transport of Ca^{2+} and HCO_3^- , from which they concluded that a significant portion of dissolved AgLime constituents may leach through the soil and be transported by rivers to the ocean. Upon reaching the ocean, much of the HCO_3^- will precipitate as CaCO_3 , which will release 0.6 moles of CO_2 for every mole of CaCO_3 precipitated (Ware et al. 1991).

Considering these different soil-based reaction pathways, in addition to the transport of bicarbonate down the soil profile to water bodies (e.g. rivers, lakes, ocean) and

subsequent partial release of CO₂ during precipitation of bicarbonate to CaCO₃, West and McBride (2005) estimated net CO₂ release from lime application to US soils to be about 50% of the theoretical maximum. This lower estimate is mainly due to the initial uptake of CO₂ during dissolution of lime by H₂CO₃, which offsets a proportion of the CO₂ released.

6.2 Derivation of country-specific emission factors and activity data

Our literature search found only two studies reporting EF_{LIME} and EF_{DOLOMITE} values (West and McBride, 2005; Cho et al. 2019). West and McBride (2005) estimated country-specific EF values of 0.059 and 0.064 t C/ t lime or dolomite, respectively, which are lower than the IPCC default value of 0.12 (IPCC, 2006). Their values have been adopted by the US Environmental Protection Agency (EPA, 2016, cited by Cho et al. 2019) for estimating CO₂ emissions from lime usage, as the IPCC encourages individual countries to derive country-specific EF_{LIME} and EF_{DOLOMITE} values for lime and dolomite, respectively (IPCC, 2006).

Cho et al. (2019) proposed a country-specific EF_{LIME} value for Korean upland soils. These researchers measured ¹³CO₂ fluxes for 2 years from ¹³C-CaCO₃ applied at different rates (0-2 t/ha/year) to a single upland soil. Approximately 0.026 t C/t CaCO₃ was directly lost as CO₂ from the soil. When including CO₂ emissions from the oceans following transport of bicarbonate to oceans and subsequent release of CO₂ during precipitation of bicarbonate to CaCO₃ (see section 6.1 above), the total CO₂ EF_{LIME} value for Korean upland soils may be close to 0.039 t C/ t CaCO₃ (Cho et al. 2019). These workers proposed that this value, which is lower than the IPCC value of 0.12 t C/t CaCO₃, is adopted for these upland soils.

6.3 Potential improvements to GHG inventory reporting

There may be justification for determining country-specific EF_{LIME} and EF_{DOLOMITE} values for New Zealand's agricultural soils, given the large error associated with the default value. However, such an undertaking is likely to be resource-hungry, given these field studies should probably be conducted over 2 years (Cho et al. 2019) or more, and the large range of New Zealand soil types with contrasting buffering capacities.

While this report mainly focuses on emission factors, it is important to include a comment on the activity data used for reporting CO₂ emissions from lime and dolomite. The purity of the lime and dolomite (i.e. the CaCO₃ content of the quarried products) will influence the amount of CO₂ emitted per tonne of lime or dolomite. A country-specific Tier 2 approach that accounts for the purity could be adopted to provide greater accuracy of the

activity data used for estimating CO₂ emissions (IPCC, 2006). The degree of purity will vary from one quarry to another. For example, lime from Ravensdown quarries range from 69 to 97% purity on a wet weight basis, i.e. as applied to land (Ravensdown, 2019). Accounting for the purity of lime and dolomite will improve the accuracy of the New Zealand agricultural GHG inventory. However, a Tier 2 approach will require monitoring, reporting and verification of activity data (IPCC, 2006).

7. Conclusions

Nitrous oxide emissions factors (EF₁) for AS and AP fertilisers

- We identified 16 studies that documented N₂O emission factors for AS or AP applied to soils in temperate climates, providing 30 N₂O EF values. Of these, 29 related to AS while only one EF₁ value was found for DAP. Based on the collated data, the mean N₂O EF₁ value for AS was 0.35%.
- Our dataset contained 17 studies where both AS and urea were applied to soils. The mean EF₁ values for AS and urea were 0.38% and 0.57%, respectively.
- There may be justification for determining a country-specific EF₁ value for AS fertilisers, as the current IPCC default value of 1% is likely an over-estimate of N₂O emissions from this fertiliser form.
- A single New Zealand study showed EF₁ values were similar for DAP and urea fertiliser, at ca 1%. Given New Zealand uses a country-specific EF₁ value of 0.59% for urea, the current use of 1% for DAP is likely an over-estimate of annual average N₂O emissions from this fertiliser form. Further work is necessary to confirm this, however.
- We were unable to find any MAP fertiliser studies that met the scope of the review.

Ammonia volatilisation (Frac_{GASF}) values for AS and AP fertilisers

- We identified 15 suitable field studies that provided 58 Frac_{GASF} values, where 17 related to DAP and 41 related to AS.
- Mean Frac_{GASF} values were 9.7% and 7.1% for AS and DAP, respectively.
- Soil pH has a significant influence on NH₃ volatilisation from AS and DAP.
- Under New Zealand's acidic to neutral soil pH conditions, there is sufficient evidence to suggest that NH₃ losses are minor from AS fertiliser, while losses from DAP are approximately 50% of those from urea.
- We were unable to locate any field studies relating to MAP fertiliser.

Carbon dioxide EF_{LIME} and EF_{DOLOMITE} values

- We identified two studies proposing country-specific EF_{LIME} and EF_{DOLOMITE} values.

- Proposed EF_{LIME} values were 0.039 and 0.059 t C/t lime for, respectively, Korean upland soils and the US as a mean EF. These values were lower than the IPCC default value of 0.12, which is considered to represent the maximum potential emission.
- A proposed US country-specific $EF_{DOLOMITE}$ value was 0.064 t C/t dolomite, which is lower than the IPCC default value of 0.13.
- Carbon dioxide emissions from lime and dolomite application to soil are likely to be lower than the maximum potential loss mainly due to the initial uptake of CO_2 during dissolution of lime.
- To improve the accuracy of the national GHG inventory, country-specific EF_{LIME} and $EF_{DOLOMITE}$ values could be developed, although the costs may be prohibitive.
- A further improvement could be made through the adoption of country-specific activity data that accounts for the purity of lime and dolomite.

Potential improvements to GHG inventory calculations in relation to NH_4^+ -based fertiliser, lime and dolomite

1. There may be justification for determining a single country-specific EF_1 value for NH_4^+ -based fertilisers, as the collated data suggests EF_1 values are broadly similar for AS, AP and urea N fertiliser forms.
2. Under New Zealand's acidic to neutral soil pH conditions, the data would suggest NH_3 volatilisation is minor from AS fertiliser, while losses from DAP are approximately 50% of those from urea. There is justification for determining country-specific $Frac_{GASF}$ values for AS and DAP fertilisers.
3. Adoption of country-specific activity data accounting for the purity of lime and dolomite could be investigated. This should include an assessment of how to meet IPCC monitoring, reporting and verification requirements in relation to lime and dolomite purity.

8. Acknowledgements

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10. Appendix 1

Table A1: Nitrous oxide emission factors (EF₁, %) for ammonium sulphate and ammonium phosphate fertilisers. Data constrained to field experiments in temperate countries.

| Fertiliser Form | Land use | Country | N fertiliser rate applied (kg N/ha) | Measurement period (d) | EF ₁ (% of N applied lost as N ₂ O) | Urea EF ₁ (% of N applied lost as N ₂ O) (where available) | Reference |
|-----------------|-----------|-------------|-------------------------------------|------------------------|---|--|---------------------------|
| AS | bare soil | USA | 250 | 96 | 0.11 | 0.12 | Breitenbeck et al. (1980) |
| AS | bare soil | USA | 125 | 96 | 0.18 | 0.14 | Breitenbeck et al. (1980) |
| AS | pasture | Canada | 120 | 21 | 0.11 | - | Mkhabala et al (2008) |
| AS | pasture | Canada | 120 | 21 | 0.37 | - | Mkhabala et al. (2008) |
| AS | pasture | Canada | 120 | 21 | 0.04 | - | Mkhabala et al. (2008) |
| AS | pasture | China | 100 | NA | 0.27 | - | Peng et al. (2011) |
| AS | pasture | China | 100 | NA | 0.15 | - | Peng et al. (2011) |
| AS | pasture | Netherlands | 320 | NA | 0.32 | - | Schils et al. (2010) |
| AS | pasture | Netherlands | 330 | NA | 0.15 | - | Schils et al. (2010) |
| AS | pasture | Netherlands | 330 | NA | 0.14 | - | Schils et al. (2010) |

| | | | | | | | |
|----|---------|-------------|-----|-----|-------|------|-----------------------------|
| AS | pasture | Netherlands | 80 | 24 | 0.05 | 0.05 | Velthof et al. (1997) |
| AS | pasture | Netherlands | 80 | 28 | 0.2 | 0.05 | Velthof et al. (1997) |
| AS | pasture | Netherlands | 50 | 31 | 1 | 0.7 | Velthof et al. (1997) |
| AS | pasture | New Zealand | 600 | 84 | 1.09 | 1.08 | Bhandral et al. (2007) |
| AS | pasture | New Zealand | 600 | 84 | 0.25 | 0.16 | Bhandral et al. (2007) |
| AS | pasture | Scotland | 360 | NA | 0.3 | 1.4 | McTaggart et al. (1993) |
| AS | pasture | Scotland | 360 | 365 | 0.18 | 0.8 | Clayton et al (1997) |
| AS | pasture | Scotland | 360 | 365 | 0.28 | 1.4 | Clayton et al (1997) |
| AS | pasture | Scotland | 360 | 365 | 0.11 | 0.76 | McTaggart et al (1997) |
| AS | barley | Scotland | 360 | 365 | 0.27 | 1.39 | McTaggart et al (1997) |
| AS | barley | USA | 200 | 95 | 0.155 | - | Mosier et al. (1986) |
| AS | maize | Brazil | 120 | 130 | 0.27 | 0.13 | Martins et al (2015) |
| AS | maize | USA | 200 | 120 | 0.36 | - | Mosier et al. (1986) |
| AS | melons | Spain | 175 | 120 | 1.30 | - | Sánchez-Martin et al (2008) |
| AS | melons | Spain | 175 | 120 | 0.43 | - | Sánchez-Martin et al (2008) |

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|-------------|----------|-------------|-----|-----|------|------|-----------------------|
| AS | rapeseed | France | 170 | 163 | 0.55 | 0.42 | Henault et al (1998) |
| AS | wheat | Germany | 220 | 365 | 0.32 | 0.51 | Lebender et al (2014) |
| AS | wheat | Germany | 220 | 365 | 0.94 | 0.32 | Lebender et al (2014) |
| AS | wheat | Germany | 220 | 365 | 0.38 | 0.34 | Lebender et al (2014) |
| AS solution | wheat | Germany | 130 | 365 | 0.03 | - | Deppe et al (2016) |
| AS solution | wheat | Germany | 130 | 365 | 0.4 | - | Deppe et al (2016) |
| AS solution | wheat | Germany | 130 | 365 | 0.22 | - | Deppe et al (2016) |
| AS solution | wheat | Germany | 130 | 365 | 0.37 | - | Deppe et al (2016) |
| DAP | pasture | New Zealand | 150 | 84 | 1.0 | 1.1 | Zaman et al (2008) |

Table A2: Ammonia volatilisation (Fra_{CGASF}) values (%) for ammonium sulphate and ammonium phosphate fertilisers. Data constrained to field experiments in temperate countries.

| Fertiliser Form | Land use | Country | N fertiliser rate applied (kg N/ha) | Measurement period (d) | Soil pH | Fra _{CGASF} (% of N applied lost as NH ₃) | Urea Fra _{CGASF} (% of N applied lost as NH ₃) (where available) | Reference |
|-----------------|-----------|-----------|-------------------------------------|------------------------|---------|--|---|-------------------------|
| AS | bare soil | Australia | 100 | 27 | 8.9 | 33.8 | 11.8 | Schwenke et al (2014) |
| AS | bare soil | Australia | 100 | 27 | 8.3 | 6.7 | 6.9 | Schwenke et al (2014) |
| AS | bare soil | Australia | 80 | 34 | 7.6 | 3.1 | 13.8 | Schwenke et al (2014) |
| AS | bare soil | Australia | 80 | 34 | 7.9 | 5.8 | 19.1 | Schwenke et al (2014) |
| AS | bare soil | Australia | 100 | 27 | 9.3 | 18.6 | 8 | Schwenke et al (2014) |
| AS | bare soil | Australia | 100 | 27 | 8.8 | 6.5 | 8.1 | Schwenke et al (2014) |
| AS | bare soil | Australia | 80 | 35 | 8.0 | 7.1 | 6.3 | Schwenke et al (2014) |
| AS | bare soil | Australia | 80 | 34 | 7.5 | 8.7 | 5.4 | Schwenke et al (2014) |
| AS | bare soil | Australia | 100 | 33 | 8.7 | 11.3 | 16.3 | Schwenke et al (2014) |
| AS | bare soil | Australia | 100 | 32 | 8.0 | 4.1 | 11.4 | Schwenke et al (2014) |
| AS | bare soil | Belgium | 100 | 14 | 8.0 | 29 | - | Vermoesen et al. (1992) |
| AS | bare soil | Belgium | 100 | 10 | 8.0 | 8.5 | - | Vermoesen et al. (1992) |

| | | | | | | | | |
|----|-----------|-------------|-----|----------------|-----|------|------|-------------------------|
| AS | bare soil | Belgium | 100 | 16 | 8.0 | 9.8 | - | Vermoesen et al. (1992) |
| AS | bare soil | Belgium | 100 | 10 | 8.0 | 27.7 | - | Vermoesen et al. (1992) |
| AS | bare soil | Belgium | 100 | 14 | 8.0 | 30.7 | - | Vermoesen et al. (1992) |
| AS | bare soil | Belgium | 200 | 7 | 8.0 | 58.2 | 23.9 | Vermoesen et al. (1992) |
| AS | bare soil | Belgium | 200 | 7 | 8.0 | 18.3 | 7.8 | Vermoesen et al. (1992) |
| AS | bare soil | Belgium | 200 | 14 | 8.0 | 23 | 13.9 | Vermoesen et al. (1992) |
| AS | bare soil | New Zealand | 100 | 10 | 5.9 | 0.6 | 21.1 | Black et al. (1989) |
| AS | pasture | Australia | 100 | 20 | 7.0 | 3.9 | 30.8 | Schwenke et al (2014) |
| AS | pasture | Australia | 100 | 26 | 8.2 | 8.8 | 22.3 | Schwenke et al (2014) |
| AS | pasture | New Zealand | 30 | approx. 9 days | 5.8 | 0.6 | 11.2 | Black et al (1985) |
| AS | pasture | New Zealand | 30 | approx. 9 days | 5.8 | 0.2 | 7.4 | Black et al (1985) |
| AS | pasture | New Zealand | 30 | approx. 9 days | 5.8 | 1.3 | 15 | Black et al (1985) |
| AS | pasture | New Zealand | 30 | approx. 9 days | 5.8 | 2.1 | 12.6 | Black et al (1985) |
| AS | pasture | New Zealand | 30 | 11 | 6.1 | 0.3 | 7.3 | Black et al (1984) |
| AS | pasture | New Zealand | 30 | 11 | 6.1 | 1 | 26.7 | Black et al (1984) |

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|-----|---------------|-------------|------|----|-----|-------|-------|--------------------------|
| AS | wheat & grass | Denmark | 90 | 20 | 6.1 | 5 | 24 | Sommer and Jensen (1993) |
| AS | blueberry | Canada | 35 | 12 | 4.4 | 1.9 | 2.2 | Thyssen et al (2006) |
| AS | blueberry | Canada | 35 | 12 | 3.9 | 1.5 | 5.4 | Thyssen et al (2006) |
| AS | blueberry | Canada | 35 | 12 | 4.8 | 2.6 | 5.1 | Thyssen et al (2006) |
| AS | blueberry | Canada | 35 | 12 | 5.1 | 1.9 | 2.1 | Thyssen et al (2006) |
| AS | maize | Brazil | 120 | 37 | 5.2 | 3.5 | 3.5 | Martins et al (2015) |
| AS | rice | USA | 134 | 20 | 7.6 | 5.6 | 25.6 | Norman et al (2009) |
| AS | rice | USA | 134 | 20 | 7.6 | 4.6 | 21.2 | Norman et al (2009) |
| AS | wheat | USA | 134 | 18 | 7.2 | 0.159 | 2.619 | Massey et al (2012) |
| AS | wheat | USA | 168 | 33 | 6.7 | 17 | 46 | del Moro et al (2017) |
| AS | wheat | Japan | 63.6 | 9 | 5.6 | 0.2 | - | Hayashi et al (2011) |
| AS | wheat | China | 122 | 41 | 8.2 | 8.5 | 12 | Huo et al (2015) |
| DAP | pasture | New Zealand | 30 | 11 | 6.1 | 2.2 | 7.3 | Black et al (1984) |
| DAP | pasture | New Zealand | 30 | 11 | 6.1 | 10 | 26.7 | Black et al (1984) |

| | | | | | | | | |
|-----|-----------|-------------|-----|----------------|-----|------|------|--------------------------|
| DAP | pasture | New Zealand | 30 | approx. 9 days | 5.8 | 3.1 | 11.2 | Black et al (1985) |
| DAP | pasture | New Zealand | 30 | approx. 9 days | 5.8 | 2.2 | 7.4 | Black et al (1985) |
| DAP | pasture | New Zealand | 30 | approx. 9 days | 5.8 | 8.2 | 13.4 | Black et al (1985) |
| DAP | pasture | New Zealand | 30 | approx. 9 days | 5.8 | 5.8 | 15 | Black et al (1985) |
| DAP | pasture | New Zealand | 30 | approx. 9 days | 5.8 | 7 | 12.6 | Black et al (1985) |
| DAP | pasture | New Zealand | 150 | 14 | 5.7 | 1.4 | 4.2 | Zaman et al (2008) |
| DAP | pasture | Denmark | 90 | 20 | 6.1 | 9.9 | 17.8 | Sommer and Jensen (1993) |
| DAP | pasture | Denmark | 90 | 20 | 6.1 | 16.6 | - | Sommer and Jensen (1993) |
| DAP | blueberry | Canada | 35 | 12 | 4.4 | 1.4 | 2.2 | Thyssen et al (2006) |
| DAP | blueberry | Canada | 35 | 12 | 3.9 | 2.3 | 5.4 | Thyssen et al (2006) |
| DAP | blueberry | Canada | 35 | 12 | 4.8 | 3.3 | 5.1 | Thyssen et al (2006) |
| DAP | blueberry | Canada | 35 | 12 | 5.1 | 2.3 | 2.1 | Thyssen et al (2006) |
| DAP | wheat | Denmark | 90 | 20 | 6.1 | 19.4 | 29.8 | Sommer and Jensen (1993) |
| DAP | wheat | Denmark | 90 | 20 | 6.1 | 9.4 | 28.4 | Sommer and Jensen (1993) |
| DAP | wheat | Denmark | 90 | 20 | 6.1 | 16.8 | 24.1 | Sommer and Jensen (1993) |

