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Lachgas (N_2O) is een broeikasgas met op mondiaal niveau een aandeel van 6% in de emissies van broeikasgassen. Bemeste landbouwgronden zijn een belangrijke bron van N_2O. Er is een literatuurstudie uitgevoerd naar N_2O-emissie uit landbouwgronden met focus op de emissie uit verschillende typen kunstmest en de mogelijkheden om de emissie uit kunstmest te beperken. De N_2O-emissie uit kunstmest draagt voor 0,8% bij aan de totale broeikasgasemissie in Nederland. Uit de literatuur volgt dat toediening van kunstmest onder gemiddelde en relatief droge omstandigheden in de bodem leidt tot een beperkt risico op N_2O-emissie voor zowel grasland als bouwland. Het risico op N_2O-emissie neemt toe als nitraathoudende kunstmeststoffen, zoals kalkammonsalpeter en urean, onder natte omstandigheden aan grasland (alle grondsoorten) en bouwland (met name klei- en veengrond) worden toegediend. Het toedienen van een ammoniummeststof (eventueel met nitrificatieremmer) of ureum onder natte omstandigheden of het uitstellen van bemesting van de nitraathoudende kunstmest tot drogere omstandigheden zijn mogelijkheden om N_2O-emissie te beperken. De zogenaamde 4R-strategie om de benutting van nutriënten uit meststoffen te verhogen, kan ook leiden tot een lagere N_2O-emissie, namelijk N-toediening met het juiste type, juiste hoeveelheid, juiste tijdstip en juiste plaats.

Nitrous oxide (N_2O) is a greenhouse gas contributing to 6% of the global greenhouse effect. Fertilized agricultural soils are a major source of N_2O. A literature study on N_2O emission from agricultural soils was carried out focussing on the effect of different types of mineral nitrogen (N) fertilizers and strategies to mitigate N_2O emission from fertilizers. The N_2O emission from mineral N fertilizer application contributes to 0.8% of the total greenhouse gas emission in the Netherlands. The study shows that application of mineral N fertilizer under moderate and relatively dry conditions results in a relatively low risk of N_2O emission from both grassland and arable land. However, during wet conditions, application of nitrate containing mineral fertilizers such as (calcium) ammonium nitrate and urean to grasslands (all soil types) and arable crops on clay and peat soils increases the risk of N_2O emission. To decrease the risk of N_2O emission during wet conditions, an ammonium based fertilizer (possibly with a nitrification inhibitor) or urea can be used. Alternatively, the application of nitrate based fertilizer should be postponed until drier periods. The 4R strategy to increase nutrient use efficiency of fertilizers will also reduce N_2O emission, i.e., N application with the Right type, at the Right rate, at the Right time, and in the Right place.

Keywords: agriculture, emission, mineral fertilizer, manure, nitrous oxide, soils

Photo cover: Eduard Hummelink

Contents

Summary

OCI Nitrogen BV has requested that Wageningen Environmental Research carry out a literature study on nitrous oxide (N_2O) emission from agricultural soils that focusses on the effect of different types of mineral N fertilizers and strategies to mitigate N_2O emission from fertilizers.

Concentrations of atmospheric N_2O have risen from 270 ± 7 ppb in 1750 to 324.2 ± 0.1 ppb in 2011. It is estimated that 30% of the N_2O in the atmosphere is the result of human activity mainly originating from agricultural sources. Nitrous oxide is a greenhouse gas that currently contributes to 6% of total radiative forcing. CO_2 contributes to 75% and methane (CH_4) to 17% of this total figure. Agriculture accounts for approximately 75% of total N_2O emissions. The dominant global sources of N_2O emissions are manure application to grasslands (22%) and synthetic fertilizers (18%). Nitrous oxide also depletes stratospheric ozone and N_2O emission is currently the single most important ozone depleting emission. It is expected that N_2O will remain the largest ozone depleting emission throughout the 21st century.

In the Netherlands, N_2O emission from agriculture contributes 6.1 Mton CO_2 equivalents or 3.1% of the total greenhouse gas emissions. The emission of N_2O from agriculture amounts to 74% of the total N_2O emission in the Netherlands. The N_2O emission from mineral fertilizer applied to agricultural soils amounts to 1.6 Mton CO_2-equivalents or 0.8% of the total greenhouse gas emission and 19.7% of the total N_2O emission in the Netherlands. Since 1990, a sharp reduction of N_2O emission from agriculture and industrial processes (i.e. nitrate fertilizer production) has resulted in a strong decrease in nitrous oxide emission in the Netherlands. The decrease of N_2O emission from agricultural soils in the Netherlands since 1990 can be attributed to the manure policy which has led to a decrease in the amount nitrogen (N) applied to soils, nitrate leaching, and ammonia emission. The N_2O emission from mineral N fertilizer decreased by 0.9 Mton (more than 30%) between 1990 and 2015. In the early nineties, the introduction of rules to abate ammonia emission required the injection of slurry into agricultural soil resulting in an increase of N_2O emission from livestock manure.

The main sources of N_2O production in soils are nitrification, denitrification, nitrifier denitrification and chemical denitrification. Soil type and conditions, weather conditions, and N management have a large effect on the N_2O producing soil processes. Rapid changes in soil mineral N contents (e.g. through application of fertilizers and manure), available carbon contents in soil (e.g. through application of crop residues and manure), oxygen concentrations (e.g. through rainfall, groundwater fluctuations, and biological oxygen consumption in the soil) and temperature induce strong fluctuations in N_2O emission. Highest N_2O production is found in fertilized soils during relatively wet soil conditions, especially in soils rich in organic matter (e.g. grassland soils, peat soils or soils to which organic matter is applied). There are also many interactions between controlling variables that affect N_2O emission. The many variables and interactions between these make the overall effect on N_2O emission difficult to predict. Analysis of the dataset of emission factors in the Netherlands led to the use of country specific emission factors for mineral fertilizers, i.e., 0.8% of the fertilizer N applied for mineral soils and 3.0% of the fertilizer N applied for peat soils.

Statistical analyses of data contained within the global database with measurements of N_2O emissions showed no significant effect of fertilizer type on N_2O emission. However, several studies in which different mineral fertilizers are compared often show differences. Studies on grassland soils point to higher N_2O emissions from nitrate based fertilizers than from fertilizers only containing ammonium, especially during wet conditions. The denitrification capacity of grassland is high because of the high organic matter contents. Adding nitrate to grassland during wet conditions or before rainfall events increases the risk of high N_2O emission. Studies on arable soils point to similar or lower N_2O emissions from nitrate based fertilizers than urea and ammonium based fertilizers, especially under relatively dry conditions. Urea may increase N_2O emission during relatively dry conditions because of ammonia toxicity in nitrifying bacteria resulting in accumulation of nitrite (NO_2^-) and increased N_2O production.

The denitrification capacity of arable land is low and lower than that of grasslands because of the low organic matter content. Application of livestock slurry increases the denitrification capacity of arable land. The emission of N_2O from arable land is higher for livestock slurry than for calcium ammonium nitrate application. The differences between different fertilizer types on N_2O emission are not included in the Dutch monitoring protocol (all fertilizers have the same emission factor). However, it may be expected that the strict targets for reducing greenhouse gas emissions will result in the inclusion of the effect of different nutrient management strategies in protocols. The 4R strategy to increase nutrient use efficiency of fertilizers will also reduce N_2O emission, i.e., N application with the Right type, at the Right rate, at the Right time, and in the Right place.

Right type

Results from literature show that the N use efficiency of (calcium) ammonium nitrate is on average higher than that of regular urea and ammonium based fertilizers. This is mainly due to higher ammonia losses from urea and ammonium based fertilizers compared to nitrate containing fertilizers. Adding a urease inhibitor to urea decreases the risk of ammonia emission. Ammonium nitrate fertilizer application results in less acidification of the soil than ammonium and urea fertilizer application which is beneficial for crop quality and the species composition of grassland, and results in less demand for lime. Soil acidification may also increase the risk of N_2O emission when using ammonium and urea based fertilizers relative to (calcium) ammonium nitrate application.

Emission of N_2O from urea and ammonium fertilizers on arable soils is similar to or higher than that of nitrate fertilizers. Nitrous oxide emission from manure on arable sandy soils is much higher than that of mineral N fertilizers probably due to an increase in the denitrification capacity of the soil resulting from the organic matter content of manure. Nitrate fertilizer should not be applied just after manure application because the fresh organic matter of the manure can increase N_2O emission from the applied nitrate.

Application of nitrate fertilizer should be avoided on soils with a high denitrification capacity (high amounts of easily available organic matter) during wet conditions or just before expected heavy rainfall. These include grasslands, peat soils and arable land on clay soils. Options to decrease N_2O emission during these conditions include postponing the application of nitrate fertilizer or applying an ammonium fertilizer or livestock slurry during wet conditions. Grassland can rapidly absorb N, especially in late spring, summer and early autumn, and mineral N contents will decrease over a number of days following N application. Thus, the longer the period without rainfall following nitrate application, the lower the risk of N_2O emission.

The use of ammonium based fertilizers with a nitrification inhibitor can further reduce N_2O emission. The most well-known inhibitors, DCD, and DMPP can reduce N_2O emission by approximately 30 to 50%, with the highest effects seen in grassland. Addition of a nitrification inhibitor may also decrease N_2O emission from ammonium nitrate fertilizer, but it is doubtful whether N_2O emission can be heavily reduced during wet conditions when denitrification activity is high. Although several compounds may have inhibitory effects on denitrification, there are, unlike nitrification inhibitors, no commercial denitrification inhibitors available. Compounds that may have some inhibitory denitrification effects include heavy metals, salts and organic compounds. However, it is not known whether these compounds maybe used as denitrification inhibitors as their mode of action and specificity are currently unclear.

Right rate

The fertilizer application rate should be balanced with the N requirement of the crop as over fertilization increases the risk of N_2O emission. If manure or other organic fertilizers are used, the amount of available N should be accounted for in the application of mineral N fertilizer. Separating N fertilization into several applications limits overall mineral N content in the soil and reduces periods of elevated mineral N content, decreasing the risk of N_2O emission. In wet periods on grasslands, separating the recommended N fertilization into smaller applications may decrease N_2O emission.

Right time

The risk of N_2O emission is highest when the mineral N content of the soil is elevated. Therefore, shortening the period of elevated soil mineral N contents after fertilizer or manure application decreases the risk of N_2O emission. Therefore, N should be applied during or just before the crop growing period. The risk of N_2O emission increases when the moisture content of the soil increases for both ammonium, urea, and nitrate based fertilizers. Grasslands and peat soils have a high denitrification capacity, i.e., they contain easily available organic matter. Application of a nitrate fertilizer to these soil types during wet conditions should be avoided because of the high risk of N_2O emission. An ammonium based fertilizer (possibly with a nitrification inhibitor) can be used to decrease the risk of N_2O emission during wet conditions or the application of the nitrate based fertilizer can be postponed to drier periods.

Application of manures, regular urea and urean (a solution of urea and ammonium nitrate) and the application of ammonium fertilizer to calcareous soils result in a risk of ammonia emission which decreases the N use efficiency of these fertilizers. Application during rainy conditions decrease the risk of ammonia emission. However, application of fertilizers and manures during rainy conditions will increase the risk of N_2O emission. Large losses of ammonia decrease the N use efficiency and, depending on the N application rate, increase the need for additional N fertilizers which heightens the risk of nitrate leaching. Ammonia is also a source of indirect N_2O emission meaning that a reduction in ammonia emission will also reduce N_2O emission.

Right Place

Surface application of fertilizers and manures decreases N_2O emission relative to incorporation or injection methods. Surface application increases the risk of ammonia emission, however, the risk of ammonia emission for calcium ammonium nitrate is much smaller than for regular urea, urean, livestock manure and ammonium fertilizers (when applied to calcareous soils). Ammonia is also a source of indirect N_2O emission meaning that ammonia emission reduction will also reduce N_2O emission.

1 Introduction

Nitrous oxide (N_2O) is a greenhouse gas that is also harmful to stratospheric ozone (depletion of the ozone layer). Fertilized soils are a major source of N_2O.

OCI Nitrogen BV has requested that Wageningen Environmental Research carry out a literature study on N_2O emission from agricultural soils. Topics to be included in this study are:
- A description of the mechanisms of N_2O production in soils;
- A description of the factors controlling N_2O emission from soils, including the effect of nitrogen (N);
- An overview of the N_2O emission from different types of mineral N fertilizers and animal manure;
- Options to mitigate N_2O emission from agricultural soils; and
- An overview of nitrification and denitrification inhibitors and their effectiveness in decreasing N_2O emission.

Chapter 2 gives an overview of the Global Warming Potential of N_2O, the main N_2O sources, and monitoring of N_2O emission. Chapter 3 describes the processes of the variables influencing N_2O emission from agricultural soils, Chapter 4 deals with the agricultural value of N fertilizers and manures, Chapter 5 provides an overview of the effects of mineral fertilizers and manures on N_2O emission, and Chapter 6 includes options for mitigation of N_2O emission from fertilizers and manures, including the use of inhibitors.

2 Nitrous oxide

2.1 Nitrous oxide

Nitrous oxide (N$_2$O; popular name laughing gas) is a colourless non-flammable gas. It is a natural gas that occurs in small amounts (± 300 µg per L or ppb) in the atmosphere. Nitrous oxide is also used in surgery because it has anaesthetic and pain reducing effects. It is also used as an oxidizer to increase the power of engines.

Atmospheric concentrations of nitrous oxide have risen from 270 ± 7 ppb in 1750 to 324.2 ± 0.1 ppb in 2011 (IPCC, 2013. See Figure 1 for the trend in concentration from 1978 to 2011). It is estimated that 30% of the N$_2$O in the atmosphere is the result of human activity which is mainly attributed to agriculture (IPCC, 2013).

Nitrous oxide is a greenhouse gas. The Global Warming Potential (GWP) is used to compare the global warming impacts of different gases. The GWP indicates how much energy the emissions of 1 ton of a gas will absorb over a given period of time, relative to the emissions of 1 ton of carbon dioxide (CO$_2$). The GWP depends on the absorption of infrared radiation by a given species, the spectral location of its absorbing wavelengths, and the atmospheric lifetime of the species. Nitrous oxide has a GWP 265 times that of CO$_2$ over a 100 year timescale (IPCC, 2013[1]) because of its long residence time (121 years) and strong absorption capacity (for comparison, methane has a GWP of 28).
The concentration of N$_2$O is much smaller (measured in ppb) than CO$_2$ (measured in ppm) and therefore the total greenhouse effect of N$_2$O is much smaller than that of CO$_2$. The radiative forcing[2] of N$_2$O is currently 0.17 ± 0.03 W m^{-2} (6% of total radiative forcing; IPCC, 2013). The radiative forcing of CO$_2$ is 1.82 ± 0.19 (64%) and that of CH$_4$ 0.48 ± 0.05 W m^{-2} (17%).
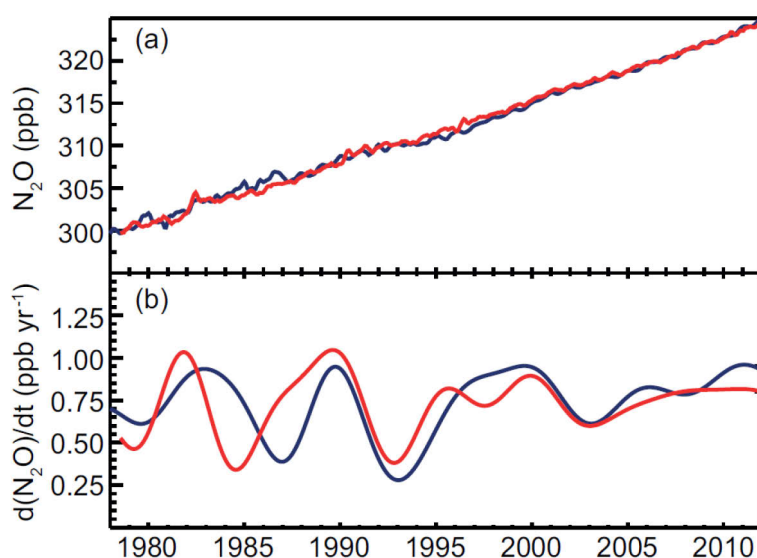
Figure 1   a) Globally averaged N$_2$O dry-air mole fractions from AGAGE (red) and NOAA/ESRL/GMD (blue) stations at monthly resolution. (b) Instantaneous growth rates for globally averaged atmospheric N$_2$O (IPCC, 2013).

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[1] The GWP of N$_2$O was 298 for a 100 year timescale according to the IPCC (2007).
[2] IPCC: 'Radiative forcing is a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system and is an index of the importance of the factor as a potential climate change mechanism. In this report radiative forcing values are for changes relative to preindustrial conditions defined at 1750 and are expressed in Watts per square meter (W/m^2).'

N_2O is also a stratospheric ozone depleting gas (Figure 2). Emissions of chlorofluorocarbons (CFCs) have strongly decreased because of the Montreal Protocol and signs of ozone stabilization have been observed. Currently, N_2O emission is the single most important ozone depleting emission and is expected to remain the most important throughout the 21st century (Ravishankara *et al.*, 2009; Wuebbles, 2009).
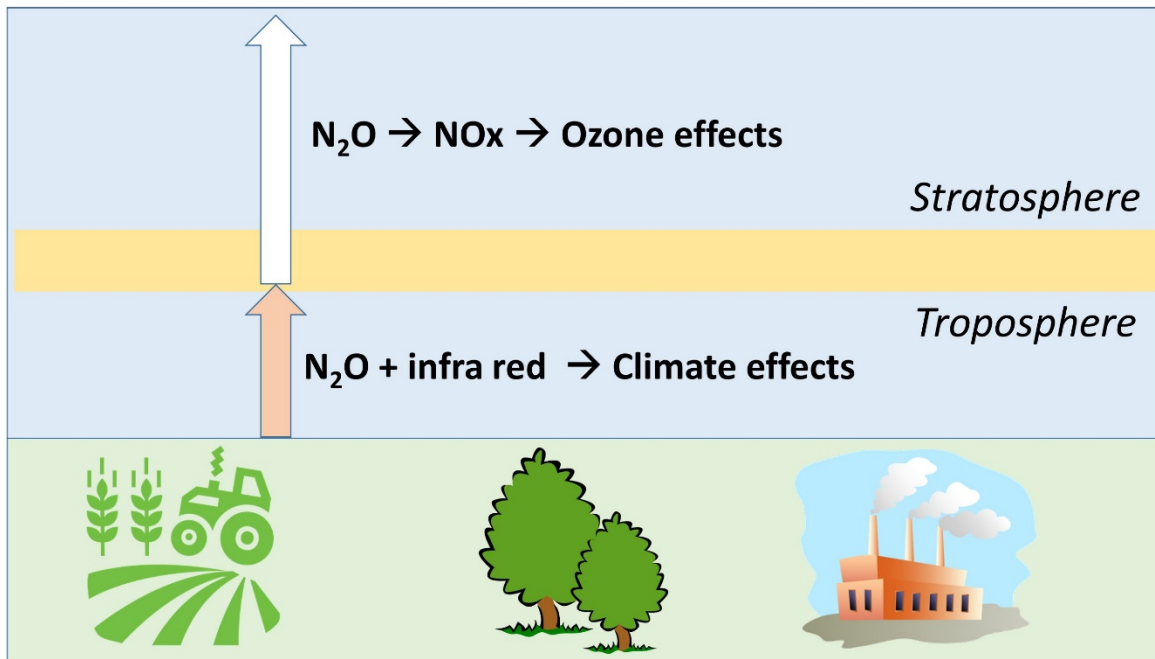
Figure 2   *Nitrous oxide is a greenhouse gas (troposphere) and ozone depleting gas (stratosphere) (After Wuebbles, 2009).*

2.2   Sources of nitrous oxide

2.2.1   Global

Nitrous oxide emissions account for about 6% of total greenhouse gas emissions on a global scale (Figure 3). Agriculture, including indirect N_2O emissions[3], accounts for about 75% of total N_2O emissions (Figure 3).

The main global sources of N_2O emissions are manure application to grasslands (pastures, rangeland and paddocks) and synthetic fertilizers (22% and 18%, respectively in 2016; Figure 4).

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[3] Indirect N_2O emissions are emissions of N_2O from volatilized ammonia (NH_3) and leached nitrate (NO_3^-).

Contribution to 2016 greenhouse gas emissions per emission category
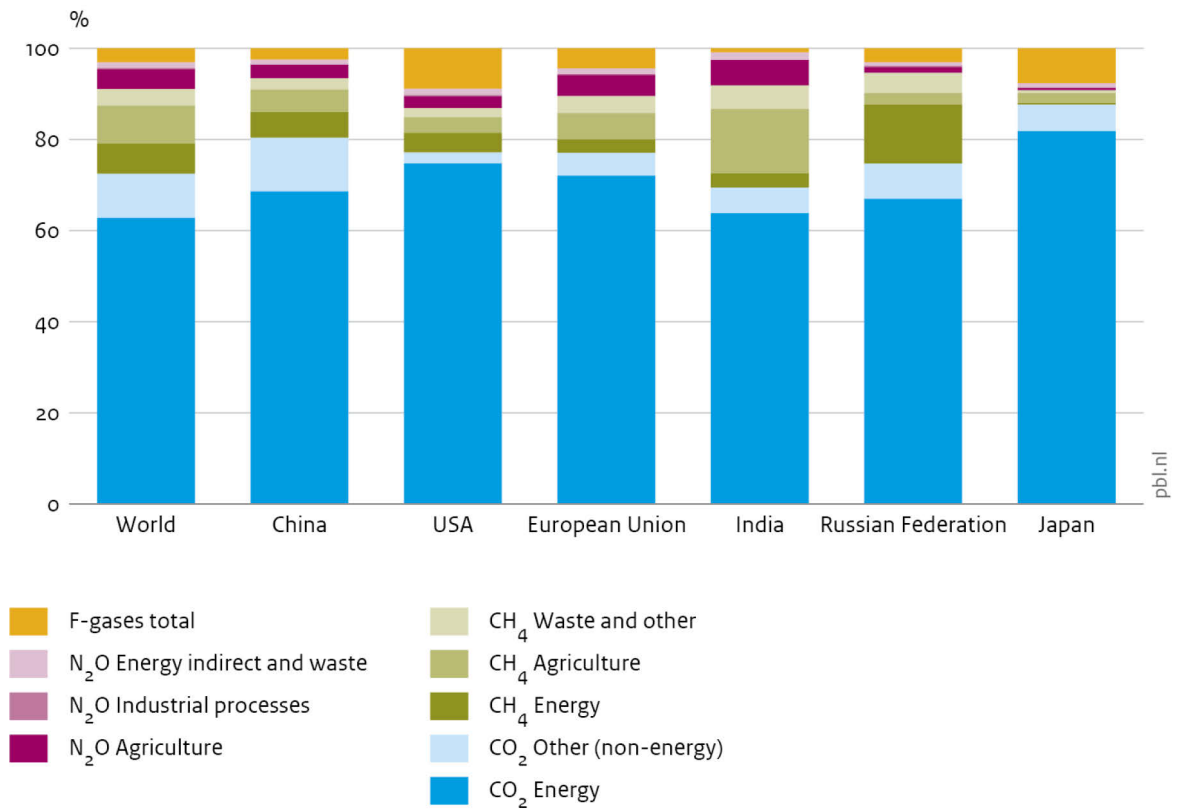
Source: EDGAR v4.3.2. (EC-JRC/PBL 2017); IEA (2017); BP (2017)

Figure 3 *Greenhouse gas emissions per category in the world and for several regions/countries (Olivier et al., 2017).*

Global N_2O emissions per source category
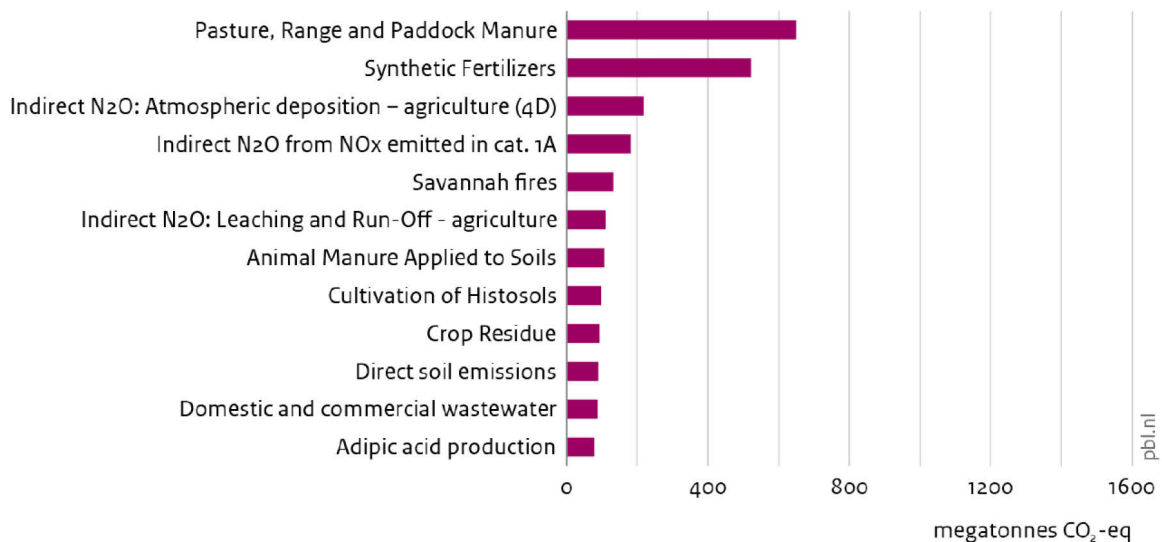
Figure 4 *Top 12 sources of nitrous oxide. Nitrous oxide emission are expressed in megatonnes CO_2 equivalents (Olivier et al., 2017).*

2.2.2   The Netherlands

In the Netherlands, N_2O emission from agriculture contributes to 3.1% of the total greenhouse gas emissions (Table 1). The emission of N_2O from Dutch agriculture amounts to 74% of the total N_2O emission (Table 1).

The N_2O emission from mineral fertilizers applied to agricultural soils amounts to 1.6 Mton CO_2-equivalents, that is 0.8% of the total greenhouse gas emission in the Netherlands and 19.7% of the total Dutch N_2O emission (Table 1). The direct N_2O emission from organic N fertilizer which excludes excretion during grazing is 0.6% of the total greenhouse gas emission and 15.1% of the total N_2O emission in the Netherlands.

The N_2O emission in the Netherlands has strongly decreased since 1990 (Figure 5) due to a strong reduction in N_2O emission from agriculture and industrial processes (i.e. nitrate fertilizer production; Figure 6). The decrease in N_2O emission from agricultural soils seen since 1990 resulted from a reduction in direct N_2O emission from mineral fertilizer and grazing, and reduced indirect emission from ammonia and nitrate leaching (Figure 7). These decreasing trends have mainly resulted from the manure policy in the Netherlands which led to a reduction in the amount N applied to soils, nitrate leaching, and ammonia emission. However, the obligatory injection of slurry in the early nineties to abate ammonia emission has resulted in an increase in N_2O emission from the category organic N fertilizers (Figure 7). The influence of application technique on N_2O emission is described in the following Chapter. The N_2O emission from mineral N fertilizer has decreased with 0.9 Mton (more than 30%) between 1990 and 2015 (Table 1).
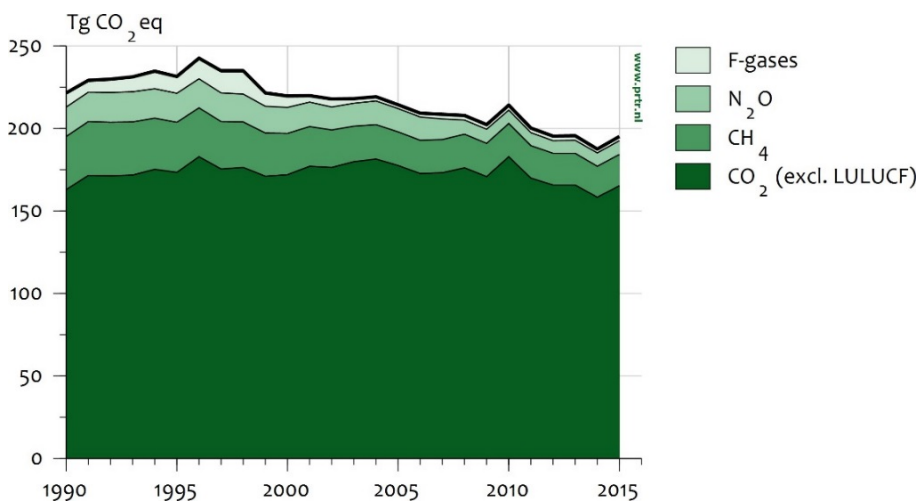
Figure 5   *Greenhouse gases in the Netherlands: trend and emission levels (excl. Land Use, Land Use Change, and Forestry; LULUCF), 1990– 2015 (Coenen et al., 2017).*
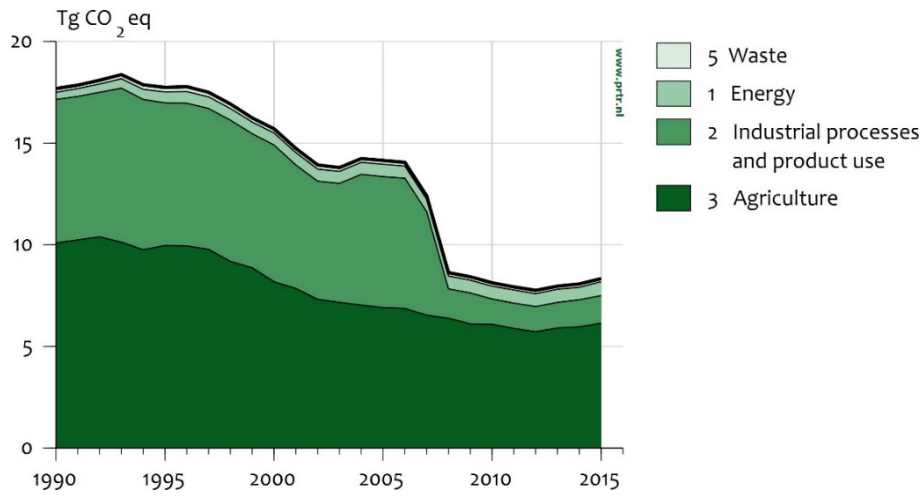
Figure 6 *N₂O emissions in the Netherlands: trend and emission levels per sector, 1990–2015 (Coenen et al., 2017).*
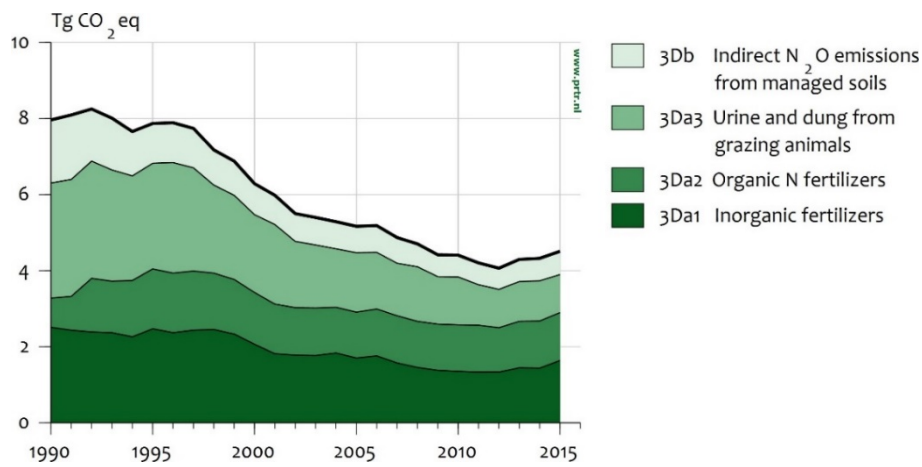
Figure 7 *Category 3D Agricultural soils in the Netherlands: trend and emission levels per source category, 1990–2015 (Coenen et al., 2017).*

Table 1 *Greenhouse gas emission in the Netherlands; emissions from sector 3, Agriculture, in Mton CO$_2$-eq (Coenen et al., 2017).*

Sector/category	Gas	Key*	Base year	2014	2015	Difference 2015-2014	Contribution to total in 2015 (%)		
			Tg CO$_2$-eq				by sector	of total gas	of total CO$_2$-eq
3. Agriculture	CO$_2$	-	0.2	0.1	0.1	0.0	0.4	0.0	0.0
	CH$_4$	-	15.0	12.6	13.0	0.4	67.7	68.4	6.7
	N$_2$O	-	10.1	6.0	6.1	0.2	32.0	73.7	3.1
	All	-	25.3	18.6	19.2	0.6	100.0		9.8
3A. Enteric fermentation	CH$_4$	-	9.2	8.2	8.5	0.3	44.3	44.8	4.4
3A1. Cattle	CH$_4$	-	8.2	7.3	7.6	0.3	39.6	40.0	3.9
3A1. Mature dairy cattle	CH$_4$	L, T	5.2	5.0	5.2	0.2	27.2	27.5	2.7
3A1. Other mature cattle	CH$_4$	non key	0.2	0.2	0.2	0.0	0.8	0.8	0.1
3A1. Growing cattle	CH$_4$	L	2.8	2.2	2.2	0.0	11.5	11.6	1.1
3A2. Sheep	CH$_4$	-	0.3	0.2	0.2	0.0	1.0	1.0	0.1
3A3. Swine	CH$_4$	L2	0.5	0.5	0.5	0.0	2.5	2.5	0.2
3A4. Other livestock	CH$_4$	non key	0.2	0.2	0.2	0.0	1.3	1.3	0.1
3B. Manure management	CH$_4$	-	5.8	4.4	4.5	0.1	23.4	23.6	2.3
	N$_2$O	L, T2	0.9	0.7	0.7	0.0	3.5	8.1	0.3
	All	-	6.7	5.0	5.2	0.2	26.9		2.6
3B1. Cattle	CH$_4$	L,T	1.8	2.2	2.3	0.1	11.8	11.9	1.2
2B2. Sheep	CH$_4$	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3B3. Swine	CH$_4$	L,T	3.5	2.1	2.1	0.0	11.0	11.1	1.1
3B4. Poultry	CH$_4$	T	0.5	0.1	0.1	0.0	0.4	0.4	0.0
3B4. Other livestock	CH$_4$	non key	0.0	0.0	0.0	0.0	0.2	0.2	0.0
3B1-4. Direct emissions	N$_2$O	-	0.5	0.4	0.5	0.0	2.4	5.4	0.2
3B5. Indirect emissions	N$_2$O	-	0.4	0.2	0.2	0.0	1.2	2.7	0.1
3D. Agriculture soils	N$_2$O	-	9.2	5.3	5.5	0.2	28.5	65.6	2.8
3Da. Direct N$_2$O emissions from agricultural soils	N$_2$O								
3Da1. Inorganic fertilizers	N$_2$O	L,T	7.5	4.7	4.9	0.1	25.3	58.3	2.5
3Da2. Organic N fertilizers	N$_2$O	-	2.5	1.4	1.6	0.2	8.5	19.7	0.8
3Da3. Urine and dung from grazing animals	N2O	-	0.8	1.2	1.3	0.0	6.5	15.1	0.6
3Da4. Crop residues	N2O	-	3.0	1.1	1.0	-0.1	5.2	12.0	0.5
3Da6. Cultivation of organic soils	N2O	-	0.4	0.2	0.2	0.0	1.0	2.3	0.1
3Db. Indirect N2O Emissions from managed soils	N2O	-	0.8	0.8	0.8	0.0	4.0	9.3	0.4
3G. Liming	CO2	L,T	1.6	0.6	0.6	0.0	3.2	7.3	0.3
		T2	0.2	0.1	0.1	0.0	0.4	0.0	0.0
National Total GHG emissions (excl. CO2 LULUCF)	CO2		162.9	158.3	165.3	7.1			
	CH4		32.3	18.8	19.0	0.2			
	N2O		17.7	8.1	8.3	0.3			
	All		223.1	187.6	195.2	7.7			

2.3 Monitoring

2.3.1 Intergovernmental Panel on Climate Change (IPCC)

The N_2O emissions from agricultural soils consist of direct emissions from N application to soils, and indirect emissions from N leaching and run-off and from ammonia and nitrogen dioxide (NH_3 and NO_x) emissions. The Intergovernmental Panel on Climate Change (IPCC) has provided a general framework for the calculation of the emission of greenhouse gases (including N_2O) at the national level (2006 IPCC Guidelines for National Greenhouse Gas Inventories. https://www.ipcc-nggip.iges.or.jp/public/2006gl/ Volume 4 Agriculture).

The method for mineral fertilizers is described in Chapter 11: https://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/4_Volume4/V4_11_Ch11_N2O&CO2.pdf

The method for manure management is described in Chapter 10: https://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/4_Volume4/V4_11_Ch11_N2O&CO2.pdf

The following N sources are included in the methodology for estimating direct N_2O emissions from managed soils (IPCC, 2006):
- Mineral (synthetic) N fertilizers;
- Organic N applied as fertilizer (e.g. animal manure, compost, sewage sludge, rendering waste);
- Urine and dung N deposited on pasture, range and paddock by grazing animals;
- N in crop residues (above ground and below ground), including residues from N-fixing crops and from pasture renewal;
- N mineralisation associated with loss of soil organic matter resulting from changes in land-use or management of mineral soils; and
- Drainage/management of organic soils.

The N_2O emission of each source is calculated according to the amount of N in each source (e.g. the amount of N applied with mineral fertilizers) and the N_2O emission factor as a percentage of the N applied. Countries can used default emission factors (Tier 1 and Tier 2 approach) or country specific emission factors (Tier 3 approach). The Netherlands uses country specific emission factors for direct N_2O emission (see next section) and IPCC defaults for indirect N_2O emission.

The default IPCC N_2O emission factor for mineral fertilizer and manure is 1%, for grazing by cattle 2%, for leaching 0.75% of the N leached and for ammonia volatilization 1% of the volatilized ammonia.

2.3.2 The Netherlands

The calculation of N_2O emission from fertilizers and manures in the Netherlands is based on country specific emission factors expressed in % of the N applied. Velthof and Mosquera (2011a) created a database with N_2O emission factors derived from field experiments in the Netherlands. The emission factors are calculated as:

*N_2O-N emission factor (in %) = [(N_2O-N emission from fertilized soil) − (N_2O-N emission from unfertilized soil)]/(N applied) * 100,*

where N_2O-N emission and N applied are expressed in kg N per ha.

Emission factors were only used if they were obtained in field experiments that included replicates and an unfertilized control. This method of calculating emission factors is in agreement with the method proposed by the IPCC. For monitoring studies of more than 1 year duration, separate emission factors for each year were included in the database.

Table 2 shows the number of N_2O emission factors for each N source and the mean, standard error, minimum and maximum emission factor. The N sources include mineral N fertilizers, livestock manures, urine excreted during grazing and crop residues. In total, there are 153 experimentally

derived emission factors in the Netherlands resulting in an average emission factor of 1.3% of N applied with a standard error of 0.2%. In some experiments, N_2O emission was only measured for a short period lasting less than a full 6 months growing season. The average emission factor is 1.2 ± 0.1% (n = 130) if these shorter experiments are removed.

The average emission factor of experiments lasting longer than 6 months (Table 2) was higher for peat soils (4.5 ± 0.9%) than for clay soils (1.3 ± 0.2%) and sandy soils (0.7 ± 0.1%). The average emission factor was somewhat higher for grassland (1.4 ± 0.2%) than for arable land (1.0 ± 0.2%). The effect of soil type is discussed in the following Chapter.

Table 2 N_2O-N emission factors for N sources derived from field experiments in the Netherlands (mean, standard error[*], minimum and maximum). Emission factors are presented for the entire dataset and for a dataset with experiments that lasted at least a whole growing season (> 6 months) (Velthof and Mosquera, 2011a). [4]

	Total data set					Experiments > 6 months				
	n	N_2O emission factor, % of N				n	N_2O emission factor, % of N			
		mean	st error	min	max		mean	st error	min	max
N source										
Ammonium sulphate	6	0.3	0.1	0.1	1.0	3	0.2	0.1	0.1	0.3
Ammonium sulphate + DCD	2	0.1	0.0	0.1	0.1					
Calcium Ammonium Nitrate (CAN)	52	1.3	0.2	-0.2	8.3	44	1.0	0.2	-0.2	4.5
CAN + cattle slurry	19	0.6	0.2	0.1	3.1	19	0.6	0.2	0.1	3.1
CAN + grazing	8	3.0	0.8	0.8	6.8	8	3.0	0.8	0.8	6.8
Cattle slurry	35	0.5	0.1	-0.6	2.0	31	0.6	0.1	-0.6	2.0
Calcium Nitrate	3	5.8	3.4	0.1	12.0					
Pig slurry	8	2.0	0.8	0.1	7.0	8	2.0	0.8	0.1	7.0
Sugar beet leaves	2	0.2	0.1	0.1	0.3	2	0.2	0.1	0.1	0.3
Urea	3	0.3	0.2	0.1	0.7					
Urine patch	7	1.6	0.2	0.9	2.1	7	1.6	0.2	0.9	2.1
Urine/dung	8	4.2	1.3	1.0	11.4	8	4.2	1.3	1.0	11.4
Total	153	1.3	0.2	-0.6	12.0	130	1.2	0.1	-0.6	11.4
Soil										
Clay	39	1.1	0.2	-0.6	4.6	35	1.3	0.2	-0.6	4.6
Peat	12	4.5	0.9	1.5	11.4	12	4.5	0.9	1.5	11.4
Sand	102	1.0	0.2	-0.2	12.0	83	0.7	0.1	-0.2	7.0
Total	153	1.3	0.2	-0.6	12.0	130	1.2	0.1	-0.6	11.4
Land use										
Arable land	49	1.0	0.2	-0.6	7.0	49	1.0	0.2	-0.6	7.0
Grassland	104	1.5	0.2	0.0	12.0	81	1.4	0.2	0.0	11.4
Total	153	1.3	0.2	-0.6	12.0	130	1.2	0.1	-0.6	11.4
N application rate, kg N per ha		264	175	50	880		293	173	50	880

[*]a measure of uncertainty in the emission factors.

The emission factors for calcium ammonium nitrate (CAN) applied to clay soil are higher than for CAN applied to sandy soils, especially for arable land (Table 3). Emissions for livestock manure were (somewhat) smaller for clay soils than sandy soils (Table 3). The emission factors for CAN applied to grassland on peat soil were higher than those for CAN applied to grassland on mineral soils. The average emission factor for CAN on peat soil is 3.0 ± 0.6% (n =4).

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[4] Dolfing *et al.* (unpublished), Schils *et al.* (2008), Schils *et al.* (2010), Van Groenigen *et al.* (2005), Van Groenigen *et al.* (2004), Velthof *et al.* (1996), Velthof *et al.* (1997), Velthof *et al.* (2003), Velthof *et al.* (2010a), and Velthof & Mosquera (2011).

Table 3   *Average and standard errors of N$_2$O emission factors for CAN and livestock manure (low ammonia emission application technique and broadcast surface application) for arable and grassland in the Netherlands (experiments > 6 months), split in factors for sand, clay, and peat soils (Velthof and Mosquera, 2011a).*

Soil	N source	Manure application technique	Land use								
			Arable land			Grassland			All		
			Average	se	n	Average	se	n	Average	se	n
Clay	CAN		1.7 ± 0.6		5	1.1 ± 0.3		9	1.3 ± 0.3		14
	Livestock manure	Low emission	1.1 ± 0.3		7	0.3 ± 0.1		2	0.9 ± 0.3		9
		Surface				0.1 ± 0.1		2	0.1 ± 0.1		2
	Average		1.3 ± 0.3		12	0.8 ± 0.2		13	1.1 ± 0.2		25
Sand	CAN		0.2 ± 0.1		9	0.7 ± 0.2		17	0.5 ± 0.1		26
	Livestock manure	Low emission	1.5 ± 0.5		14	0.3 ± 0.1		5	1.2 ± 0.4		19
		Surface	0.6 ± 0.2		6	0.1 ± 0.0		3	0.5 ± 0.2		9
	Average		0.9 ± 0.2		29	0.5 ± 0.1		25	0.7 ± 0.1		54
Average mineral soils			1.0 ± 0.2		41	0.6 ± 0.1		38	0.8 ± 0.1		79
Peat	CAN					3.0 ± 0.6		4	3.0 ± 0.6		4

On the basis of the analysis of the dataset of emission factors in the Netherlands, it was recommended that specific emission factors are used for manures applied to grassland and arable land on mineral soils (Table 4). The average emission factors in Table 4 were used to calculate N$_2$O emissions in the Netherlands (Vonk *et al.*, 2018). The emission factor that is used in the Netherlands for CAN and other fertilizer types in mineral soils is somewhat smaller than the IPCC default factor of 1%. The 3% emission factor for peat soil is higher than the IPCC default of 1%.

The emission factor for CAN is used for all fertilizer types. In the previous monitoring protocol (before 2013), an emission factor of 0.97% for mineral soils and 1.94% for peat soil was used for nitrate containing fertilizers, and 0.48% for mineral soils and 0.97% for peat soils for ammonium fertilizers. However, the number of measurements for ammonium fertilizers is small meaning that no fertilizer type specific emission factors are currently used.

Table 4   *Average N$_2$O emission factors (in % of N applied) and standard errors for CAN and livestock manure in the Netherlands based on the dataset with emission factors obtained from experiments in the Netherlands. The emission factors for manure applied to peat soil were calculated from results from an incubation study (Velthof and Mosquera, 2011a).*

Soil type	Source	Application technique	Land-use		
			Arable land	Grassland	All
Mineral soils	CAN		0.7 ± 0.3 (n=14)	0.8 ± 0.1 (n=26)	0.8 ± 0.1 (n=40)
	Livestock manure	Low emission	1.3 ±0.3 (n=21)	0.3 ± 0.1 (n=7)	1.1 ± 0.2 (n=28)
		Surface	0.6 ± 0.2 (n=6)	0.1 ±0.02 (n=5)	0.4 ± 0.2 (n=11)
Peat soil	CAN			3.0 ± 0.6 (n=4)	
	Livestock manure	Low emission		1[*]	
		Surface		0.5[*]	

[*]   estimated from an incubation study.

3 Processes and controlling factors

3.1 Processes

The biological processes nitrification, denitrification, and nitrifier denitrification, and the chemical process chemical denitrification are the main mechanisms through which N_2O is produced. These processes are discussed in this chapter.

3.1.1 Nitrification

Nitrification is the oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) and nitrate (NO_3^-); Figure 8. Bacterial species that are involved in the first step (transformation of NH_4^+ to NO_2^-) generally belong to *Nitrosomonas* and those involved in the second step (transformation of NO_2^- to NO_3^-) to *Nitrobacter*.

Nitrification occurs under aerobic (oxygen rich) conditions. The majority of bacteria involved are autotrophs and use CO_2 as a source of carbon. Hydroxylamine (NH_2OH) is an intermediate product of nitrification. Nitrous oxide is a by-product of nitrification that is produced at low O_2 concentrations. Some nitrifiers use organic carbon (C) as an energy source in a process called heterotrophic nitrification.
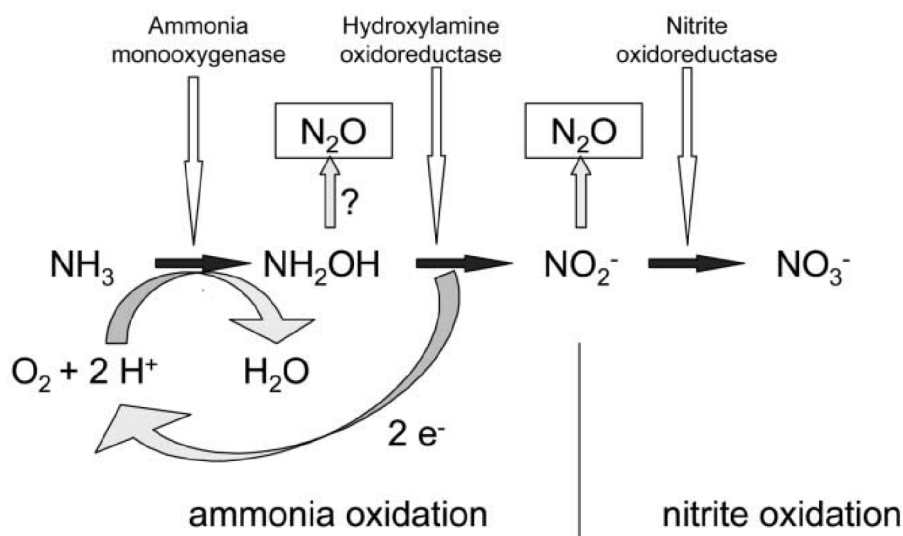
Figure 8   *Pathway of nitrification (Wrage et al., 2001).*

3.1.2 Denitrification

3.1.2.1   Biological denitrification

Using available carbon sources as a source of energy, denitrifying bacteria produce N_2O under anaerobic conditions during the stepwise reduction of NO_3^- to dinitrogen (N_2) (Firestone *et al.*, 1989). Several intermediates are developed during denitrification (Figure 9): NO_2^-, nitric oxide (NO), N_2O and N_2. All these products may be released during denitrification. Reactions are regulated by the enzymes nitrate reductase and nitrite reductase (Figure 9; Coyotzi *et al.*, 2017). The reactions are carried out by denitrifying bacteria that are widely distributed across the bacterial taxa. Examples of these include *Pseudomonas, Bacillus, Thiobacillus, Propionibacterium* (Firestone, 1982). These predominantly heterotrophic microorganisms are facultative anaerobes that are able to use NO_3^- instead of oxygen as an electron acceptor in respiration to cope with low oxygen or anaerobic conditions (Wrage *et al.*,

2001). Bacteria are mostly responsible for emission of N_2O in soils (Syakila & Kroeze, 2011; Reay et al., 2012), however, fungi are also able to denitrify (Matsuoka et al., 2017). Nitrous oxide is a regular intermediate in denitrification which contrasts with nitrification where N_2O is a by-product.
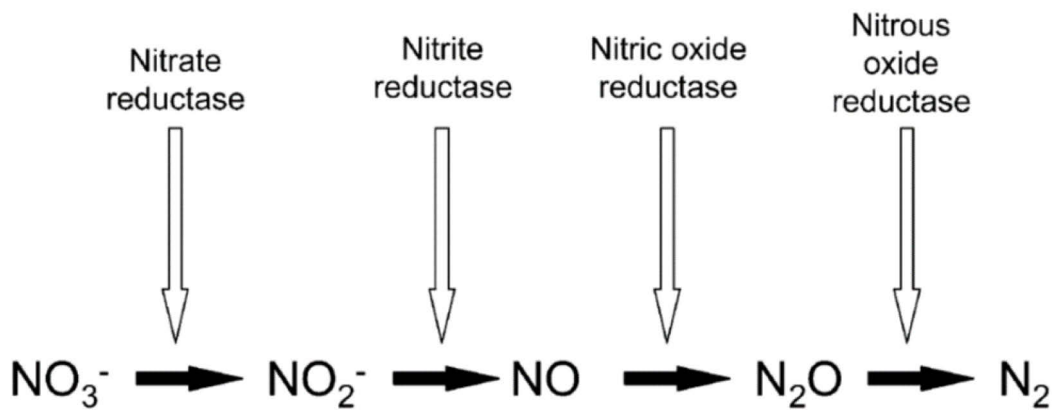
Figure 9   Pathway of denitrification (Wrage et al., 2001).

3.1.2.2   Chemical denitrification

Chemical denitrification is the process by which NO_2^- and NH_2OH are chemically reduced to N_2O (Figure 10; (Chalk and Smith, 1983; Heil et al., 2016). Several reactions are involved, i.e., self-decomposition of NO_2^-, reactions of NO_2^- with reduced metal cations, nitrosation of soil organic matter by NO_2^-, a reaction between NO_2^- and NH_2OH, and the oxidation of NH_2OH by iron (Fe^{3+}) or manganese (MnO_2).

In most soils, the oxidation of NO_2^- to NO_3^- proceeds faster than the conversion of NH_3 to NO_2^- meaning that NO_2^- does not accumulate. Under alkaline conditions (high pH), NH_3 is formed from NH_4^+. NH_3 is toxic for the bacteria that transform NO_2^- into NO_3^- resulting in accumulation of NO_2. This process may increase N_2O emission through chemical denitrification. Emission of N_2O from accumulated NO_2^- may occur after application of urea fertilizer to all soil types and ammonium fertilizer to calcareous soils, and in urine patches on grazed grassland.
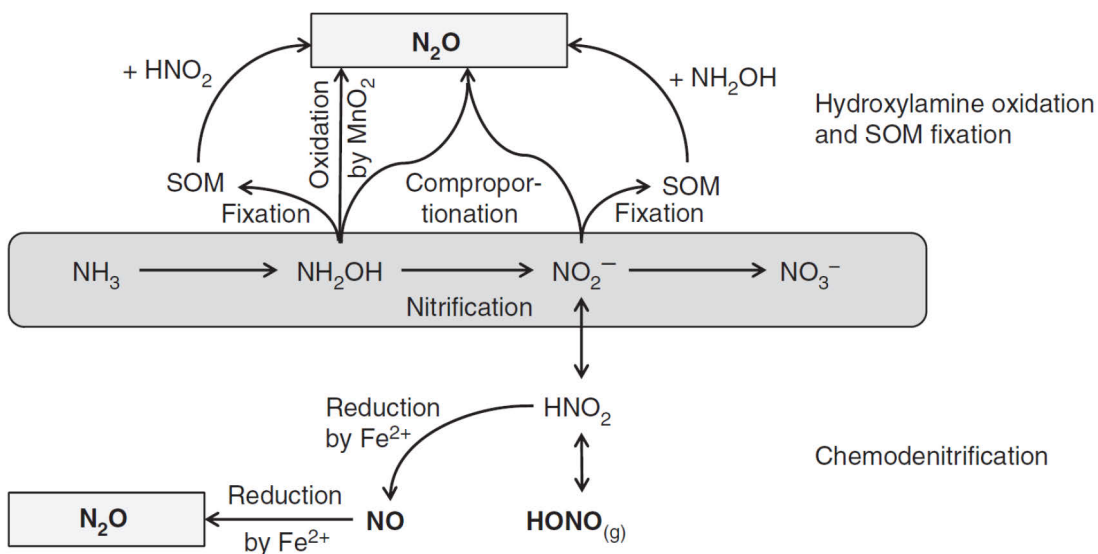

Figure 10   Pathways of chemical denitrification (Heil et al., 2016).

3.1.3   Nitrifier denitrification

Nitrifier denitrification is the pathway of nitrification in which NH_4 is oxidized by autotrophic nitrifiers to NO_2^- followed by the reduction of NO_2^- to NO, N_2O and N_2 (Figure 11; Wrage *et al.*, 2001; 2018). Due to experimental difficulties and a lack of awareness of nitrifier denitrification, not much is known about this mechanism of N_2O production. Experiments indicate that nitrifier denitrification occurs at relatively high ammonium concentrations, low O_2 and low C contents.
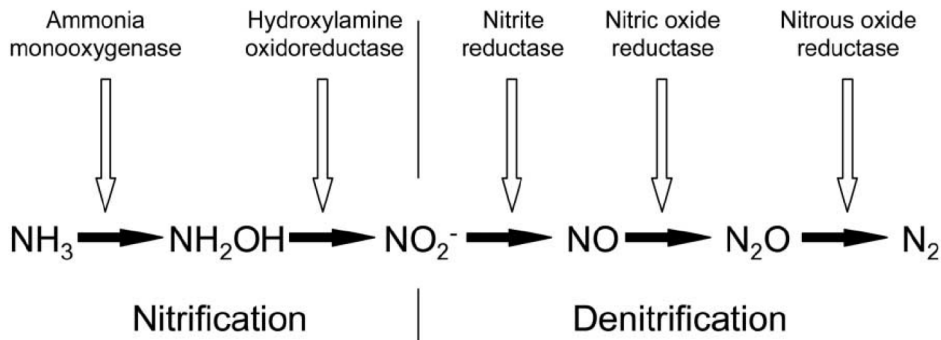
Figure 11   *Pathway of nitrifier denitrification (Wrage et al., 2001).*

3.2   Controlling factors

Soil type and conditions, weather conditions, and N management have a large effect on N_2O production in soils (Butterbach-Bahl *et al.*, 2013; Lesschen *et al.*, 2011). Rapid changes in soil contents of mineral N (e.g. by application of N fertilizers and manure), available carbon (e.g. by application of crop residues and manure), oxygen (e.g. rainfall, groundwater fluctuations, and biological oxygen consumption in the soil) and temperature can result in strong fluctuations in N_2O emission (Figure 12). Highest production is found in fertilized soils during relatively wet soil conditions and especially in soils rich in organic matter (e.g. grassland soils, peat soils or soils to which organic matter containing products are applied).

In general, the total N losses by denitrification (N_2 + N_2O + NO) increase with increasing temperature, available C content, pH and nitrate contents and decreasing oxygen content (Table 5). However, for N_2O emission, it is also important to consider the proportion of N_2O to total N denitrification loss. The N_2O/N_2 ratio of denitrification products increases when nitrate concentration, oxygen concentration or available carbon increases and temperature or pH decreases (Table 5). This demonstrates the complexity of predicting N_2O emission. It should be noted that even at suboptimal conditions for denitrification (low oxygen, low pH and low temperature), relatively high N_2O emission may occur.

The nitrification rate increases with increasing ammonium content, oxygen content, or temperature and decreasing pH. The highest N_2O production is generally found during suboptimal conditions for nitrification, e.g., during wet conditions. These are also conditions in which N_2O production during denitrification is highest. Therefore, it is difficult to determine whether the mechanism of N_2O production is nitrification or denitrification in wet soils containing both ammonium and nitrate.

A more in depth description of the factors controlling N_2O emission is given in the following sections.

Table 5 *Effects of factors on denitrification rate and N_2O/N_2 ratio on the end products of denitrification (Based on Delwiche, 1981; Firestone, 1982; Firestone et al., 1989; Knowles, 1982).*

	denitrification	N_2O/N_2 ratio
Increasing nitrate content	+	+
Increasing oxygen content	-	+
Increasing available organic carbon	+	+
Increasing temperature	+	-
Decreasing pH	-	+
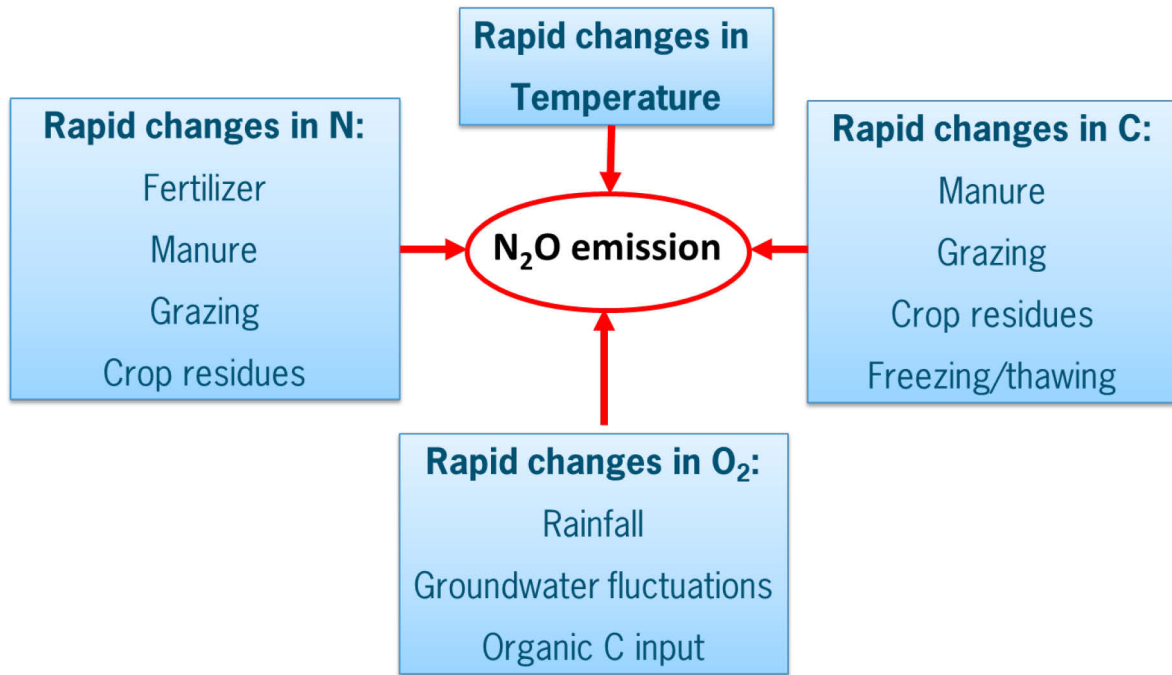
Figure 12 *Factors controlling N_2O emission from soils.*

3.2.1 Nitrogen type and concentration

Mineral or organic N fertilizer type affects N_2O in several ways, i.e.

- via the type of applied N (urea, NO_3^-, NH_4^+, and/or organic N) and the effects on nitrification and denitrification;
- via the presence of available carbon (stimulates denitrification and oxygen consumption in the soil);
- via the addition of other compounds (nutrients, metals, lime, water) affecting biological, chemical and physical soil processes, including pH and salt concentration (EC), and
- via the application technique (soil compaction, placement/concentration of N and C in the soil).

Emissions of N_2O from N fertilizer types are shown in the following Chapter. The rate of denitrification increases with increasing nitrate content. The portion of N_2O that is released during denitrification (relative to N_2) increases with increasing nitrate concentration (Table 5).

Emission factors used in the monitoring of N_2O emission (% N applied) assume that there is a linear relationship between N application rate and N_2O emission. However, as demonstrated in the examples in Figures 13 and 14, this is not always the case. In these experiments, the emission factors increased with increasing N application rate. This non-linear response of N_2O emission to N application rate is not accounted for in the IPCC guidelines or the protocol for the Netherlands.
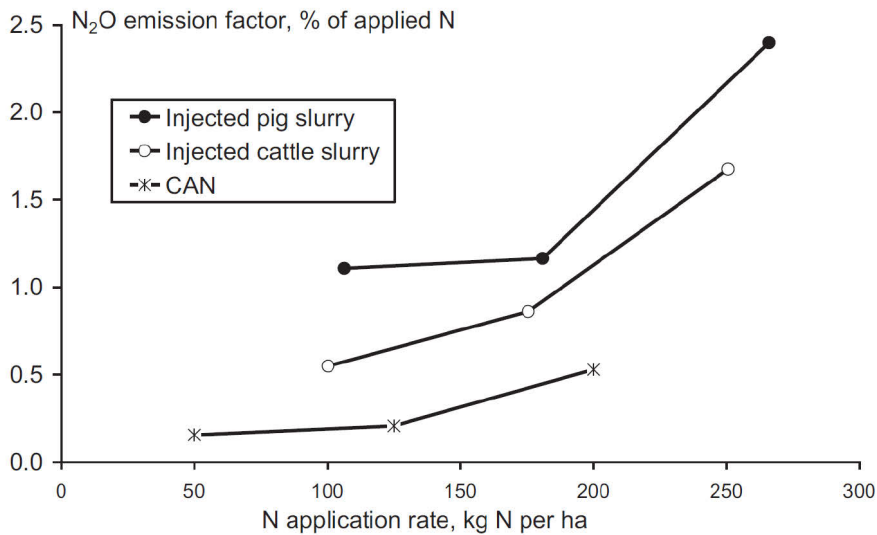
Figure 13 *Relation between the N application rate of injected pig and cattle slurries and calcium ammonium nitrate (CAN) application and the N$_2$O emission factor for maize on a sandy soil (Velthof and Mosquera, 2011b).*
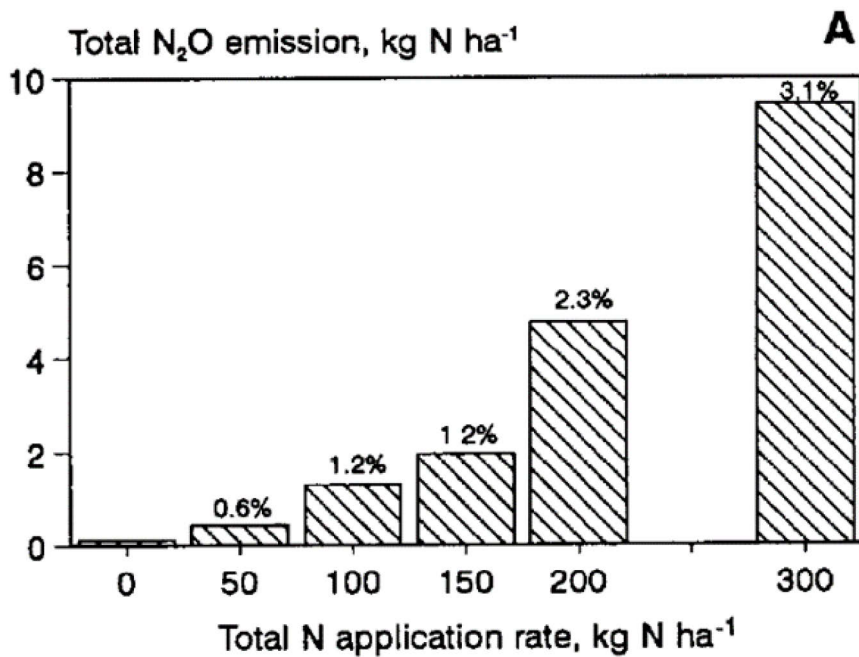
Figure 14 *Relation between the N application rate of calcium ammonium nitrate and the N$_2$O emission factor for grassland on a sandy soil (Velthof et al., 1996). The percentages near the bars indicate the emission factor.*

3.2.2 Carbon/organic matter

Easily degradable organic matter is an energy source for denitrification. Therefore, the presence of organic matter in soil and the application of organic matter via manure or crop residues affects denitrification and N$_2$O emission.

Potential denitrification rates (i.e. denitrification measured in soil with an excess of nitrate during incubation under anaerobic conditions at 20 °C) are highest in soils and soil layers with the highest organic matter content, i.e., higher in peat soils than in mineral soils, higher on grassland than on arable land (Velthof, 2003), and higher in top soil layers than in deep soil layers (Table 6).

Table 6   *Potential denitrification rates in Dutch soils (Assinck et al., 2005).*

| | Average potential denitrification, mg N kg^{-1} d^{-1} | | | | | |
| | Grassland | | | | Maize land | |
Layer, cm	Peat	Clay	Loam	Sand	Loam	Sand
0 – 20	267	151	65	26	20	11
20 - 40	317	125	30	4	9	4
40 - 60	116	5	1	0.1	1	0.1
60 - 80	61	0.9	0.3	0.5	0.3	0
80 - 100	39	0.6	0.2	0.2	0.1	0

3.2.3   Moisture content and aeration

Figure 15 schematically shows that during nitrification and denitrification the highest N_2O production occurs under intermediate soil moisture conditions (about 60% water-filled pore space). The N_2O emission is low during dry and extremely wet conditions (saturated soil).

Rainfall or irrigation can increase N_2O emission for a short period (several hours), as shown in Figure 16. This risk is highest just after N fertilizer application. The higher the mineral N content in the soil, the larger the risk that rainfall will increase N_2O emission.
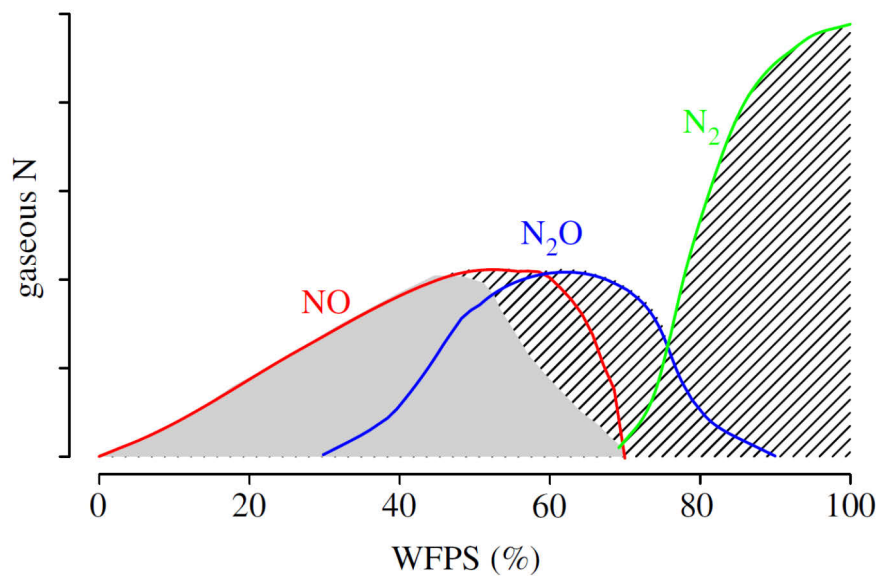
Figure 15   *Proposed relative contributions of nitrification (solid grey shading) and denitrification (hatched shading) to gaseous N emissions as a function of water-filled pore space (WFPS). (Pilegaard, 2013).*
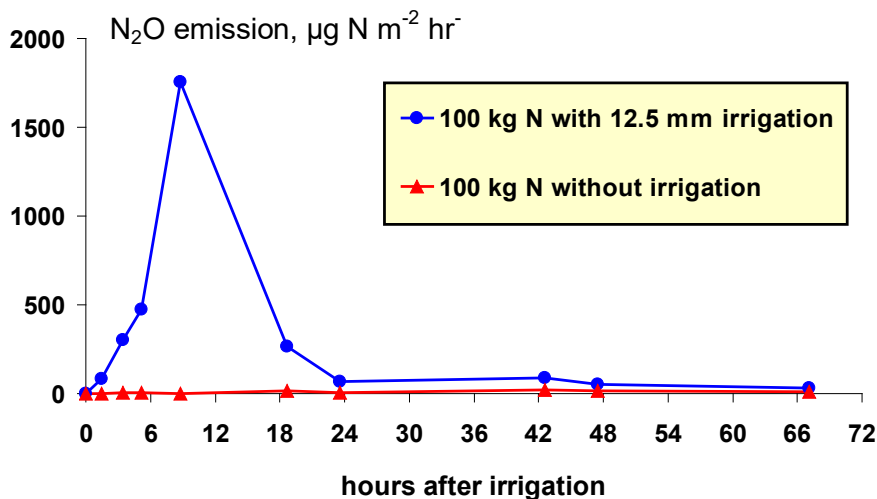
Figure 16   *Emission of N₂O from grassland after application of 100 kg N per ha as calcium ammonium nitrate with and without 12.5 mm irrigation water (Van der Bolt, unpublished results).*

3.2.4   Temperature

Denitrification rate increases with increasing temperature. The portion of intermediate N₂O relative to N₂ that is released during denitrification decreases with increasing temperature (Table 5). Significant N₂O emissions may occur at low temperature.

During cycles of freezing and thawing a significant amount of N₂O may be released (Kaiser *et al.*, 1998). The mechanism governing this is not yet clear, but it may be related to an increase in accessibility of organic matter (Christensen and Christensen, 1991).

3.2.5   pH

The rate of chemical reduction of N₂O to N₂ in soil is slower at low soil pH (Granli & Bøckman, 1994; Liu *et al.*, 2014). Therefore, liming can decrease N₂O emissions (Shaaban *et al.*, 2018). According to Eurofins Agro (soil laboratory in the Netherlands), approximately one in three maize fields feature a pH value below 5, which may be considered low if the guideline of pH 5.5 for sandy soils is observed.[5] Liming may improve yield and N uptake, as well as reducing N₂O emission.

3.2.6   Soil type and structure

Soil type and structure influence N₂O emission via different mechanisms involving O₂ concentration, available carbon, water and gas transport, and pH. These factors influence the rates of mineralisation, nitrification and denitrification, and the N₂O/N₂ ratio of the end products of nitrification and denitrification. Soil cultivation affects the aeration of the soil which in turn affects the rates of these N transformation processes and emission of N₂O. The effect of soil cultivation on N₂O emission (decrease or increase) will depend on the local conditions and are difficult to predict.

The N₂O emission from peat soils is much higher than that of mineral soils because the organic matter contents and groundwater levels (wet conditions) are much higher in peat soils than in sandy soils.

3.2.7   Interactions between factors

There are also many interactions between the factors that control N₂O emission. These interactions make the overall effect on N₂O emission difficult to predict. Models are mostly based on emission factors that are a highly simplified presentation of reality. Some process-based models predict N₂O emission, but the accuracy is uncertain if the environmental conditions for which the model is applied differs from the conditions for which the model has been parametrized. The model DNDC (DeNitrification DeComposition) is the most widely used model for N₂O (e.g. Gilhespy *et al.*, 2014).

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[5]   http://eurofins-agro.com/nl-nl/expertise/bemesting/artikelen/bekalken-het-voorjaar-zinvol-niet

4 Agricultural value of nitrogen fertilizers and manures

4.1 Nitrogen use efficiency of mineral fertilizer types

The results of several decades of research on efficiency of mineral N fertilizers in the Netherlands were summarized in a review paper by Van Burg *et al.* (1982).

The main conclusions with regard to the use efficiency of mineral N fertilizers applied to arable land were:
- The average N efficiency of urea in experiments was 0.90 – 0.95 compared to CAN. The N efficiency of urea was lowest on calcareous clay soils, most probably because of ammonia emission.
- The average N efficiency of urean (a solution of urea and ammonium nitrate) was similar to that of CAN.
- The variation in N efficiency of urea and urean was large. This was attributed to large variations in ammonia emissions from these fertilizers (high ammonia emission during dry weather conditions and low ammonia emission during wet weather conditions).

The main conclusions of Van Burg *et al.* (1982) with regard to the use efficiency of mineral N fertilizers applied to grassland were:
- The average N efficiency of ammonium sulphate compared to CAN was 0.90 on clay, 0.85 on peat, and 0.91 on sand.
- The differences in N efficiency between ammonium sulphate and CAN are dependent on weather conditions. Nitrate leaching from CAN reduces its efficiency under wet conditions whereas ammonium sulphate may cause burning of leaves during dry conditions.
- Repeated application of ammonium sulphate acidifies the soils which negatively affects the mineral composition of grass (lower magnesium and calcium contents) and the botanical composition of the sward (see Section 4.3).
- The average N efficiency of urea was much lower than that of CAN (0.75 – 0.85) and was attributed to ammonia emission from urea.
- The relative N efficiency of urea was higher than that of CAN during very wet conditions which was probably due to low ammonia emission from urea and elevated nitrate leaching from CAN.
- The efficiency of urean was less than that of CAN which also was attributed to ammonia emission. There was a large variation in effectiveness of urean due to the high impact of weather conditions on ammonia emission.

Bussink & Oenema (1996) examined the efficiency of urea and CAN applied to grassland in the Netherlands and parts of the UK (Northern Ireland and England). In the Netherlands, the apparent yield of grassland treated with urea was on average 92 and 86% of CAN on sand and clay soils, respectively. There were no differences observed between urea and CAN on peat soils. In England and N. Ireland, the apparent yield of grassland with urea was the same as CAN during the first grass cut, but 97% in N. Ireland and 91% in England for the second cut. It was concluded that rainfall strongly effected the agronomic N use efficiency of fertilizers and that differences between the three countries could be attributed to differences in rainfall. It was calculated that application of urea to grassland in the Netherlands was more economically profitable when rainfall exceeded 6 mm within three days following application at the first cut and 9.5 mm within three days following application at the second cut.

Den Boer *et al.* (2011) produced a review of mineral N fertilizers which was partly based on the paper by Van Burg *et al.* (1982). The authors concluded that:
- Fertilizers based on nitrate and ammonium have a higher efficiency than those based on ammonium and urea.
- The average efficiency of urea compared to CAN is 90% and of urea with an urease inhibitor, 95%.
- Fertilizers in solid form (prills or granules) have a higher yield and N uptake than liquid fertilizers.

- The efficiency of liquid urea based fertilizers, including urean, is lower than that of liquid ammonium nitrate.
- The efficiency of ammonium based fertilizers with an added nitrification inhibitor is higher than CAN at the first dressing in early spring. This is especially the case for wet conditions that promote nitrate leaching and denitrification of nitrate applied with CAN.

A series of field experiments were carried out in 2004 and 2005 in the UK during which the crop response to different mineral fertilizers was determined. The main conclusions of these field experiments were (Dampney *et al.*, 2006):
- Granular urea was commonly a less efficient source of N for winter cereal crop uptake than ammonia nitrate. This was most likely due to ammonia volatilisation. Use of granular urea in practice would justify around 20% higher N application rates to achieve the same cereal crop yield and quality.
- Differences in early spring between urean and ammonia nitrate applied to silage crops were small. This was probably due to significant rainfall just after N application.
- Liquid urean was a less efficient source of fertilizer-N for winter cereals than granular urea. Use in practice would justify around 30% higher N application rates.
- Addition of urease inhibitor (nBTPT, trade name Agrotain) appeared to improve the efficiency of urea based fertilizers.

Bhogal *et al.* (2003) summarized the main results of experiments carried out in the UK before 2000 and obtained similar results to Dampney (2006), i.e., there is a variable and on average lower N efficiency for urea and urean compared to CAN.

Forestal *et al.* (2017) reported that there was a tendency that grassland yields in Ireland were slightly higher when urea was applied in spring compared with CAN (103.5% of CAN yield) and that summer yields following urea application were slightly lower than CAN (98.4% of CAN yield). There was no significant difference in annual grassland yield when CAN, urea and urea + NBPT were used throughout the growing season. The N offtake was higher for CAN and urea + NBPT than for urea alone in three of the five experiments (Table 7). This was attributed to a higher ammonia emission from urea.

Table 7   *The main effects of fertilizer type on N offtake (kg N per ha per yr) averaged across N rates and harvest dates (Forestal et al., 2017).*

Fertilizer type	Location and year				
	Johnstown Castle 2013	Moorepark 2013	Johnstown Castle 2014	Moorepark 2013	Hillsborough 2014
CAN	58.9 a[a]	76.9 a	62.7 a	78.9	54.9
Urea	53.5 b	74.2 b	56.7 b	76.4	53.0
Urea + NBPT	57.0 a	77.3 a	62.2 a	79.6	55.6
Standard error of mean	1.93	1.16	1.67	1.82	1.07

[a] N offtake values with different letters within columns are significantly different according to F-protected L.S.D. test ($P \leq 0.05$).

Van Geel *et al.* (2011) presents a desk study on N fertilization strategies for potatoes. The paper summarises the results of different studies on the effect of N fertilizer types:
- Liquid fertilizers showed no higher efficiency than solid fertilizers in general. Liquid fertilizer may have a slightly higher N efficiency under dry conditions where irrigation is not possible.
- Cultan (Controlled uptake long-term ammonium nutrition; urea and ammonium sulphate solution) application did not result in higher yields than CAN.
- Potato yields were on average higher with CAN application than with urean or urean with an added urease inhibitor.

Postma *et al.* (2009) carried out field experiments with potatoes showing that, on average, the yields obtained with new types of fertilizer (including ammonium fertilizer with nitrification

inhibitor, liquid urea based fertilizer, and slow release fertilizer) and new fertilization strategies were similar to that of CAN (yield differences of 1-2%).

4.2 Nitrogen use efficiency of manures

The N use efficiency of manure is on average lower than that of mineral fertilizers. This is mainly because a part of the N in manure is present as organic N and because of the ammonia emission from manure. Only part of the organic N will be mineralised during the growing season to mineral N available for plant uptake. In addition, organic N will be mineralised in the years following application. Therefore, the N use efficiency of manure will improve with time. Ammonia emission starts immediately after manure application and will continue for a few days. Losses of ammonia from manure range from 3% of the mineral N in slurry injected deep into soil to more than 70% for broadcast slurry (Table 8).

The relative N use efficiency of cattle slurry to CAN applied to grassland in the Netherlands with a low ammonia emission application technique is about 50 to 60% (1st year) and 80% (long-term) (Schröder *et al.*, 2008; CBGV, 2017). The values for arable land are somewhat lower because the N uptake period of arable crops is shorter than that of grassland. The N efficiency of pig slurry is somewhat higher than that of cattle slurry because the mineral N fraction of total N is higher in pig slurry than in cattle slurry. The review of Webb *et al.* (2013) examining relative N efficiency of manures in the EU shows low values for some countries (less than 50%). This is because manures are broadcast in many countries and the N efficiency of broadcast manures is much smaller than that of injected or incorporated manure (Huijsmans *et al.*, 2015).

Table 8 *Emission factors for ammonia with manure application used for calculation of ammonia emission in the Netherlands, in % of ammoniacal nitrogen (Van Bruggen et al., 2017).*

Grassland	
sod injector (in trenches in the soil)	19.0
slurry tanker (partly in trenches in the soil and partly on the soil)	22.5
spreader (in strips on the soil)	26.0
Above ground	74.0

Arable land	
manure injection	2.0
sod injector (in trenches in the soil)	24.0
slurry tanker (partly in trenches in the soil and partly on the soil)	30.0
spreader (in strips on the soil)	36.0
incorporated in 1 operation	22.0
incorporated in 2 operations	46.0
above ground manure and sewage sludge	69.0

4.3 Acidification

Transformations of N are an important source and sink of hydrogen ions or protons (Table 9). Acidification (generation of protons) reduces the fertility of the soil (decreases the availability of nutrients such as phosphorus, calcium, magnesium and molybdenum), affects microbial transformations in the soil, and causes the release of toxic compounds including aluminium and manganese (e.g. Bolan *et al.*, 2003). This may cause a depression of crop growth and yields. Low soil pH promotes the production of N_2O during nitrification and denitrification (Section 3.2.5).

Ammonium based fertilisers acidify soils as a result of a combination of nitrification, ammonium uptake by plants, and/or ammonia volatilization (Table 9). Nitrate based fertilizers increase the pH of

soils due to a combination of nitrate uptake by plants and/or denitrification. In addition to the type of N fertiliser, soil acidification is dependent on crop type, soil type, weather conditions (leaching) and other N sources (Bolan *et al.*, 2003). The acidifying effect of fertilizers applied to agricultural soils can be estimated from their chemical composition in combination with a quantification of the nitrogen cycle in the agricultural system under consideration. In the Netherlands, the acidifying effect of fertilizers is estimated using an ionic balance equation referred to as the 'Pierre-Sluijsmans equation' (Harmsen *et al.*, 1990). Table 10 shows the acidifying effects of several N fertilizers. Manures contain high ammonium concentrations which have an acidifying effect either through uptake or nitrification. Organic N in manure leads to alkalinisation if it is mineralized. The total effect of manure on acidification depends on rates of inputs and uptake of cations and anions by the crop, specifically NH_4 and NO_3, and the rate of denitrification affecting nitrate leaching.

Liming is used to decrease soil acidification and to optimize plant growth in carbonate free soils. The major sources of lime used in agriculture are limestone ($CaCO_3$) and dolomite ($CaMgCO_3$). However, other compounds may also reduce soil acidification (burned lime, rock phosphate, sugar beet pulp). Dissolution of lime in soils leads to dissolution of carbonates and release of CO_2. Countries are obliged to report the CO_2 emission of limestone and dolomite used in agriculture in annual inventories delivered to the UNFCCC. The method used in the Netherlands is described by Vonk *et al.* (2018). Lime use in agriculture produces relatively small amounts of CO_2, much smaller than the N_2O emission from agriculture, for example.

Table 9 *Generation (acidification) and consumption (alkalinisation) of protons (H^+) during the N transformation processes (Velthof et al., 2011).*

Process	Reaction[1]	H^+, mol/mol N
Biological N-fixation	$4ROH + 2N_2 + 3CH_2O \rightarrow 4RNH_2 + 3CO_2 + H_2O$	0
Mineralization of organic N	$RNH_2 + H_2O + H^+ \rightarrow ROH + NH_4^+$	-1
Urea hydrolysis	$(NH_2)_2CO + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2$	-1
Nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$	+2
Ammonium assimilation	$ROH + NH_4^+ \rightarrow RNH_2 + H_2O + H^+$	+1
Nitrate assimilation	$ROH + NO_3^- + H^+ + 2CH_2O \rightarrow RNH_2 + 2CO_2 + 2H_2O$	-1
Ammonia volatilization	$NH_4^+ \rightarrow NH_3 + H^+$	+1
Denitrification	$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$	-1

[1] R = in the reaction mean organic C compounds.

Table 10 *Effect of fertilizer type on soil pH, expressed in base equivalent in kg CaO per 100 kg fertilizer (NMI, 2000). Negative values indicate acidification and positive values alkalinisation of the soil.*

Fertilizer type	kg CaO per 100 kg fertilizer	
	Arable land	Grassland
Ammonium sulphate	-63	-59
Ammonium nitrate	-33	-26
Calcium ammonium nitrate	-15	-10
Magnesamon	-2	3
NP fertilizers	-25 to -40[*]	
Potassium nitrate	11	14
Urea	-46	-37
Urean	-30	-24

[*] depending on the composition of the fertilizer

4.4 Conclusions

- Fertilizers based on nitrate and ammonium have, on average, a higher N efficiency than ammonium and urea fertilizers. The average efficiency of urea and urea with a urease inhibitor is 90% and 95% of CAN, respectively.
- Application of fertilizers in solid form (prills or granules) result in a higher yield and N uptake than application of liquid fertilizers.
- The higher N use of efficiency of CAN compared to urea and urean is due to higher ammonia emission from urea and urean. The differences are smallest during wet conditions (low risk of ammonia emission). The N efficiency of urea is higher than that of CAN in wet conditions in early spring. This is probably due to a low ammonia emission from urea and elevated nitrate leaching from CAN during these wet conditions.
- The N use efficiency of manure is on average lower than that of mineral fertilizers. This is mainly because a part of the N in manure is present as organic N and because of the ammonia emission from manure. Only part of the organic N will be mineralised during the growing season to mineral N available for plant uptake. In addition, organic N will be mineralised in the years following application. Therefore, the N use efficiency of manure will improve with time. Application of manure with a low ammonia emission application technique increases the N use efficiency relative to broadcasting of manure.
- Repeated application of ammonium fertilizer acidifies soil more strongly than ammonium nitrate fertilizer application. Acidification negatively affects the mineral composition of grass (lower magnesium and calcium contents) and the botanical composition of the sward. Liming is required to maintain the soil pH in this case.

5 Effects of mineral fertilizers and manures on nitrous oxide emission

5.1 Studies with different fertilizer types in the Netherlands

5.1.1 Field experiments

Velthof *et al.* (1997) compared the effects of different fertilizers and manures following their application to grassland in three experiments in the Netherlands (Table 11). Emissions were very low following applications on grassland with clay soil (< 0.1%). However, the two experiments on sandy soil were carried out under extremely wet conditions as there was heavy rainfall in the days after application in both cases. It was clear that the N_2O emission from the nitrate containing fertilizers, CAN and calcium nitrate, were much higher than that from ammonium sulphate, urea and cattle slurry. Measurements of denitrification showed that the high N_2O emission from the nitrate based fertilizers was due to denitrification (Table 11). The amount of nitrate added with calcium nitrate was twice that of CAN, but the difference in N_2O emission factor was less than a factor 2 between these fertilizers. More specifically, in one experiment there was no effect and in the other experiment a factor 1.4 difference was calculated.

Table 11 *Emission of N_2O and total N losses by denitrification from grassland (in % of applied N) after application of different types of fertilizers or manure (at 80 kg N per ha) in three experiments lasting about three weeks (Velthof et al., 1997).*

Fertilizer	Clay soil, 13 mm rain; 6.0 ºC	Sandy soil 42 mm rain; 8.2 ºC		Sandy soil 68 mm rain; 16.0 ºC	
	N_2O	N_2O	Denitrification	N_2O	Denitrification
Calcium ammonium nitrate	< 0.1	5.2	14.1	8.3	8.3
Calcium nitrate	< 0.1	5.2	12.4	12.0	10.5
Ammonium sulphate	< 0.1	0.2	0.6	1.0	0.0
Ammonium sulphate + nitrification inhibitor DCD	-	<0.1	0.2	0.1	0.0
Urea	< 0.1	< 0.1	1.1	0.7	1.9
Cattle slurry; surface-applied	-	< 0.1	0.4	< 0.1	0.4
Cattle slurry; injected	-	0.1	0.0	< 0.1	0.0

The N_2O emission from CAN was compared with cattle slurry (grassland) and pig slurry (maize fields) in field experiments carried out by Velthof and Mosquera (2011b). The main results (Table 12) are:
- The N_2O emission was higher for CAN than for cattle slurry on grassland. This suggests that the presence of nitrate in CAN was an important factor controlling N_2O emission from grassland.
- The N_2O emission from CAN was lower than from pig slurry on maize fields. This suggests that the presence of nitrate in CAN was not a dominating factor controlling N_2O emission on arable land. The much higher N_2O emission from pig slurry on maize fields was most probably due to the addition of available carbon to the slurry. Carbon is an energy source for denitrifying bacteria; see Section 3.2.2. Van Groenigen *et al.* (2004) also found a higher N_2O emission from cattle slurry than from CAN applied to maize fields in the Netherlands which was attributed to the effect of carbon addition to the soil with cattle slurry.
- Injection of slurry increased N_2O emission which was most likely due to a combination of two factors: injection reduces ammonia emission so that more mineral N remains in the soil, and oxygen concentrations near soil where slurry is injected is lower than concentrations near surface applied slurry.

Table 12 *Average N$_2$O emission factors, % of N applied (Velthof and Mosquera, 2011b).*

Object	N$_2$O emission factor, % of N		
	Grassland clay soil	Grassland sandy soil	Maize fields sandy soil
CAN	2.2	1.2	0.1
Cattle slurry; shallow injection	0.3	0.5	0.9
Cattle slurry; surface applied	0.1	0.1	0.4
CAN + injected cattle slurry	0.8	1.0	*
Pig slurry; injected	*	*	3.6
Pig slurry; surface applied	*	*	0.9

Figure 17 shows the pattern of N$_2$O emission on grassland and maize fields. On maize fields there is one peak of N$_2$O per year just after N application which can last several weeks. The magnitude and length of the peak is affected by rainfall. This can be seen when the three years in Figure 17 are compared. The same amount of N was applied during each year, but emissions were much higher in the relatively wet summer of 2007 than in the drier years of 2008 and 2009. On grassland, the peaks are much shorter, i.e., from several days to 2-3 weeks, and there are more peaks in single years. This is due to the multiple N dressings causing several peaks of N2O within years, and the rapid N uptake by grass and/or N immobilization in grassland soil indicated by narrow peaks of N2O after N application. The period during which mineral N content in the soil is elevated after N application, when the risk on N2O emission is highest, is much shorter on grassland than on maize fields. Clearly, only a few peaks of N2O emission during single years occur on grassland and maize fields (and other arable crops). These are observed during wet periods in the first weeks after N application. Mitigation strategies should focus on these periods where the risk of N$_2$O emission is highest.
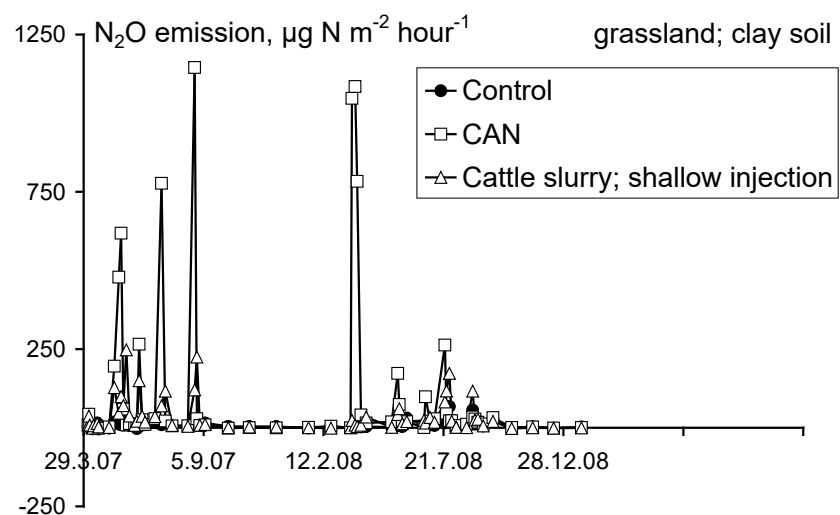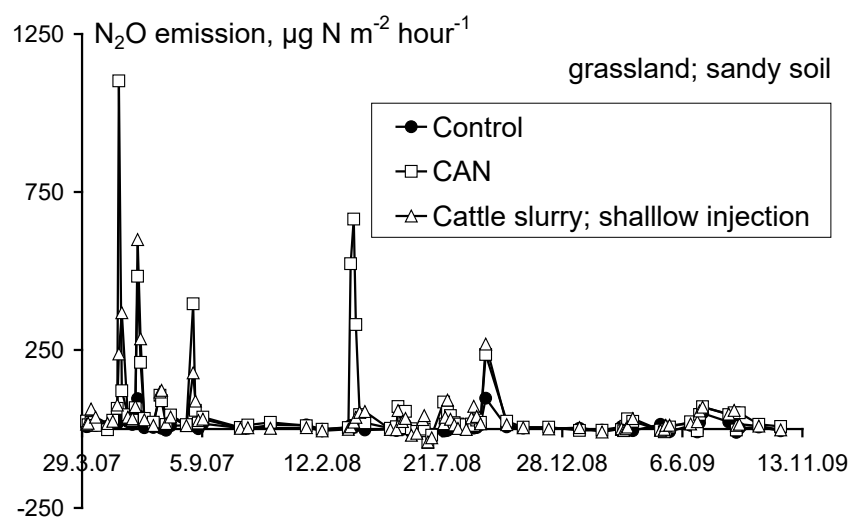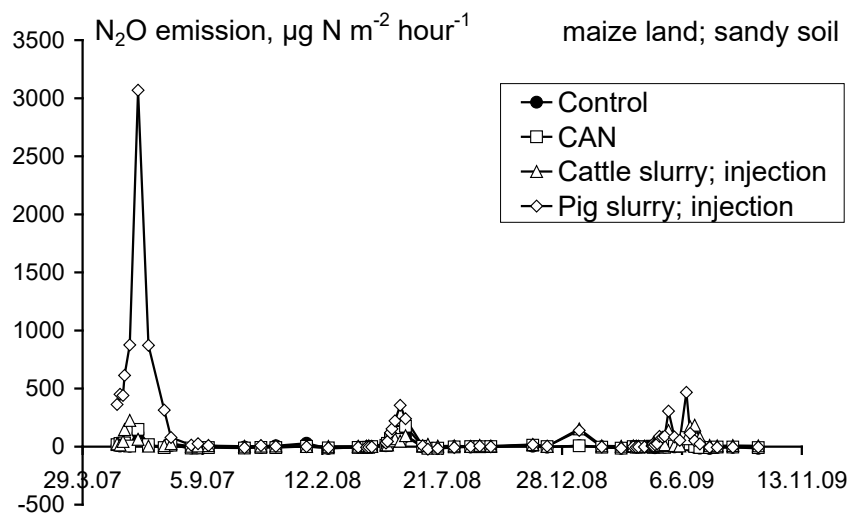
Figure 17 *Fluxes of N₂O from unfertilized control, CAN, and (shallow) injected slurry on maize fields on sand (upper figure), grassland on sand (middle figure) and clay soil (lower figure); Velthof and Mosquera, 2011b.*

5.1.2   Laboratory experiments

The results of an incubation experiment where identical conditions were applied in each treatment showed very large differences between manure types (Figure 18). Emission of N_2O was highest after application of slurry from fattening pigs and sows. Animal manures are a mixture of mineral N, salts, water, and easily mineralizable and resistant organic N and C compounds. There are large differences in composition between animal manures due to differences in animal species and nutrition. These differences in composition result in large differences in N_2O emission. In general, the degradability of organic C in pig slurry is higher than that of cattle slurry and poultry manure. This is probably a major cause of the higher N_2O emission from pig slurries.
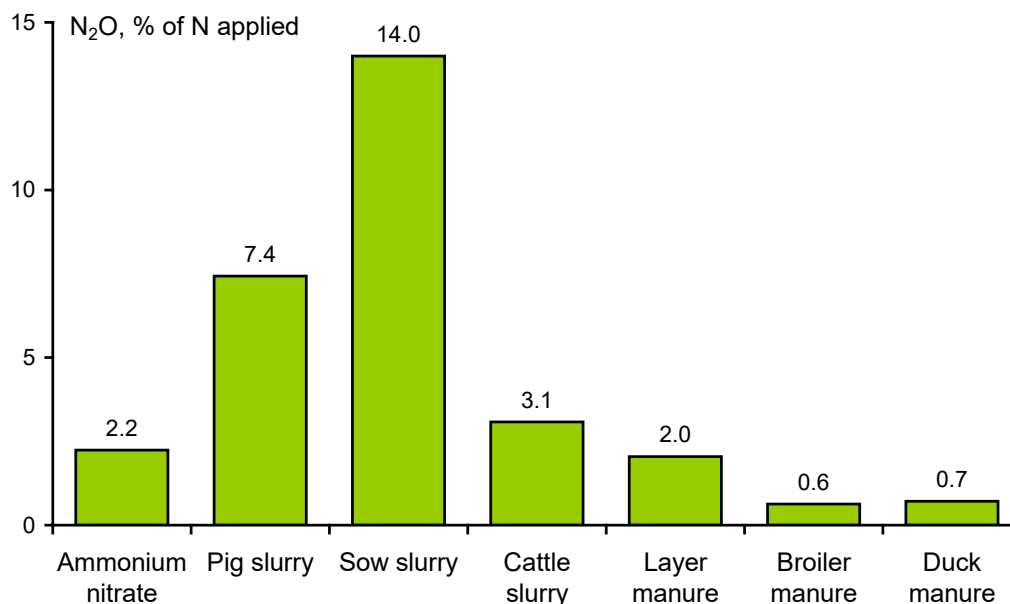
Figure 18   *Emission of N_2O from ammonium nitrate and several manure types in an incubation experiment by Velthof et al. (2003).*

Velthof and Hummelink (2011) carried out several incubation experiments under controlled conditions. These types of study give a good insight into processes and controlling factors, but cannot be directly translated to the field because of differing conditions, e.g., crop presence. The experiments were carried out at 20 °C and at field capacity. Field capacity is defined as the soil moisture content after excess water has percolated into deeper soil layers following rainfall.

CAN showed higher N_2O emission than urea, urean and pig slurry for sand and peat, and lower N_2O emission for clay on grassland soils (Figure 19). This reveals the complexity of predicting N_2O emissions resulting from the many factors that play a role in controlling N_2O emissions.

Incorporation of fertilizers and manures increased the emission of N_2O in all cases except for urean (Figure 20). This is because oxygen concentration is lower in the soil than on the soil surface. Moreover, ammonia emission is higher from surface applied manures and mineral N content in soil is lower after surface application in comparison with incorporation methods. The N_2O emission of CAN was lowest on arable soil indicating that denitrification was a less important source of N_2O than nitrification under these experimental conditions and/or that available C was limiting denitrification in this experiment. The higher N_2O emission from urea, urean and mineral concentrate may be related to inhibition of nitrification resulting from high ammonia concentration. Ammonia toxicity inhibits the oxidation of nitrite to nitrate during nitrification resulting in an accumulation of nitrite and potential N_2O production (see also Section 3.1.2.2 Chemical denitrification in the previous Chapter).
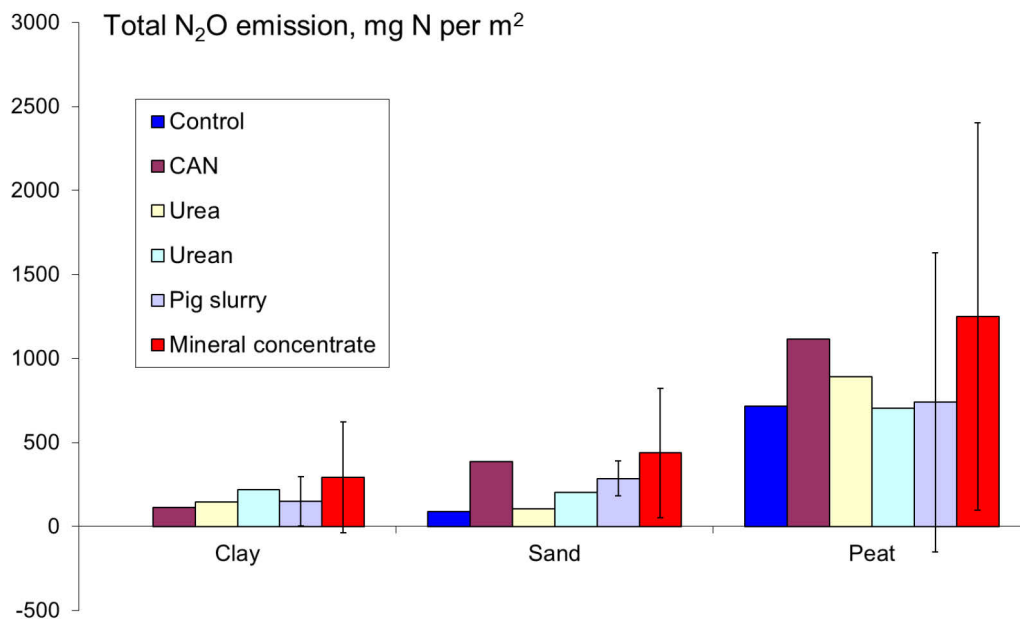
Figure 19   *Total N₂O emission from surface applied CAN, urea, urean, injected pig slurry, and injected mineral concentrate of the liquid fraction of pig slurry, after application to grass sward on clay, sand, and peat soil in a pot experiment under controlled conditions. The results from pig slurry and mineral concentrates are the average ± standard deviation of four manure treatment installations (Velthof and Hummelink, 2011).*
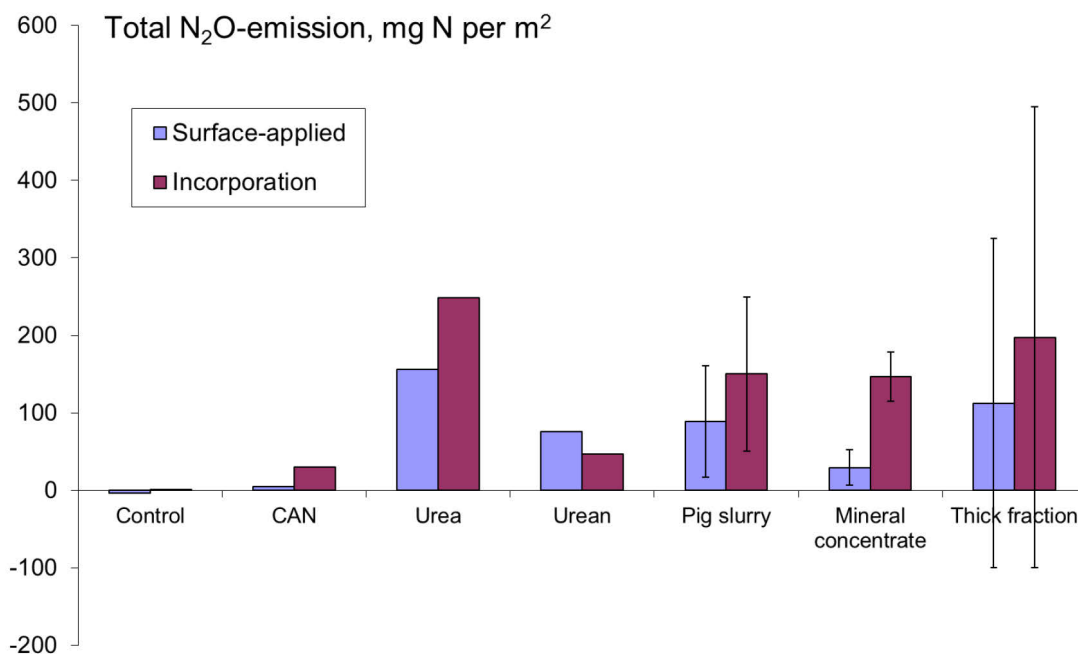
Figure 20   *Total N₂O emission from CAN, urea, urean, pig slurry, mineral concentrate of the liquid fraction of pig slurry, and the thick fraction of pig slurry after both surface application and incorporation to arable sandy soil in an incubation study under controlled conditions. The results from pig slurry, mineral concentrates, and thick fraction are the average ± standard deviation of four manure treatment installations (Velthof and Hummelink, 2011).*

5.2 Studies outside the Netherlands

A literature study was carried by Velthof and Mosquera (2011a) to summarize the results of studies performed outside the Netherlands. The study focused on experiments in which emission factors of CAN and livestock manure were derived and included the effects of application technique. Urea was not included in this review study.

Table 13 presents a summary of the results of the literature study. The average emission factor for CAN on grassland was 0.7 ± 0.2% and on arable land 0.7 ± 0.3%. Remarkably, the emission factor of ammonium nitrate was much higher than that of CAN (2.3% on grassland and 2.1% on arable land). The exact reason for this is not clear. It may suggest that the liming effect of CAN has decreased N_2O emission. It is known that N_2O emissions are relatively high when conditions are acidic (e.g. Russenes *et al.*, 2016). However, the limited number of studies in which CAN was tested restricts our ability to come to firm conclusions. Currently, no studies exist where ammonium nitrate and CAN are tested together. The average emission factor for manures on grassland was 0.8 ± 0.4% and that of arable land 0.6 ± 0.1%.

Velthof and Mosquera (2011a) summarized the results of studies carried out outside the Netherlands in which N_2O emission factors of different fertilizers and manures were derived in the same experiment (Table 14). This gives a better indication of the difference in N_2O emission between fertilizers because conditions are controlled. Emission of N_2O from CAN was clearly higher than from cattle manure in three studies on grassland, lower than ammonium fertilizer in two studies and similar to cattle manure in one experiment. The three studies in which higher emissions were found for nitrate fertilizers were all carried out in the UK (Egginton & Smith, 1986; Clayton *et al.*, 1997).

Table 13 *Summary of N_2O-N emission factors (in % of N) derived from literature excluding studies from the Netherlands (Velthof and Mosquera, 2011a).* [6]

Fertilizer	Grassland			Arable land		
	average	se.	n	average	se.	n
Manures	**0.8**	**0.4**	**19**	**0.6**	**0.1**	**24**
Cattle manure	0.3	0.1	13	0.4	0.1	14
Pig manure	0.3	0.1	4	0.8	0.2	7
Mineral fertilizers	**1.9**	**0.3**	**81**	**1.9**	**0.4**	**59**
Ammonium fertilizers	0.3	0.1	12	2.2	1.7	2
Ammonium nitrate	2.3	0.3	42	2.1	0.4	48
Calcium ammonium nitrate	0.7	0.2	7	0.7	0.3	7
Calcium, sodium of potassium nitrate	2.3	0.9	20	1.4	0.9	2

Roche *et al.* (2016) found no significant differences in N_2O emissions between CAN and urea in a field study under spring barley in Ireland. Adding a nitrification inhibitor reduced N_2O emission from urea, but an urease inhibitor did not reduce N_2O emissions relative to CAN.

A study by Harty *et al.* (2016) in Ireland evaluated the impact of switching fertilizer formulation from CAN to urea based products on grassland (urea, urea + urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT), and urea + nitrification inhibitor dicyandiamide; DCD). The results showed that N_2O emissions were highest for CAN, also when the indirect N_2O emission from ammonia was

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[6] References: Abbasi and Adams (2000); Ambus *et al.* (2001); Anger *et al.* (2003); Arah *et al.* (1991); Ball *et al.* (2000); Burford *et al.* (1981); Chadwick *et al.* (2000); Christensen (1983), Clayton *et al.* (1994); Clayton *et al.* (1997); Clemens *et al.* (1997); Colbourn and Harper (1987); Colbourn *et al.* (1984); Conrad *et al.* (1983); Dobbie and Smith (2003a); Dobbie *et al.* (1999); Eggington and Smith (1986); Ellis *et al.* (1998); Glatzel and Stahr (2001); Goossens *et al.* (2001); Hénault *et al.* (1998a); Jambert *et al.* (1997); Jørgensen *et al.* (1997); Kaiser *et al.* (1996); Kaiser *et al.* (1998b); Kamp *et al.* (1998); McTaggart *et al.* (1997); Misselbrook *et al.* (1998); Mogge *et al.* (1999); Petersen (1999); Rodhe *et al.* (2006); Ryden (1981); Seiler and Conrad (1981); Skiba *et al.* (1992); Skiba *et al.* (1998); Slemr *et al.* (1984); Smith *et al.* (1998a, b); Van Cleemput *et al.* (1994); Webster and Dowdell (1982); Weslien *et al.* (1998); Wulf *et al.* (2002); Yamulki and Jarvis (2002); Yamulki *et al.*(1995).

accounted for (Figure 21). The authors concluded that switching from CAN to stabilised urea formulations was found to be an effective strategy to reduce N_2O emissions, particularly in wet, temperate grassland. This is in agreement with Velthof et al. (1997), Clayton et al. (1997), Dobbie and Smith (2003), Jones et al. (2007) and Smith et al. (2012). From a review of UK studies, Smith et al. (2012) concluded that there was some evidence of lower N_2O emissions from urea than from ammonium nitrate or CAN. This is due to high N_2O emissions from grassland when nitrate based fertilizers are applied during wet conditions. Nitrous oxide emission is lower for CAN and higher for urea than for nitrate based fertilizers during drier conditions.

Table 14 *Results of studies in which different fertilizers and manure were applied, excluding studies from the Netherlands (Velthof and Mosquera, 2011a).*

Land-use	Reference	N type	Application rate, kg N/ha	N_2O-N emission factor, % of N		n
				average	se.	
Grassland	Ellis et al. (1998)	Cattle manure	45	0.1		1
		Ammonium nitrate	60	0.1		1
	Egginton & Smith (1986)	Cattle manure	298-1230	0.3	0.2	2
		Nitrate	100-400	3.6	3.3	2
	Egginton & Smith (1986)	Cattle manure	700	0.5		1
		Nitrate	700	1.9		1
	Clayton et al. (1997)	Ammonium	360	0.3	0.1	2
		Ammonium nitrate	360	0.8	0.4	2
		Nitrate	360	0.8	0.4	2
	Conrad et al. (1983)	Ammonium	100	0.2	0.1	8
		Nitrate	100	0	0	5
	Seiler & Conrad (1981)	Ammonium	100	0.5	0.2	2
		Nitrate	100	0.3	0.2	2
Arable land	Clemens et al. (1997)	Cattle manure	56	0.7	0.1	3
		Calcium ammonium nitrate	56	0.3	0.2	4
	Petersen (1999)	Cattle and pig manure	152	0.6		1
		Calcium ammonium nitrate	100	0.6		1
	Henault et al. (1998a)	Ammonium	170	0.6		1
		Ammonium nitrate	170	0.9	0.3	2
		Nitrate	170	0.4		1

Measurements in the UK by Bell et al. (2015) showed a much higher N_2O emission from arable cropping systems at a wet Scottish site than at drier English sites (Figure 22). Climate and soil mineral N influenced N_2O emissions from arable land. There was no significant difference in N_2O emission factor between urea and ammonium nitrate on arable land. Application of ammonium nitrate in more frequent smaller doses reduced emissions at all sites compared to one larger nitrogen application. Adding a nitrification inhibitor to ammonium nitrate significantly reduced N_2O emission from these arable soils.

A study on winter wheat in northwest Germany by Lebener et al. (2014) concluded that nitrification was the predominant process for N_2O production under mainly dry conditions. Under these conditions, urea and ammonium sulphate caused higher N_2O emissions during the growth period compared to CAN. The emission factors based on one year for the three sites examined in this study were:
• Site 1: 0.51% urea, 0.32% ammonium sulphate and 0.23% CAN
• Site 2: 0.32% urea, 0.94% ammonium sulphate and 0.05% CAN
• Site 3: 0.34% urea, 0.38% ammonium sulphate and 0.37% CAN
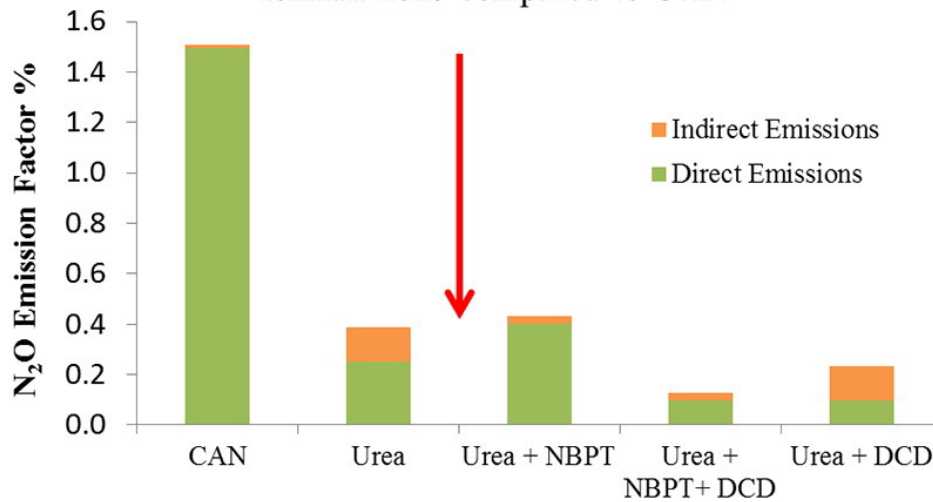
Figure 21 *Emission factors of N$_2$O from CAN, urea and urea with NBPT and/or DCD applied to grassland in Ireland (Harty et al., 2016).*
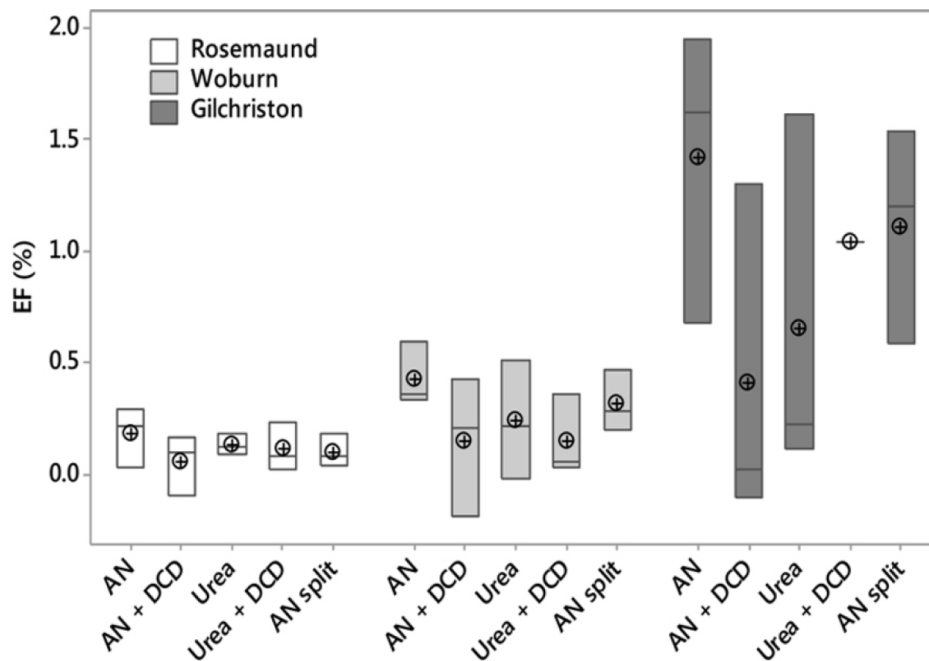
Figure 22 *Emission factors of N$_2$O from ammonium nitrate (AN) and urea for arable cropping systems at three sites in the UK (Gilchriston in Scotland and two sites in England). AN and urea were also applied with the nitrification inhibitor DCD. The AN split indicates more frequent N application in smaller dressings (Belle, 2015).*

5.3 Synthesis

Statistical analyses on measurements of N$_2$O emissions from the global database (Bouwman, 1996; Stehfest and Bouwman, 2006) showed no significant effect of fertilizer type on N$_2$O emission. However, several studies in which different mineral fertilizers are compared in one experiment often show large differences between fertilizers (see previous paragraphs). Incubation studies show that differences in N$_2$O emission between nitrate and ammonium based fertilizer are due to the soil

moisture content (e.g. Pathak and Nedwell, 2001). The N_2O emission from nitrate containing fertilizers is higher than from ammonium based fertilizers under wet conditions.

Studies on grassland soils point at higher N_2O emissions from nitrate based fertilizers than from fertilizers that only contain ammonium, especially under wet conditions. The N_2O emission from nitrate based fertilizer applied to grassland is also higher than from cattle slurries. It is clear that the denitrification capacity of grassland is high because of the large amount of easily degradable organic matter contents available at these sites. Adding nitrate to grassland during wet conditions or before rainfall events will increase the risk of high N_2O emission.

Studies on arable soils point at similar or lower N_2O emission from nitrate based fertilizers than urea and ammonium based fertilizers, especially under relatively dry conditions. The denitrification capacity of arable land is low because of the low easily degradable organic matter content at these sites. Urea may increase N_2O emission during relatively dry conditions because of the ammonia toxicity of nitrifying bacteria which leads to nitrite accumulation. Application of livestock slurry increases the denitrification capacity of arable land. The emission of N_2O from arable land is often higher for livestock slurry than for CAN.

6 Mitigation of nitrous oxide emission from fertilizers and manures

6.1 Nitrification inhibitors

6.1.1 Types of nitrification inhibitor

Nitrification inhibitors inhibit the transformation of ammonium to nitrite by *Nitrosomonas* bacteria and thereby the production of N_2O during nitrification (Figure 8). In addition, N_2O production through denitrification of nitrate released during nitrification is also reduced when nitrification is inhibited.

Table 15 presents an overview of the nitrification inhibitors mentioned in literature. There are three important brands of nitrification inhibitors (Slangen and Kerkhoff, 1984; Chien *et al.*, 2009; Trenkel, 2010; Kumar *et al.*, 2015):
- 'ENTEC' inhibitors from BASF using 3,4-dimethyl pyrazole phosphate (DMPP) (Zerulla *et al.*, 2001)(http://entecfertilizers.com.au/). Using the trade name 'Vizura', this inhibitor is sold as an additive for animal manure.
- 'N-serve' inhibitors using 2-chloro-6-(trichloromethyl) pyridine (Nitrapyrin) from DOW Chemical (http://research.ipni.net/page/RNAP-6379).
- 'Alzon' inhibitors using dicyandiamide (DCD) and/or 1H-1,2,4 Triazol (DCD/TZ) from SKW Piesterwitz (http://www.skwp.de/). Using the trade name 'Piadin', these inhibitors are sold as an additive for animal manures (TZ, 3-MP). DCD is also added to controlled-release fertilizers (Chissosahi, Japan).

The following nitrification inhibitors can be traded in the EU according to the EU fertilizers Regulation 2003/2003:
- Dicyaandiamide (DCD) (Regulation EU nr. 1107/2008)
- Mixture of dicyaandiamide (DCD) and 1,2,4-triazool (TZ) (DCD/TZ) (Regulation EU nr. 223/2012)
- Mixture of 1,2,4-triazool (TZ) and 3-methylpyrazool (MP) (TZ/MP) (Regulation EU nr. 223/2012)
- 3,4-dimethyl pyrazole phosphate (DMPP) (Regulation EU nr. 1257/2014)

The main producers of nitrification inhibitors are BASF (Germany), SKW Piesterwitz (Germany), DOW Chemical (US), Koch (US) and Eurochem (DMPSA) (Switzerland). There are also several producers in Japan and India.

There are a large number of patented nitrification inhibitors. Subbarao (2013) gave an up to date overview of 85 substances where older references are quoted (Slangen & Kerkhoff, 1984; Subbarao *et al.*, 2006). 1403 patents can be found using the search term 'nitrification inhibitor' in the orbit patent database. The fact that 'nitrification inhibitor' is mentioned in a patent does not necessarily mean that the patent refers directly to a nitrification inhibitor. No attempt was made to assess whether these 1403 patents are all related to nitrification inhibitors as most patents are rather complex. The publication dates vary from 1964 to 2018. The total number of patents in the years 1990, 2000 and 2010 were 76, 214 and 480, respectively. In total 945 patents are 'alive' and 458 patents are 'dead'. Of the 'dead' patents, 106 were 'revoked', 123 'expired' and 229 'lapsed'. The largest number of patents are found for (number of patents are indicated between brackets): Syngenta (185), Qingdao (60), BASF (36), SKW Piesteritz (29), Institute of Applied Ecology CAS (19+23), Kurita (22), Dow chemical (19), and Koch (19).

New nitrification inhibitors are often well known substances in a slightly different form. For example, DMPSA (Pacholski *et al.,* 2016) from Eurochem. DMPSA combines DMP with succinic acid with the result that DMP is only released if there is microbial degradation of succinic acid (Pacholski *et al.,* 2016). Another example inhibitor is potassium thiosulfate which is similar to ammonium thiosulfate (ATS) but where potassium is used instead of ammonium (Cai *et al.,* 2018). Relatively new

approaches involve combinations of nitrification inhibitors with urease inhibitors in urea (Ni *et al.,* 2018), or in combination with slow-release fertilizers.

Table 15 *Overview of nitrification inhibitors (Trenkel, 2010; Kumar et al., 2015).*

Chemical name	Popular name	Developer/ manufacturer	Commercial use	Reference
2-chloro-6-(trichloromethyl-pyridine)	Nitrapyrin/ N-Serve	Dow Chemical	y	(Bronson *et al.*, 1992)
4-amino-1,2,4-6-triazole-HCl	ATC	Ishihada Industries		(Malhi & Nyborg, 1988)
2,4-diamino-6-trichloro-methyltriazine	Cl-1580	American Cyanamid		(Bremner & Yeomans, 1986)
Dicyandiamide	DCD	Showa Denko	y	(Treweek *et al.*, 2016)
Thiourea	TU	Nitto Ryuso		(Malhi & Nyborg, 1988)
1-mercapto-1,2,4-triazole	MT	Nippon		No recent reference
2-amino-4-chloro-6-methyl-pyramidine	AM	Mitsui chemicals		(Kumar *et al.*, 2015)
2-sulfanilamidothiazole	ST	Mitsui Chemicals		(Bremner & Yeomans, 1986)
2-mercapto-benzothiazole	MBT	Onodo Chemical Industries		No recent reference
3,4-dimethylpyrazole phosphate	DMPP	BASF	y	(Menéndez *et al.*, 2012)
1-amide-2-thiourea	ASU	Nitto Chemical Ind.	n	(Bremner & Yeomans, 1986)
Ammonium thiosulphate	ATS		Fertilizer	(Margon *et al.*, 2015)
3-methylpyrazole	3-MP	/SKW Piesterwitz	y	(Barneze *et al.*, 2015)
1H-1,2,4-triazole	HPLC			(Barneze *et al.*, 2015)
5-ethylene oxide-3-trichloro-methly1,2,4-thiodiazole	Dwell, etridiazol, Terrazole	Olin Mathieson/Uniroyal Chemical	fungicide	(Carrasco *et al.*, 2004)
1-carbamoyl-3-methyl-pyrazole	CMP			No recent reference
Neem (Azadirachta indica tree)	Nimin		y	(Datta & Adhya, 2014)
Karanjin				(Datta & Adhya, 2014)
Calcium carbide				(Bronson *et al.*, 1992)
N (2,5 dichlorphenyl) succinic acid monoamide	DCS			(Skiba & Smith, 1993)
Polyolefin coated urea	POCU			(Delgado & Mosier, 1996)
3,4 dimethylpyrazol succinic acid	DMPSA	Eurochem		(Pacholski *et al.*, 2016)
Potassium thiosulfate	KTS		fertilizer	(Cai, 2018)

The effect of nitrification inhibitors is strongly influenced by soil and soil moisture contents. In some experiments nitrification inhibitors were completely ineffective (van der Weerden *et al.,* 2016; Nauer *et al.,* 2018). The reason for this is unknown. An antagonistic effect has been demonstrated between the nitrification inhibitors 3,4-dimethylpyrazole phosphate and the fungicide iprodione (Zhang, 2018). Efforts to improve knowledge of the interactions between nitrification inhibitors and chemicals for crop protection may help improve our understanding of the differing effectiveness of inhibitors. Synergism between nitrification inhibitors has been studied for ATS and DCD (Goos, 1992). This combination did not produce synergistic effects. Guanyl thiourea (GTU) and DCD in combination with urea have also been studied to assess combination effects. The inhibitory effect on nitrification was improved when urea was combined with both products (Duncan, 2017).

In addition to specific chemicals that are used as nitrification inhibitors, there are a number of substances which are used in fertilizers which also have an inhibiting effect on nitrification inhibitors. Examples of these are chloride in KCl or NH_4Cl (Golden *et al.,* 1981; Souri, 2010). Some nitrification inhibitors can be added as a coating around the fertilizer prill, e.g., DCD and methyl pyrimidine (Subbarao 2006). There are also a number of natural substances which act as nitrification inhibitors (Kumar *et al.,* 2015). For example, in India an oil is extracted from the seeds of the neem plant and commercially applied (Azadirachta indica A. Juss.). The extract is used in the production of Neem oil-coated urea (NOCU) (Opoku *et al.,* 2014). In addition, a number of studies show that black carbon or

'Biochar' may have an inhibitory effect on N_2O emission. However, a meta-study of 40 individual studies indicate that this effect is not certain (Verhoeven *et al.,* 2017).

Some crops are able to produce nitrification inhibitors during a process called biological nitrification inhibition (BNI). This has been demonstrated in a tropical grass species, for rice (Sun *et al.,* 2016), wheat (O'Sullivan *et al.,* 2016), millet, peanut and sorghum (Subbarao *et al.,* 2013; Li *et al.,* 2018). It is possible to extract and use BNI substances from plants. During a two year field study, BNI demonstrated similar nitrification inhibiting effects as DCD (Zhang *et al.,* 2015).

6.1.2 Effect on N_2O emission

The effect of nitrification inhibitors on N_2O emission has been reviewed during several meta-studies of literature. Akiyama *et al.* (2010) calculated the average effect of a number of substances on N_2O emission (Table 16). These calculations show that, on average, DCD, Nitrapyrin and Ca-carbid can reduce N_2O emission by approximately 50%, and Thiosulphate and Neem by approximately 15-20%.

Table 16   *Effect of various nitrification inhibitors (Akiyama et al., 2010).*

Nitrification inhibitor	Crop	Decrease of N_2O emission (%) (*number of observations*)
DCD	Paddy rice	36 (*9*)
	Grassland	50 (*17*)
	Grass-upland	25 (*15*)
Nitrapyrin	Diverse	50 (*10*)
Ca-carbide	Diverse	50 (*8*)
Thiosulphate	Diverse	20 (*4*)
Neem	Diverse	15 (*8*)

Gilsanz *et al.* (2016) reviewed the effects of the most well-known inhibitors on N_2O emissions (DCD and DMPP) in a meta-analysis (Table 17). Both nitrification inhibitors can reduce N_2O emission by approximately 30 to 50% with the highest effects seen for grassland. The high effect for grassland occurs because N is absorbed rapidly. This means that the nitrification inhibitor needs to be effective over a relatively short time period only (up to two weeks). Conversely, it can take several weeks after application before arable crops take up N from the soil in significant amounts.

Following the publication of the meta-analysis by Gilsanz *et al.* (2016), a few additional studies have been published in which the effect of nitrification inhibitors on N_2O emission has been determined (Table 18). Pacholski *et al.* (2016) and Guardia *et al.* (2018) demonstrated that the addition of the nitrification inhibitor DMPSA (3,4 dimethylpyrazol succinic acid) reduced N_2O emission from CAN by 63%. This result was obtained in a study in Spain with an irrigated maize crop showing that nitrification was the main source of N_2O in this study (Guardia *et al.*, 2018). Remarkably, emissions from applied nitrate were also significantly reduced in the DMPSA based treatment suggesting that this inhibitor also affects N_2O production during denitrification. Torralbo *et al.* (2017) concluded that DMP based nitrification inhibitors stimulate the reduction of N_2O to N_2 by the enzyme nitrous oxide reductase during the denitrification process. Further research involving changes in microbial function is required to confirm the findings of Guardia *et al.* (2018) and to develop understanding of the possible influence of pyrazole ($C_3H_3N_2H$) based nitrification inhibitors on denitrifying communities and the final products of denitrification. It was concluded that the use of nitrate based fertilizers or DMPSA with ammonia based fertilizers can reduce N_2O losses in irrigated agro-ecosystems.

Studies show that the effect of nitrogen inhibitors on crop varies strongly, with some studies showing large effects and others no effects at all (Duncan *et al.*, 2017). This variation is probably due to variations in climate, soil type, crop type, and soil and crop management. The N use efficiency generally increases at increasing crop yield, and this may reduce the need for N fertilizer. This decreases emission of N_2O.

Table 17 *Effect of well-known nitrification inhibitors on N_2O emission: DCD and DMPP (Gilsanz et al., 2016).*

Nitrification inhibitor	Crop	Decrease Cof N_2O emission (%)*
DCD	Paddy rice	34 *(14)*
	Arable	36 *(8)*
	Grassland	48 *(52)*
	Grassland-upland	32 *(15)*
DMPP	Arable	38 *(9)*
	Grassland	46 *(8)*
	Grassland-upland	35 *(5)*

*number of observations given in brackets

Table 18 *Recent studies in which effects of nitrification inhibitors have been tested.*

Inhibitor	Fertilizer and conditions	Decrease of N_2O emission (%)	Reference
DMPSA	CAN	63	Pacholski *et al.*, 2016; Guardia *et al.*, 2018
Urease (2-NPT) and nitrification inhibitor (DCD/1 H-1,2,4-Triazol)	Urea, fallow, 50 days	65	Ni *et al.*, 2018
DMPP	Urea, grassland, 3 seasons	0	Nauer *et al.*, 2018
DMPP	Urea, rice, various amounts of DMPP, 4 months	39-94	Yin *et al.*, 2017
DMPP, DMPSA	Ammonium sulphate, lab, 51 days, 2 soil moisture contents	20-95, 22-90	Torralbo *et al.*, 2017
DMPP	Urine of sheep, 9 weeks	Not significant	Marsden *et al.*, 2017
DMPP	Urea, grassland, 21 days	Not significant	Friedl *et al.*, 2017
DCD in animal manure and urea	Animal manure, grassland, 367 days Urea, grassland, 367 days	Not significant	van der Weerden *et al.*, 2016
DMPP	Urea, grass	76	Suter *et al.*, 2016

All individual studies in Table 19 are selected from Gilsanz *et al.* (2016) and compare fertilizers containing nitrate with other fertilizers. All studies except one show that nitrification inhibitors also reduced the N_2O emission from ammonium nitrate (AN) and calcium ammonium nitrate (CAN). This is probably due to an inhibition of nitrification of the ammonium part of (C)AN. However, denitrification may also be affected by nitrification inhibitors as demonstrated by Guardia *et al.* (2018). The effect of rainfall on N_2O emission has not been assessed in these studies. Therefore, it is not clear whether nitrification inhibitors also affect N_2O emission from (C)AN applied to grassland under wet conditions. DCD was shown to be more effective in reducing N_2O emission from urea than from ammonium nitrate in 4 out of 6 experiments conducted by Misselbrook *et al.* (2014) and in the study of McTaggart *et al.* (1997). In studies in which animal manure and ammonium nitrate were compared, DCD performed better for animal manure while DMPP worked better for CAN (Macadam *et al.*, 2003). Comparisons between (C)AN and urea for arable land were only available in one study (Misselbrook *et al.*, 2014). This study showed that, on average, nitrification inhibitors were more highly effective in reducing N_2O emission from urea than from CAN.

In conclusion, the most well-known nitrification inhibitors, DCD and DMPP, are able to strongly reduce N_2O emission from ammonium fertilizers. However, reductions vary widely from about 20 to 80%. It has also been shown that nitrification inhibitors can reduce the N_2O emission from (C)AN. This is probably due to the inhibition of nitrification of the ammonium part of (C)AN. However, denitrification may also be affected by nitrification inhibitors.

Table 19 *Effect of nitrification inhibitors on fertilizers containing nitrate and comparisons with other N fertilizers. The fertilizers ammonium sulphate (AS), ammonium sulphate nitrate (ASN) ammonium nitrate (AN) and calcium ammonium nitrate (CAN) are compared to cattle slurry (CS) and urea (U).*

Fertilizer	Inhibitor	Crop/soil	Decrease in N$_2$O emission (%)	Reference
AN	DCD	Grass	42	Macadam *et al.*, 2003
CS			60	
CS	DMPP		58	
CAN			61	
AS	DCD	Grass, sandy loam	41	McTaggart *et al.*, 1997
U			57	
AS			41	
U			55	
AN			35	
ASN	DMPP	Grass, clay loam	9	Menéndez *et al.*, 2006
CS			29	
CAN	DCD	Grass, clay loam	42	Merino *et al.*, 2002
CS			60	
AN	DCD	Grass, sandy loam	33	Misselbrook *et al.*, 2014
U			31	
AN		Grass, clay	44	
U			69	
AN		Grass, clay loam	39	
U			111	
AN		Arable, sandy loam	15	
U			48	
AN		Arable, clay	13	
U			63	
AN		Arable, clay loam	41	
U			37	
AS	DMPP	Grass, sandy loam	15	(Linzmeier *et al.*, 2001)
AN			20	
U	DCD	Grass	39	(McTaggart *et al.*, 1997)
AN			-12	

6.2 Denitrification inhibitors

A wide range of bacterial species can denitrify and several enzymes are involved in this process (See section 3.12). Therefore, inhibition of denitrification is much more difficult (less specific) than inhibition of nitrification. Moreover, if a chemical compound is not specific in its inhibition of enzymes in the denitrification process, it can inhibit the reduction of N$_2$O to N$_2$, which results in an increase of N$_2$O emissions.

Although, several compounds may have inhibitory effects on denitrification, there are, unlike nitrification inhibitors, no commercial denitrification inhibitors available. Silicates have shown to inhibit denitrification (Song *et al.,* 2017). Silicates are sometimes used as fertilizers in paddy rice fields because silicon is a (non-essential) plant nutrient. Compounds that may have some inhibitory denitrification effects include heavy metals, salts and organic compounds. However, it is not clear whether these compounds maybe used as denitrification inhibitors as their mode of action and specificity are not clear. Moreover, it is also not clear whether inhibition is complete and over what duration inhibition occurs. Toxic compounds (e.g. Toluene, azide) may have unwanted side effects on other biological processes in the soil and negatively affect soil biodiversity and/or crop production. The results summarised in the previous section show that DMP based nitrification inhibitors also decreased N$_2$O emission from nitrate by stimulating the reduction of N$_2$O to N$_2$ by nitrous oxide reductase during the denitrification process.

6.3 Slow release fertilizers

Slow and controlled release versions of N fertilizers such as S-coated urea (SCU) or polymer coated urea (PCU) may increase N efficiency (Subborao, 2006). A number of studies demonstrate that coating urea based fertilizers reduces N_2O emission (e.g. Di Bella *et al.* (2017) for PCU-Agromaster and Maharjan and Venterea (2013) for PCU). However, other studies demonstrate no effect (e.g. Rose, 2017 for DMPP and PCU applied to rice and Akiyama *et al.* (2013) for PCU).

No references to publications testing the effect of coating of ammonium nitrate based fertilizers on N_2O emission were found during a search of the literature.

6.4 Nutrient management

There are a number of nutrient management strategies available that aim to decrease N_2O emission (Venterea *et al.,* 2012; Oenema *et al.,* 2014). The 4R strategy increases the nutrient use efficiency of fertilizers as well as reducing N_2O emission. It encourages N application with the Right type of fertilizer, at the Right rate, at the Right time, and at the Right place on the basis of site, soil and crop type specific knowledge and information (http://www.ipni.net/4R).

6.4.1 Right type

Results from literature show that the N use efficiency of (calcium) ammonium nitrate is on average higher than that of regular urea and ammonium based fertilizers (Chapter 4). This is mainly due to higher ammonia losses from urea and ammonium based fertilizers compared to nitrate containing fertilizers. In addition, the application of ammonium nitrate fertilizer results in less soil acidification than ammonium and urea fertilizer application. This decreases the demand for lime and is beneficial for crop quality and the botanical composition of grassland (Chapter 4). Soil acidification may also increase N_2O emission. This means that the risk of N_2O emission due to acidification is greater for ammonium and urea based fertilizers than for CAN.

Emission of N_2O from urea and ammonium fertilizers on arable soils is similar or higher to that of nitrate fertilizers. Emission from manure applied to arable crops on sandy soils is often higher than that of mineral N fertilizers. This is probably due to the application of organic matter with manure that increases denitrification capacity. Nitrate fertilizer should not be applied just after the application of manure because the fresh organic matter contained in manure can increase N_2O emission from the applied nitrate.

Application of nitrate fertilizer should be avoided during wet conditions or just before expected heavy rainfall on soils with a high denitrification capacity (high amounts of easily available organic matter) such as grasslands and peat soils. Measures to decrease N_2O emission during these (potentially) wet conditions are the postponement of nitrate fertilizer application or the application of an ammonium fertilizer or livestock slurry instead. Grassland can rapidly absorb N, especially in late spring, summer and early autumn resulting in a decrease of mineral N content during the initial days following N application. The risk of N_2O emission after N application decreases if there is no or limited rainfall during this period. The application of ammonium based fertilizers with a nitrification inhibitor can further reduce N_2O emission. Addition of a nitrification inhibitor may also decrease N_2O emission from ammonium nitrate fertilizer, but it is doubtful that N_2O emission can be strongly reduced during wet conditions with high denitrification activity.

In conclusion, Figure 23 shows a decision support tree that determines mineral N fertilizer types with reduced risk of N_2O emission assuming that manure is applied as per common agricultural practice. (Calcium) ammonium nitrate is the mineral N fertilizer with, on average, the highest N use efficiency (Chapter 4), lowest risk of acidification (Chapter 4; reduces risk of N_2O emission), and is a fertilizer that can be surface applied (reduces risk of N_2O emission; Figure 20). Application of (calcium) ammonium nitrate under moderately and relatively dry conditions (where soil moisture content is at

field capacity[7] or less) results in a relatively low risk of N_2O emission on both grassland and arable land. However, the application of nitrate containing mineral fertilizers such as (calcium) ammonium nitrate and urean to grasslands (all soil types) and arable land on clay and peat soils should be avoided during wet conditions. An ammonium based fertilizer (possibly with a nitrification inhibitor) or urea can be used to decrease the risk of N_2O emission during wet conditions. The application of the nitrate based fertilizer should otherwise be postponed to drier periods.
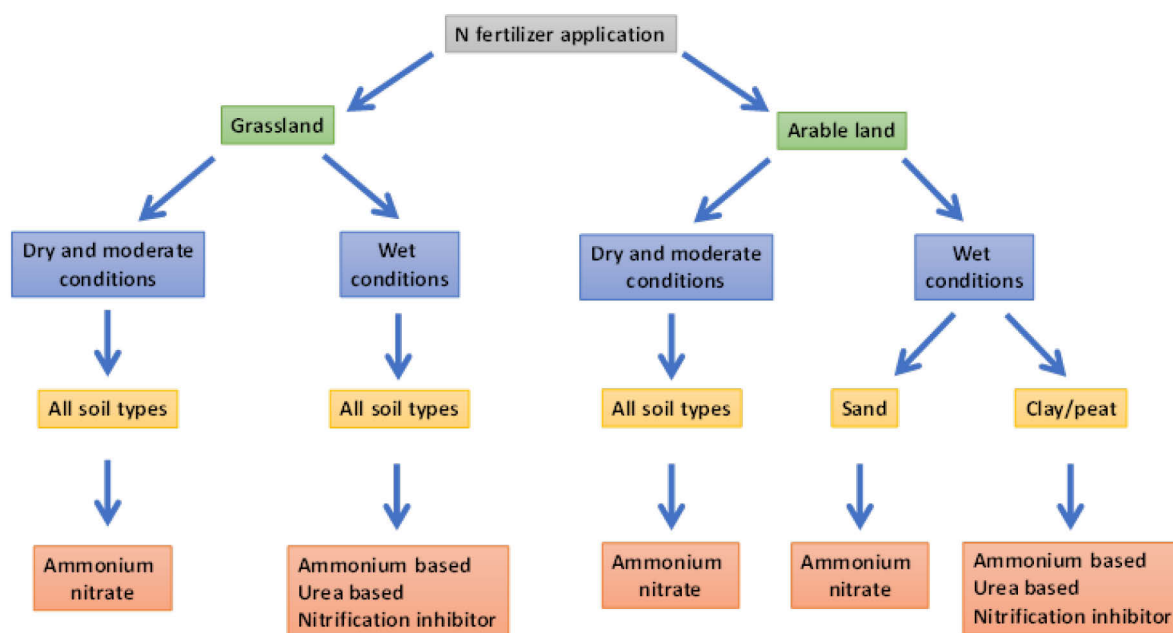
Figure 23   *Decision support tree to determine mineral N fertilizer types that decrease the risk of N_2O emission (Velthof, unpublished).*

6.4.2   Right rate

The application rate should be balanced with the N requirement of the crop as over-fertilization increases the risk of N_2O-emission. Van Groenigen *et al.* (2010) argued that agricultural management practices to reduce N_2O emissions should, instead of aiming to minimize N application rates, focus on optimizing fertilizer-N use efficiency under median rates of N input. The amount of available N should be accounted for in the application of mineral N fertilizer if manure or other organic fertilizers are used.

Splitting N application up into several dressings limits the content of mineral N in the soil and minimises the period of elevated mineral N content. This decreases the risk of N_2O emission. Splitting the recommended N rate into two smaller dressings may decrease N_2O emission during wet periods on grasslands.

6.4.3   Right time

The risk of N_2O emission is highest when the mineral N content of the soil is elevated. Therefore, shortening the period of elevated soil mineral N content after fertilizer or manure application decreases the risk of N_2O emission. The N should be applied during or just before the crop growing period.

The risk of N_2O emission increases when the moisture content of the soil increases for ammonium, urea, and nitrate based fertilizers. Application of a nitrate fertilizer to soils with a high denitrification

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[7]   Soil moisture content after excess water has drained away in a freely drained soil (within 1 to 2 days after the soil has been saturated).

capacity (grasslands and peat soils) should be avoided during wet conditions due to the high risk of N_2O emission. Soils with a high denitrification capacity are those that contain easily available organic matter. An ammonium based fertilizer (possibly with a nitrification inhibitor) can be used to decrease the risk of N_2O emission during wet conditions. The application of nitrate based fertilizer should otherwise be postponed to drier periods.

Application of manures, urea and urean and application of ammonium fertilizer to calcareous soils lead to a high risk of ammonia emission which decreases the N use efficiency of these fertilizers. These fertilizers should be applied during rainy conditions to decrease ammonia emission. High ammonia losses decrease the N use efficiency and, depending on the N application rate, increase the need for additional N fertilizers which increases the risk of nitrate leaching. Ammonia is also a source of indirect N_2O emission suggesting that ammonia emission reduction will also reduce N_2O emission.

6.4.4 Right Place

Surface application of fertilizers and manures decreases N_2O emission relative to incorporation or injection. Surface application will increase the risk of ammonia emission but this risk is much smaller for CAN than for urea, urean, ammonium fertilizers and livestock manure. Ammonia is also a source of indirect N_2O emission suggesting that ammonia emission reduction will also reduce N_2O emission.

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