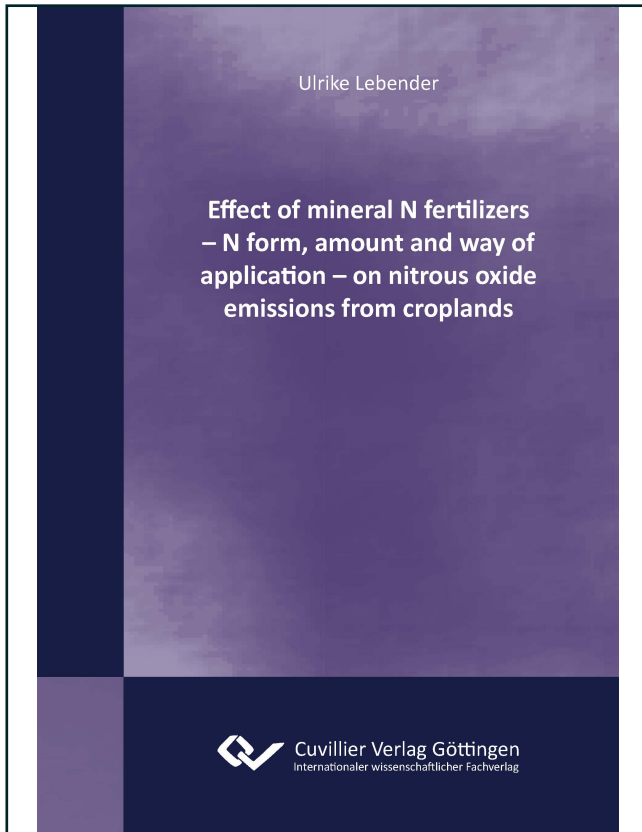




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Effect of mineral N fertilizers - N form, amount and way of application - on nitrous oxide emissions from croplands



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2 General Introduction

2.1 Nitrous Oxide (N₂O)

Nitrous oxide (N₂O) is an environmentally important atmospheric trace gas and contributes to the anthropogenic greenhouse effect. In addition, it is a precursor to photochemical nitric oxide (NO) production in the stratosphere which leads to stratospheric ozone depletion. The relative importance of N₂O as an ozone depleting substance has increased since global emissions of chlorofluorocarbon (CFC's) decreased as a result of the Montreal Protocol (Crutzen, 1981, Ravishankara et al., 2009). Though less abundant than carbon dioxide in the atmosphere, N₂O is 298 times more powerful than carbon dioxide in trapping heat calculated on a 100 year timespan (IPCC, 2007). The residence time of N₂O in the atmosphere is estimated to be 114 years (Montzka et al., 2002). Overall, N₂O contributes about 7.9 % to the anthropogenic greenhouse effect, despite its relatively low atmospheric concentration. The other contributing anthropogenic greenhouse gases (GHG) are methane (CH₄) with 14.3%, fluorocarbons (F-gases) with 1.1% and carbon dioxide (CO₂) with 76.7% in 2004 (IPCC, 2007). The atmospheric concentration of N₂O has increased by 20% from 270 ppb_{vol} in pre-industrial times (around 1900) (Flückiger et al., 1999) to around 322 ppb_{vol} in 2010 (Montzka et al., 2011), with a mean growth rate of 0.75 ppb yr⁻¹ over the past 10 years (2000-2010) (WMO, 2011).

Anthropogenic N₂O emissions are directly or indirectly caused by human activities. In the 1990s, these anthropogenic N₂O emissions accounted for 38% (6.7 Tg N yr⁻¹) of the total global N₂O emission from all sources (Table 1), (IPCC, 2007).

Table 1: Global sources of N₂O during the 1990s (IPCC, 2007)

Source	%	Tg N y ^{r-1}	range
Anthropogenic sources			
Fossil fuel combustion & industrial processes	10.5	0.7	0.3 - 0.9
Agriculture	42	2.8	1.7 - 4.8
Biomass and biofuel burning	10.5	0.7	0.2 - 1.0
Human excreta	3	0.2	0.1 - 0.3
Rivers, estuaries, coastal zones	25	1.7	0.5 - 2.9
Atmospheric deposition	9	0.6	0.3 - 0.9
Anthropogenic total	38*	6.7	
Natural total (soils, oceans, atmospheric chemistry)	62*	11	
Total sources	100	17.7	

* % based on the amount of total sources

Agriculture is the main source of N₂O, with agricultural soils representing the single largest source of anthropogenic N₂O emissions (Del Grosso et al., 2006). Nitrification and denitrification processes in soils are the primary sources of N₂O production (Davidson, 1991; Bremner and Blackmer, 1981).

Nitrogen fertilizer is a potential source of N₂O emissions from agricultural soils. The contribution of this source of N₂O emission will increase in future as the worldwide nitrogen fertilizer consumption will increase. Globally, the current consumption of nitrogen fertilizer is about 100 MT N yr⁻¹. This is estimated to increase by about 2.7 % during a time span of 50 years from 2000 to 2050 (Tillman et al., 2011). The reason for this increase is the rapid increase of global food demand as the global population is forecast to increase by 40%-50% during the time span 2000-2050 (Alexandratos et al., 2012; Tillman et al., 2001) to about 9 billion in 2050 (Alexandratos et al., 2012). According to the statistics of the Statistisches Bundesamt (2013) N fertilizer consumption in Germany averaged about 1.7 MT yr⁻¹ over the last 10 years.

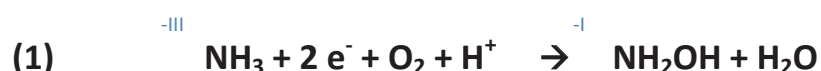


In the soil, nitrogen can undergo a number of transformations with most of the steps being exerted exclusively by microorganisms. In the process of nitrification, specialized autotrophic organisms use ammonium-N (NH_4^+) inputs or $\text{NH}_4\text{-N}$ mineralized from soil organic matter for a stepwise oxidation to nitrate to derive energy (Prosser, 1989). Under oxygen limited conditions the either previously produced nitrate from nitrification or any fertilizer applied NO_3 will be further reduced to N_2 by denitrifying microorganisms (Zumpft, 1997). However, the nitrogen added to soils can also be lost as nitrous oxide (N_2O) during nitrification as well as from denitrification.

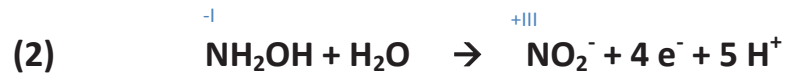
2.2 Biological processes producing N_2O in soil

Nitrification

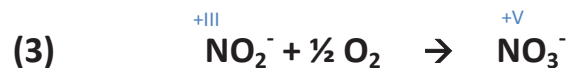
Autotrophic nitrification is the stepwise oxidation of NH_4 which is taken up by the microorganisms as ammonia (NH_3) to nitrate. It is exerted by two different functional groups of microorganisms (ammonia oxidizing bacteria and nitrite oxidizing bacteria). They use CO_2 as a carbon source and obtain their energy during the oxidation process from ammonia to nitrate (Granli and Bockman, 1994). The first step is the oxidation of ammonia (-III) to nitrite (+III) which is an aerobic respiration. During this step ammonia oxidizing bacteria (AOB) are oxidizing ammonia to hydroxylamine (-I, NH_2OH) using the enzyme ammonia monooxygenase (AMO) (Hollocher, 1981). More recently it was discovered that some archaea (AOA) are also capable of catalyzing this oxidation step (Franz et al., 2007).



Hydroxylamine is then oxidized to nitrite (NO_2^-) by the enzyme hydroxylamine oxidoreductase (HAO) (Andersson and Hooper, 1983)



Nitrite (+III) then is released to soil sol solution and serves as a substrate for nitrite oxidizing bacteria (NOB) which in turn oxidize nitrite to nitrate (+V), the end product of aerobic nitrification.



Autotrophic nitrification is the most studied process (Prosser, 1986) with the most intensively studied groups of nitrifiers, ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). The known AOB to date belong to the *Beta-* or *Gammaproteobacteria* and are classified into three genera on the basis of rRNA gene sequences (Head et al., 1993): *Nitrosomonas*, *Nitrospina* and *Nitrosococcus*. Much less is known for the classification of NOB. Some of the genera involved in nitrite oxidation include *Nitrobacter*, *Nitrospira*, *Nitrococcus* and *Nitrospina* (Teske et al., 1994).

During nitrification, N₂O can be formed either as a byproduct during ammonium oxidation, where intermediates (hydroxylamine) can chemically decompose to N₂O (Granli and Bockman, 1994), or via the so-called nitrifier denitrification under O₂ limiting conditions (Poth and Focht, 1985; Arp and Stein, 2003). Here, N₂O is an intermediate of the reduction of nitrite to N₂ (Wrage et al., 2004).

Denitrification

Denitrifiers are primarily heterotrophic microorganisms. Under oxygen-limited or anoxic conditions they are using mainly NO_3^- , NO_2^- but they can also reduce NO and N_2O instead of O_2 as an terminal electron acceptor to obtain the energy from organic compounds (e.g. dissolved organic carbon, DOC) (Zumpft, 1997). Denitrification can also be conducted by some archaea and fungi (Kobayashi et al., 1996).

N oxides, instead of oxygen, serve as the electron acceptors to generate an electrochemical gradient across the cytoplasmic membrane by the membrane bound nitrate reductase and the periplasmic nitrite reductase.

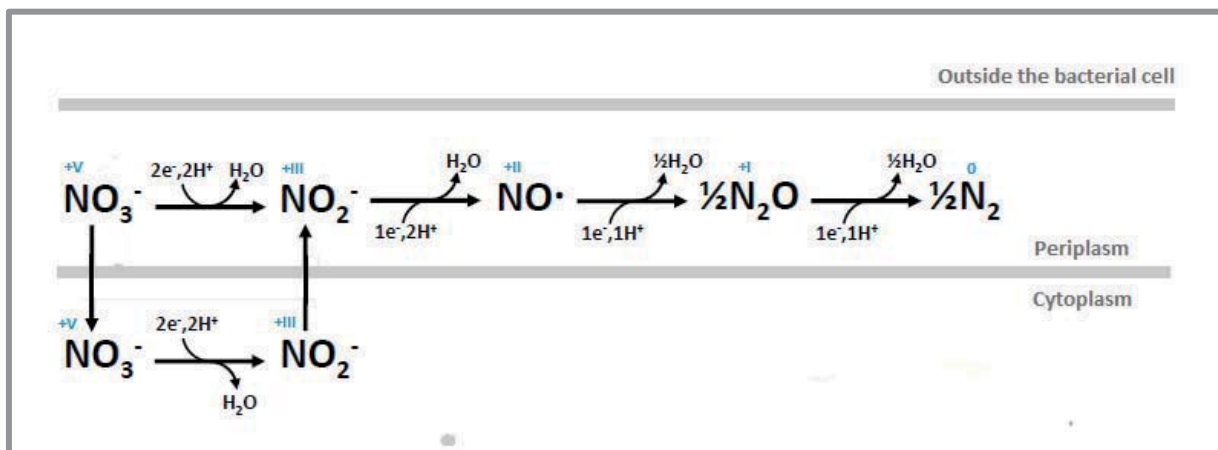


Figure 1: Bacterial denitrification in a bacterial cell adopted from Gates, 2013, pers. com.

Denitrification occurs stepwise with nitrite reductase as the key enzyme which catalyzes the first step that leads to the gaseous intermediate NO (+II) (Figure 1). In the next step NO is reduced to N_2O (+I) by nitric oxide reductase. The conversion of N_2O to N_2 (0) is the final step of a complete denitrification which is catalyzed by the labile enzyme nitrous oxide reductase.

Some bacteria produce only N_2 while others produce a mixture of N_2 and N_2O and yet others produce solely N_2O as their end product (Robertson and Kuenen, 1991). The



amounts of N_2O and N_2 released ($N_2O:N_2$ ratio) depend strongly on the microbial community in the soil as well as on soil parameters such as soil water content (O_2 availability), pH and nitrate availability.

In soils, non-microbiological reactions such as chemodenitrification can also contribute to the production of N_2O . This process is thought to be most significant when NO_2 accumulates and reacts with organic compounds and/or with metallic cations to produce NO and N_2O (Stevenson et al. 1970; Venterea and Rolston, 2000; Thorn and Mikita 2000; Wrage et al., 2001). Little is known about its contribution to total N_2O production in soils, but it is probably more significant in acidic soils (Baggs and Phillipot, 2010). However, of all the processes previously described nitrification and denitrification are considered to be the major processes producing N_2O in soils (Bouwman et al., 1996).

2.3 Main driving factors for N_2O emissions from soils

All forms of nitrogen inputs to agricultural soils, including mineral or organic fertilizer (manure) and the incorporation of crop residues, represent potential substrates for N_2O emissions,. The factors influencing N_2O emission can be divided into environmental factors which are more or less uncontrollable (e.g. temperature, precipitation) and the impact of human activities representing the controllable factors. The controllable ones are the soil nitrogen content (ammonium and nitrate concentrations) influenced by the choice of fertilizer form, the amount of nitrogen and the type of application method as well as the carbon content (application of manure or crop residues) and soil pH. Less controllable factors are the soil water content (soil aeration status), soil temperature as well as the microbial community.



Soil nitrogen

Mineral nitrogen in soil (ammonium and nitrate) serves as a substrate for nitrification and denitrification. The concentration of mineral nitrogen in the soil influences the rate of N_2O emissions. Usually, ammonium stimulates nitrification whereas nitrate promotes denitrification and influences the N_2O/N_2 ratio (Granli and Bockman, 1994). These are the most controllable factors attributed to human activity as the amount of nitrogen applied to the soil, the N form as well as the time of N application and the application method are suggested to strongly influence the amount of N_2O emitted (Smith et al., 2007).

Soil moisture

Soil moisture is an important parameter influencing N_2O emissions from soils. The soil water content controls the oxygen content in the soil and therefore determines the degree of aerobicity and anaerobicity, respectively. Water is necessary for microbial activity and as it controls the aeration in soil pores it also hinders gas exchange. The diffusion of N_2O in water is reduced by approximately four orders of magnitude when compared to the diffusion in air (Heinke and Kaupenjohann, 1999).

Water filled pore space (WFPS) is the factor that best describes the conditions determining the production and emission of N_2O from soils because WFPS takes the total pore space (TPS) into account. Since the soil water content is necessary for the microbial activity soil water is also needed by nitrifiers. The rate of nitrification increases with soil water up to a level where O_2 availability is restricted. According to the model of Davidson et al. (1991) the maximum nitrification rate is at about 50-60% WFPS; but of course as this model indicates a general



relationship between fluxes the optimum WFPS can vary depending on the soil type (Granli and Bockman, 1994). For denitrification as a semi anaerobic or anaerobic process, the optimum WFPS is much higher, with values of about 70% and higher having been reported (Bateman and Baggs, 2005; Ruser et al., 2006).

Carbon content

The content of available organic carbon is an important determinant for the denitrification rate in soil (Weier et al., 1993). Soils with high carbon contents have a greater potential for denitrification and in turn tend to form more N_2O than soils with low carbon levels. Therefore, any input of degradable organic material can create conditions which are favorable for denitrification derived N_2O emissions. Due to enhanced microbial activity O_2 is consumed and this can therefore create anoxic microsites in soil (Gök and Ottow, 1986). In the present study, the carbon content of soil was not evaluated as the soils did not differ that much in soil carbon content and the focus was mainly on the effect of nitrogen fertilization on N_2O emission from agricultural crop production.

Soil pH

Both nitrification and denitrification rates increase with soil pH increasing from acidic conditions to neutral conditions (Focht, 1974). In contrast, the product ratio of denitrification (N_2O/N_2) decreases as soil pH increases (less N_2O and more N_2) (Weier and Gilliam, 1986; Mørkved et al., 2007).

2.4 Possible N₂O mitigation options and management strategies

The main management strategies for N₂O mitigation are the management of nitrogen application, optimizing tillage, water management such as irrigation and drainage, and the more intensive use of existing farmland instead of the additional use of organic soils (Cone et al., 1995; Smith et al., 2007). The target of this study is the evaluation of the effect of nitrogen management on N₂O emissions.

Nitrogen use efficiency can be influenced by e.g. nitrogen form, N amounts in comparison to crop demand, the N fertilizer application method (broadcast vs. band application) as well as by split application of nitrogen.

N form

The effects of N fertilizer form on N₂O emissions were analyzed by Bouwman et al. (2002) in a review of published studies. They obtained the highest fertilizer induced emission factor for Urea and the lowest for CAN (Urea > AS > CAN) which is similar to the results reported by other authors (Mulvaney et al., 1997; Bergstrom et al., 2001; Gagnon et al., 2011). However, some studies have reported opposite results, with higher emissions resulting from CAN than from Urea (Velthof et al., 1997; Henault et al., 1998; Smith et al., 2012). Similarly, Stehfest and Bouwman (2006) analyzed values reported in the literature and concluded that, on average, emissions induced by UAN were lower than those by CAN, anhydrous NH₃ or Urea. To date, relatively few studies have evaluated the effect of fertilizer types on N₂O emissions in side by side experiments. Nitrification inhibitors may represent a potential mitigation option, leading to a reduction of N₂O emissions from fields. A meta-analysis showed a reduction of 38% in



N₂O emissions after the use of fertilizers containing nitrification inhibitors compared with conventional fertilizers, while fertilizers containing urease inhibitors did not significantly reduce N₂O emissions (Akiyama et al. 2010). However, nitrification inhibitors, urease inhibitors as well as other slow-release fertilizers are not evaluated in this study.

N amount

Taking the fertilizer amount which is applied to the soil into account, the potential of N₂O emission will increase with increasing nitrogen application. To identify the relationship between increasing N amounts and N₂O emissions from fields many experiments have been conducted worldwide. However, published findings are contradictory, showing either exponential increases in N₂O emissions with N amount (Chantigny et al., 1998; McSwiney and Robertson, 2005; Grant et al., 2006; Cardenas et al., 2010) if the supplied N amount was higher than crop N requirements (Zebarth et al. 2008a; Ma et al., 2010; Millar et al. 2010) or a linear relationship between N₂O emissions and N application amounts across several cropping systems like maize, potato as well as steppe (Mosier et al., 2006; Thomas et al., 2004; Gao et al., 2013; Gagnon et al., 2011; Liu et al., 2012; Peng et al., 2011). Overall, many datasets evaluating the impact of the amount of N applied on N₂O emissions consist of not more than three N fertilizer amounts which makes the interpretation of relationships between N₂O and N fertilizer amounts difficult. In this study, seven different N amounts and associated N₂O emissions were evaluated in order to increase our understanding on the relationship between N fertilizer amount and N₂O emission.