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# Mitigation of Nitrous Oxide Emissions during Nitrification and Denitrification Processes in Agricultural Soils Using Enhanced Efficiency Fertilizers

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Additional information is available at the end of the chapter

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## Abstract

Through the increasing use of nitrogen (N) fertilizers due to an increasing food demand, the agricultural sector is the main contributor of anthropogenic nitrous oxide ( $\text{N}_2\text{O}$ ) emissions, mainly through microbial processes called nitrification and denitrification. One option to mitigate  $\text{N}_2\text{O}$ , a major greenhouse gas, is to use enhanced efficiency fertilizers (EEFs). There are different types of EEFs like nitrification inhibitors or controlled-release fertilizers that aim to match the N release from fertilizers with N demands from plants. Parts of the chapter are also dedicated to organic amendments and their effects on  $\text{N}_2\text{O}$  emissions. Overall, EEFs can improve the N-use efficiency of plants, which has two positive effects. First, farmers can increase their yields, and second, environmental pollution through excessive fertilizer N can be minimized. However, the effectiveness of EEFs strongly depends on numerous factors like land use type, application method, and climate. More studies are needed to establish individual fertilizer plans that are optimized for the prevalent conditions. In conclusion,  $\text{N}_2\text{O}$  mitigation using EEFs is only advisable when “initial”  $\text{N}_2\text{O}$  emissions from conventional fertilizers are critically contributing to annual  $\text{N}_2\text{O}$  emissions. Thus, careful assessment is needed before EEFs are introduced to the system especially when economic and ecologic results are considered.

**Keywords:**  $\text{N}_2\text{O}$  emissions, enhanced efficiency fertilizers, coated urea, nitrification inhibitors, organic amendments

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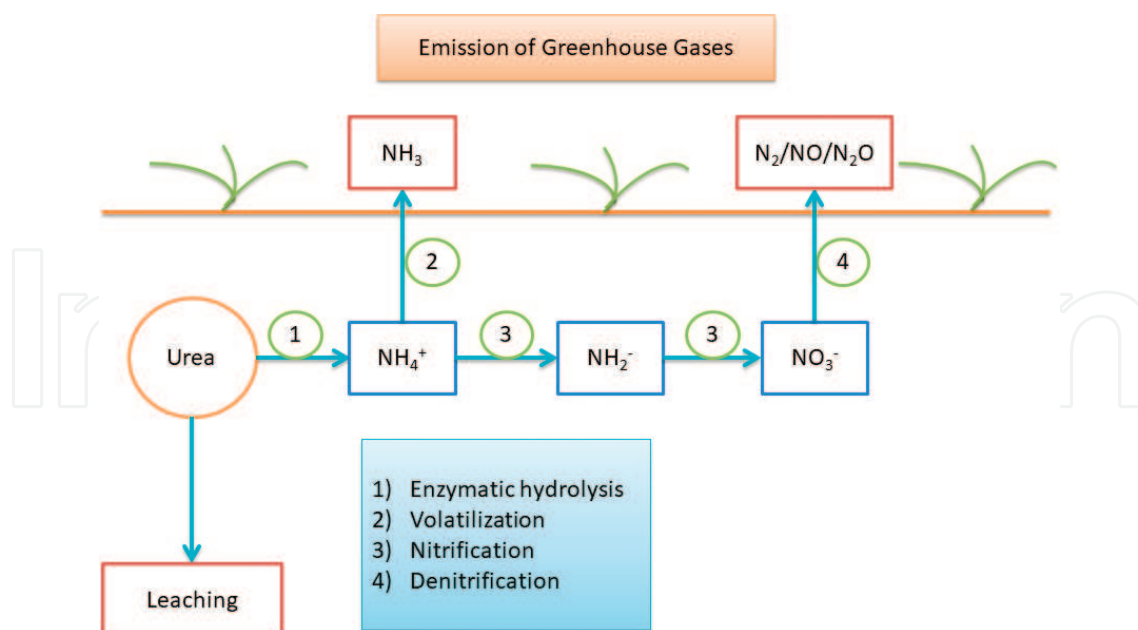
# 1. Introduction

## 1.1. Importance of fertilizer application

With an ever-increasing world population, modern agriculture faces the challenge to satisfy the increase in food demands. Fertilizers are indispensable for higher yields in agricultural food production [1]. They supply plants with primary nutrients like nitrogen (N), phosphorus (P), and potassium (K) with the focus of this chapter lying on N. Even though around 80% of the atmosphere consists of molecular N, it cannot directly be used by most plants due to it being highly stable and chemically inert [2]. Only a limited number of plants (legume plants) can fix atmospheric N through a symbiosis with N-fixing rhizobia bacteria called biological N fixation. The plant-microbe interaction results in new plant organs called root nodules, where the bacteria convert atmospheric N into available N for the plant [2, 3]. Thus, a regular replenishment of nutrients, e.g., in the form of manure, soil amendments, or organic or synthetic fertilizers, is necessary to keep the harvest quantity and quality of nonleguminous crops high [4]. The establishment of the Haber-Bosch process and with it the production of chemical N fertilizers markedly increased agricultural yields [1]. However, agricultural intensification comes with a price. To satisfy the large increases in food production, N production through the Haber-Bosch process increased by 20% from 100 in 1995 to 121 Tg N year<sup>-1</sup> in 2005 and will continue to rise with estimates of about 145 Tg N year<sup>-1</sup> in 2050 with N fertilizer production exceeding N fertilizer consumption by about 7% annually [5, 6]. This poses a huge threat to environmental systems because not all of the fertilizer N produced will actually reach the plants, be it through an overproduction of N or through direct losses of N to the environment after N fertilizer application.

## 1.2. Problems of fertilizer application

Only around half of the conventional N fertilizers applied are utilized by the plants, while the rest is lost to the environment, with around 3, 20, and 25% of N lost through accumulation in the soil, leaching to aquatic systems, and emissions to the atmosphere, respectively [6, 7]. Plants assimilate N from the soil solution as nitrate (NO<sub>3</sub><sup>-</sup>) or ammonium (NH<sub>4</sub><sup>+</sup>) ions. However, NH<sub>4</sub><sup>+</sup> can be adsorbed to the soil and is used in nitrification processes leading to a competition for N with the soil biome, whereas NO<sub>3</sub><sup>-</sup> is negatively charged and easily lost from the soil (also negatively charged) through leaching [8]. The application rates of conventional fertilizers often exceed plant demands, and about 40–70% N is lost to the environment (**Figure 1**) [5, 6, 8]. Especially, N fertilizers are susceptible to loss because of processes such as leaching, mineralization, volatilization, and other gaseous emissions (e.g., ammonium (NH<sub>3</sub>) and nitrous oxide (N<sub>2</sub>O) emissions). As a consequence, N fertilizer application can lead to heavy environmental pollution due to excessive N not taken up by the plants. Two major processes of N pollution include NO<sub>3</sub><sup>-</sup> leaching to the groundwater leading to eutrophication and N<sub>2</sub>O emission to the atmosphere via nitrification and denitrification processes of soil microbes [4].



**Figure 1.** Losses of nitrogen (red boxes) after urea application through different processes. For simplification reasons some processes of N turnover have been omitted (e.g., steps in the denitrification process, aerobic, and chemo-denitrification).

### 1.3. Enhanced efficiency fertilizers (EEFs): possible solutions for fertilizer application

Countermeasures against the environmental impact of N from fertilizer N include the use of enhanced efficiency fertilizers (EEFs). There are several types of enhanced efficiency fertilizers (EEFs). Some contain nitrification or urease inhibitors (stabilized fertilizers), while others slowly release N components (slow-release fertilizers) or release N at more predictable rates (controlled-release fertilizers) [8–11].

The use of EEFs is primarily to improve the N-use efficiency of crops. Choosing the right type of EEFs can synchronize the demands of N by the crops and the release of N by the fertilizers [12]. As an alternative approach, farmers may apply normal and/or enhanced efficiency fertilizers several times during the crop-growing season based on the requirements of the crop which is called split application [13]. However, the split application is often labor-demanding and not cost-efficient. We note that farmers normally decide to use the EEFs based on their cost performance unless they are required to use EEFs due to some environmental regulations. Thus, the mitigation of N-related environmental impacts is a secondary benefit for the farmers. There are different types of EEFs available on the market. In the next part of this chapter, we list their characteristics.

#### 1.3.1. Stabilized fertilizers

Fertilizers containing N stabilizers extend the time that the N added to the soil stays in its original form. Stabilized fertilizers like nitrification and urease inhibitors directly slow down microbial processes. For example, nitrification inhibitors (NIs) contain substances that inhibit ammonia

monooxygenase—the first enzyme involved in the oxidation process of nitrification—and thus delay the  $\text{NH}_4^+$  oxidation to  $\text{NH}_2^-$  by nitrifiers [8, 14, 15]. By slowing down the nitrification rate, plants have a higher chance of assimilating  $\text{NO}_3^-$  over a longer period which increases the N-use efficiency of the fertilizer. With reduced  $\text{NO}_3^-$  concentrations in the soil,  $\text{NO}_3^-$  leaching and  $\text{N}_2\text{O}$  loss via denitrification processes (which require  $\text{NO}_3^-$  as a substrate) are minimized [8]. In summary, NIs slow down the two main processes of  $\text{N}_2\text{O}$  production in soils with the indirect inhibition of denitrification being the most important effect since denitrification is the main contributor to  $\text{N}_2\text{O}$  emissions from agricultural soils [15]. NIs can be applied with chemical as well as organic fertilizers. Three commonly used NIs are N-(n-butyl) thiophosphoric triamide (NBPT), dicyandiamide (DCD), and 3,4-dimethylpyrazole phosphate (DMPP). NBPT is the most widely used NI due to it having a similar solubility and diffusivity as urea and thus a high effectiveness. However, under high temperature and humidity, e.g., under tropical conditions, its effectiveness might be reduced since it is rapidly degraded [8, 16]. Urease inhibitors suppress the hydrolytic action of the enzyme urease and therefore slow down the rate at which urea is hydrolyzed to  $\text{NH}_3$  which reduces volatilization losses of  $\text{NH}_3$  to the air [9]. In this chapter, the focus will lie on NIs since they are more promising in mitigating  $\text{N}_2\text{O}$  emissions than UIs [14].

### 1.3.2. Controlled-release fertilizers (CRFs)

Slow- and controlled-release fertilizer notations can be used interchangeably in most cases. One possible difference is that the nutrient release pattern of slow-release fertilizers is unpredictable due to the dependence on soil and climatic conditions, while it can roughly be predicted for controlled-release fertilizers [8]. Controlled-release fertilizers (CRFs) retard or control the release rate of nutrients to the soil which can lead to higher yields and a reduction of environmental pollution from nutrient loss through chemical modifications or coating. Coatings can be based on, e.g., sulfur, polymers, or superabsorbent/water retention materials with new and more accurate and efficient CRFs being developed on a constant basis [4, 8, 10, 11, 17, 18]. Coatings can only be applied to chemical fertilizers. Coated N fertilizers release N through a physical process like diffusion through the semipermeable coating, while slow-release fertilizers depend on chemical or biochemical processes [9]. One possible release mechanism of coated fertilizers is called multistage diffusion model where water penetrates the coating and condenses on the solid fertilizer core which dissolves the nutrients slowly. The osmotic pressure rises within the core, and the granules start to swell which leads to a slow diffusional release of the N due to a concentration and/or pressure gradient [10]. Since urea is one of the most widely used N fertilizers in the world, coated urea has been one of the most researched CRFs. Coated urea is a granule CRF which releases more N with increasing temperature and is designed to release N as close to the plant's N demand as possible. The N release can be controlled by altering the coating properties (e.g., the thickness) and thus changing the N diffusion rates. Coated urea reduces  $\text{N}_2\text{O}$  emissions by limiting the available N for microbial processes like nitrification and denitrification in the soil [9, 10, 17].

Advantages of EEFs over conventional fertilizers include higher N-use efficiency (nutrients taken up by plants compared with the amount applied) and N availability over the whole crop season. The resulting environmental benefits are decreases in  $\text{NO}_3^-$ -N loss through leaching,  $\text{NH}_3$  loss through volatilization, and  $\text{N}_2\text{O}$  emissions through microbial processes.



On the other hand, they are quite expensive, and their role in mitigating  $N_2O$  emissions is not yet fully understood with contrasting results [4, 9, 10, 17]. In conclusion, maximizing the N-use efficiency should be the goal when applying N fertilizers and EEFs in order to reduce environmental impacts like  $N_2O$  emissions and at the same time increase the yield.

### 1.3.3. Organic amendments

Even though organic fertilizers—also called organic amendments (OAs)—like plant residues, composts, or animal manure are not EEFs, they are often said to be more environmental-friendly than conventional fertilizers. The advantages of using OAs include improvement of soil C and N content, yield, and microbial biomass and activity. In addition, using OAs can recycle already fixed N [19]. Thus, animal manure and plant residue applications have been the traditional way of fertilizing agricultural fields for centuries, but recently—with the increasing demand of food—chemical fertilizers became more and more common. Still, due to the many negative effects for the environment of chemical fertilizers as well as their relatively high cost compared to OAs and unavailability in many local areas of the world, the use of OAs is rapidly increasing as well [20]. Negative environmental impacts of OAs include nutrient leaching and greenhouse gas (GHG) emissions, but their impact is much less severe than that of chemical fertilizers.

Animal manures, e.g., from livestock (cattle, pigs, or sheep) and poultry, are one of the most commonly used OAs that are rapidly increasing in quantity due to the increase in worldwide meat production. Animal manure has a substantial amount of nutrients like N, P, and K and can help to improve soil fertility and health [20]. Composts (e.g., made from crop residues or manure) are a good C source and help to enhance soil aggregate stability and prevent erosion, but most composts contain little amounts of nutrients, e.g., only 1–2% N (urea contains 46% N) which leads to the necessity of either additional addition of other fertilizers or high application rates. Also, during composting, high C and N losses occur through GHG emissions [19, 20]. Plant residues include stalks, stems, leaves, and seed pots and can function as a soil N source. Most plant residues are from cereals or legumes (e.g., red clover, winter vetch, and ryegrass). Their application method—e.g., surface application or incorporation into soil—as well as soil moisture and residue quality can have different impacts on GHG emissions with potential increases in denitrification after incorporation. Residues with a high N content and low C/N ratios like legumes might release N faster which can result in higher  $N_2O$  emissions, while high C/N ratios might decrease  $N_2O$  emissions through released N during residue degradation which stimulates microbial immobilization [20–23].

## 1.4. $N_2O$ emissions

### 1.4.1. $N_2O$ as a threat for climate and ozone layer

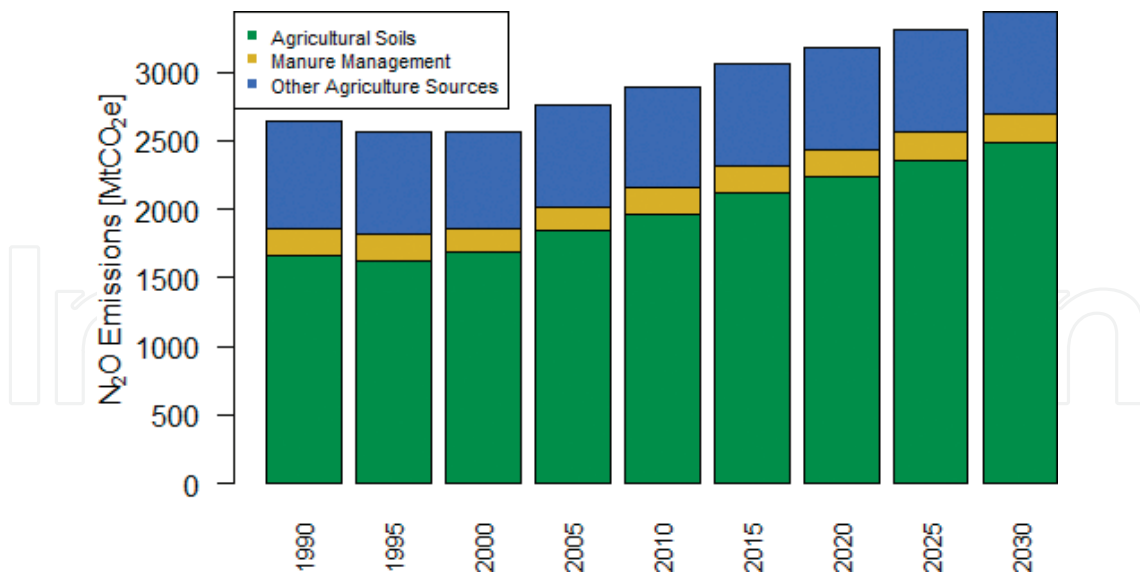
Nitrous oxide ( $N_2O$ ) is a major GHG with a global warming potential around 298 times greater than that of  $CO_2$  over a 100 year period [24, 25]. Due to the high global warming potential—which depends on its high potential of absorbing infrared light and a long atmospheric lifetime of 114 years—even low concentrations of atmospheric  $N_2O$  have strong negative impacts regarding climate change. Global emissions of  $N_2O$  occur mostly through biological processes.

Thus, factors affecting  $\text{N}_2\text{O}$  emissions from soils include oxygen ( $\text{O}_2$ ) concentration, temperature, moisture content, soil texture and type, and soil- $\text{NH}_4^+$  and soil- $\text{NO}_3^-$  concentrations that are readily available for nitrification and denitrification [26, 27]. In addition, soil organic C content and soil drainage as well as microbial community structure, abundance, and activity influence the magnitude of  $\text{N}_2\text{O}$  emissions. Agricultural management-related factors controlling  $\text{N}_2\text{O}$  emissions include fertilizer and crop type, tillage system, as well as N application rate, timing, and technique [26, 27]. It is estimated that—due to human activities— $\text{N}_2\text{O}$  emissions have increased by more than 40% compared to preindustrial levels [27]. For example, [25] estimated that global emissions have increased from 12 in 1500 to 19 Tg N year<sup>-1</sup> in 2006, with natural emissions accounting for about 55% and anthropogenic emissions accounting for about 45% in 2006.

Next to its global warming potential,  $\text{N}_2\text{O}$  also has a huge effect on the ozone layer. It is said to be the main ozone-depleting substance today and will remain the largest threat to the ozone layer throughout the twenty-first century if the current emission trend continues. Nitrous oxides ( $\text{NO}_x$ ) catalytically destroy the ozone layer, and their main source is surface  $\text{N}_2\text{O}$  emissions.  $\text{N}_2\text{O}$  already outweighs the chlorofluorocarbons—the historically dominant ozone-depleting substances—because of its abundance and continued anthropogenic emissions as well as a high ozone depletion factor of 0.017 [28]. Thus,  $\text{N}_2\text{O}$  emissions affect both the ozone layer and our climate. We need to be aware that when fighting climate change through the mitigation of  $\text{CO}_2$  emissions,  $\text{N}_2\text{O}$  emission could unintendedly rise, e.g., as a consequence of enhanced crop growth for biofuel production [28]. To avoid exchanging one GHG with another, we need to mitigate anthropogenic  $\text{N}_2\text{O}$  emissions which mainly arise from N fertilization.

#### 1.4.2. N fertilization as a source for microbially produced $\text{N}_2\text{O}$

The agricultural sector (including livestock production systems) is responsible for about 42% of the global anthropogenic  $\text{N}_2\text{O}$  emissions [15, 25, 29]. Agricultural soils are the main contributor to anthropogenic  $\text{N}_2\text{O}$  emissions, and it is estimated that emissions will continue to rise in the future (**Figure 2**) mainly due to increases in N fertilizer use and manure application [30]. The most commonly used N fertilizer is urea ( $\text{CO}(\text{NH}_2)_2$ ). When applied to the soil in the presence of water, an enzyme called urease converts urea into  $\text{NH}_4^+$ , hydroxyl ions ( $\text{OH}^-$ ), and bicarbonate ( $\text{HCO}_3^-$ ) [10, 17, 27]. The  $\text{N}_2\text{O}$  emissions from N fertilization (primarily the addition of chemical fertilizers and organic fertilizers like animal manure) mainly arise from microbial processes called nitrification (aerobic) and denitrification (anaerobic). Nitrification is the aerobic process of catabolic oxidation where  $\text{NH}_4^+$  is firstly transformed to nitrite ( $\text{NO}_2^-$ ) by *Nitrosomonas* sp. and then to  $\text{NO}_3^-$  by *Nitrobacter* and *Nitrosolobus* sp. bacteria. It is mainly influenced by the availability of  $\text{NH}_4^+$  and  $\text{O}_2$  [26, 27]. Also, many archaea species oxidize  $\text{NH}_4^+$ , and a recent study discovered that there are *Nitrospira* species that can perform the complete nitrification process (the two steps mentioned above) on their own [31]. Nitrification is a very important microbial process in the soil—especially for plant productivity and environmental quality—as it determines the form of N present. Nitrification converts the relatively immobile  $\text{NH}_4^+$  to the highly mobile  $\text{NO}_3^-$ .  $\text{NO}_3^-$  is often the major compound utilized by plants due to it being easily available, but at the same time, it can also be easily lost through leaching and denitrification [8, 27, 32].



**Figure 2.** Global N<sub>2</sub>O emissions from agriculture between 1990 and 2030 (data obtained from [35]).

Denitrification is the anaerobic process of the reduction of  $\text{NO}_3^-$  to  $\text{N}_2$  via  $\text{NO}_2^-$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}$  with high losses of  $\text{N}_2\text{O}$  to the atmosphere. Denitrification is much more temporally and spatially variable than nitrification and is influenced by  $\text{NO}_3^-$ , C, and  $\text{O}_2$  availability [8, 26, 27]. A very important, yet often overlooked, process of  $\text{N}_2\text{O}$  production is called nitrifier denitrification which, under some circumstances, can even outweigh denitrification. It is the reduction of  $\text{NO}_2^-$  by  $\text{NH}_3$ -oxidizing bacteria.  $\text{N}_2\text{O}$  emissions from  $\text{NH}_4^+$  might in some cases entirely emanate from nitrifier denitrification. Favorable environments for this process are low in oxygen and high in pH and have fluctuating aerobic-anaerobic conditions [33].

It is estimated that around half of the global anthropogenic  $\text{N}_2\text{O}$  emissions arise from N fertilization and it is thus a major concern in terms of atmospheric GHG increases [34]. The  $\text{N}_2\text{O}$  emission factor (EF) which is the “percentage of fertilizer N applied that is transformed into fertilizer-induced emissions” is estimated as 1% which means that from 100 kg of applied N, 1 kg is lost to the environment as  $\text{N}_2\text{O}$  emissions [34]. However, a 1% EF assumes a linear relationship between N application and  $\text{N}_2\text{O}$  emissions while [34] rather suggest an exponential curve which would indicate that global  $\text{N}_2\text{O}$  emissions are underestimated in general. In addition, it is predicted that agricultural  $\text{N}_2\text{O}$  emissions will increase by 20% until 2030 [35].

In order to mitigate  $\text{N}_2\text{O}$  emissions, we first need to quantify the  $\text{N}_2\text{O}$  budget and understand the mechanisms and processes linked with  $\text{N}_2\text{O}$  production. Stable isotope techniques offer a unique opportunity to gain insights into processes contributing to  $\text{N}_2\text{O}$  emissions, and recently laser spectroscopy approaches have highly increased our knowledge on the functioning and the controls regarding the  $\text{N}_2\text{O}$  budget [36].

By using isotopic ratio mass spectrometry, it is possible to estimate (e.g., through natural abundance measurements) and quantify (e.g., through enrichment experiments) the (microbial) processes associated with  $\text{N}_2\text{O}$  production based on  $^{15}\text{N}$  and  $^{18}\text{O}$  isotopes [37]. It is difficult to assign  $\text{N}_2\text{O}$  production to different processes mainly due to many simultaneous processes that contribute to  $\text{N}_2\text{O}$  production in different microsites of the soil. To attribute  $\text{N}_2\text{O}$



emissions to denitrification, acetylene ( $C_2H_2$ ) is added which inhibits nitrification. However, this method can underestimate denitrification because no additional  $NO_3^-$  is supplied via nitrification. In addition  $C_2H_2$  can be used as a substrate if C in the soil is limited which can lead to biased results [37]. Natural abundance approaches can be used as an estimate of the  $N_2O$  sources in soil, but the results should be handled with caution due to a fractionation in favor of  $^{14}N$  relative to  $^{15}N$  and higher fractionation during nitrification than denitrification. Thus, even though natural abundance approaches have the advantage of being noninvasive, they are not suitable for exact  $N_2O$  source partitioning and thus best be coupled with genetic and/or molecular approaches [37].

## **2. Enhanced efficiency of N fertilizers and their role in mitigating $N_2O$ emissions: comparing conventional, organic, and enhanced efficiency fertilizers**

One option to reduce N loss to the environment as  $N_2O$  gas is to use EEFs. As previously described, EEFs match the N release from fertilizers and N demands by crops. Thus, the excess accumulation of fertilizer-derived N in soils can be avoided. This fact is very important to minimize the  $N_2O$  emissions from soils because  $N_2O$  emissions are related to the microbial availability of N in soils. Even though environmental issues are important, the main reason for applying EEFs in recent years was to increase the N-use efficiency through optimized N management practices, which, e.g., can reduce the number of split applications a farmer has to do [13, 34]. The main goal for farmers is thus to decrease the amount of work and at the same time increase the yield due to an optimized N fertilizer utilization rate. The main goal for humanity however should be to combine high agricultural yields with a minimum environmental pollution [15].

### **2.1. Stabilized fertilizers**

In a meta-analysis by [14]—who evaluated the overall effectiveness of EEFs by comparing them with conventional fertilizers using datasets from field experiment data—they concluded that nitrification inhibitors (NIs) have the highest potential in mitigating  $N_2O$  emissions with a mean reduction of 38% (when compared to conventional fertilizers) and a relative constant effectiveness for different soil and land use types. The effectiveness of NIs to reduce  $N_2O$  emissions varied with land use type, e.g., mitigation in grasslands (−54%) was much higher than paddy fields (−30%). This indicates that the mitigation effectiveness of NIs depends on the mean  $N_2O$  emissions of the land use. The higher the mean  $N_2O$  emissions, the more effective are NIs in reducing them. However, in their meta-analysis, urease inhibitors (UIs) seemed to be ineffective in reducing  $N_2O$  emissions. In another meta-analysis by [32]—who assessed how NIs affect both hydrologic and gaseous N losses and N-use efficiency—NI application increased  $NH_3$  emissions by a mean of 20% but reduced N leaching,  $N_2O$  emissions, and NO emissions by 48, 44, and 24%, respectively, which led to a total net reduction of 16.5% of N released to the environment. Thus, overall, NIs seem to be a good option in reducing  $N_2O$  emissions, but their effectiveness may vary strongly on a local scale.

Many studies have assessed the effectiveness of stabilized fertilizers, but the results vary. The application of DCD and/or DMPP has shown positive results in mitigating  $N_2O$  emissions in various studies [38–40]. For example, [38] found that DCD and DMPP, two NI fertilizers in combination with urea, decreased cumulative emissions by 35 and 38%, respectively, in a 1 year experiment on a wheat-maize rotation field when compared to only urea application. In addition, yield, aboveground biomass, and nitrogen uptake increased significantly when using NIs, possibly through an increase in soil inorganic nitrogen and a shift from  $NO_3^-$  to  $NH_4^+$  forms. Other studies that assessed the effectiveness of DCD and/or DMPP concluded that they have a great potential to reduce  $N_2O$  emissions as well as  $NO_3^-$  leaching, e.g., from cow urine in grazed pastures or in intensive vegetable production systems [39, 40].

However, e.g., [41] found no significant reduction of  $N_2O$  emissions after urea + DCD application, even though urea + nitrapyrin did mitigate them in a 2 year study on an intensively used vegetable field. Recently, it is suggested that the positive effects of NIs on reducing  $N_2O$  emission might be overestimated or even reversed when the indirect  $N_2O$  emissions from increased  $NH_3$  volatilization after NI application are considered [42]. A study by [16], who quantified  $N_2O$  emissions in a 1 month field trial with maize plants on a tropical Acrisol after urea + NI fertilizer (nitrapyrin and NBPT) application, assessed this problem. They found that the urea + nitrapyrin treatment reduced cumulative  $N_2O$  emissions by 49%, while NBPT reduced the  $NH_3$  volatilization by 35% compared to the urea treatment. NBPT tended to increase  $N_2O$  emissions; however, it reduced  $N_2O$  emissions indirectly by reducing  $NH_3$  volatilization. In addition, while nitrapyrin was added after urea application during maize sowing, NBPT was added during the V5 stage of maize growth which increased maize yield significantly. The authors concluded that the combination of timing, placement, as well as the specific use of fertilizers are vital for the effectiveness of NIs to reduce  $N_2O$  emissions directly and indirectly through a reduction of  $NH_3$  volatilization as well as for higher N-use efficiency and yields. Recent studies also suggest that—even though NIs like DCD and DMPP are a good option to reduce  $N_2O$  emissions—they might have little economic benefits since they are relatively expensive and might not increase biomass and yield as expected. This is due to the usage of suboptimal N rates in many studies that focus on the effects of  $N_2O$  emissions after NI application [43].

Thus, the effectiveness of stabilized fertilizers depends on many factors. For example, in systems with a high N surplus,  $N_2O$  mitigation can simply be achieved by optimizing the N input because  $N_2O$  emissions increase strongly if N application rates are higher than the N uptake. But EEFs can be an effective way to mitigate  $N_2O$  emissions in agricultural systems that are moderately fertilized and that are adapted to the N demand of plants [15]. Ref. [15] also suggest that the optimal  $N_2O$  reduction occurs under conditions where the NI remains close to the N fertilizer, e.g., when the NI is sprayed on mineral-N fertilizer granules or is thoroughly mixed with liquid fertilizers. Thus, on pasture soils with high spatial N concentration variations due to urine and manure patches,  $N_2O$  mitigation strongly varies depending on  $N_2O$  hotspots dispatched across the soil.

In general, when long-term experiments and meta-analyses are conducted, NIs usually show a positive effect on the mitigation of  $N_2O$  emissions. Thus, high-frequency measurements over a long time period are important to accurately quantify  $N_2O$  emissions and assess the overall effectiveness of NIs because with short-term experiments and low-frequency measurements

effects may be over- or underestimated. This is due to the regulation of  $\text{N}_2\text{O}$  emissions via soil temperature, moisture, and inorganic N contents which leads to strong seasonal and even daily fluctuations [38].

In conclusion,  $\text{N}_2\text{O}$  mitigation using NIs is only advisable when “initial”  $\text{N}_2\text{O}$  emissions from conventional chemical fertilizers are critically contributing to the annual  $\text{N}_2\text{O}$  emissions. Thus, careful assessment is needed before NIs are introduced to the system especially when economic and ecologic results are considered.

## 2.2. Controlled-release fertilizers (CRFs)

Numerous studies have shown the effectiveness of CRFs like coated urea to mitigate  $\text{N}_2\text{O}$  emissions compared to conventional fertilizers [9, 44]. Ref. [9], for example, recorded a reduction of  $\text{N}_2\text{O}$  emissions of 42% with polymer-coated urea when compared with urea in no-till and strip-till environments for irrigated corn in Colorado. It was shown in a global meta-analysis that—while  $\text{N}_2\text{O}$  emissions from urea were high—coated urea had one of the lowest emission factors and manure was somewhat in the middle among all investigated fertilizers [34]. Ref. [14] found a reduction of  $\text{N}_2\text{O}$  emissions by 35% compared with conventional fertilizers when CRFs were applied. However, the effectiveness varied depending on the soil and land use type. CRFs were very effective for imperfectly drained Gleysol grassland (77%  $\text{N}_2\text{O}$  reduction) but ineffective for well-drained Andosol upland field. Land use type seems to be a strong factor controlling  $\text{N}_2\text{O}$  emissions after CRF application [14, 44–46]. Ref. [46] evaluated the effects of soil and fertilizer types on oil palm plantations using urea and coated urea and sandy loam, sandy, and peat soil. They found high variations in the  $\text{N}_2\text{O}$  emissions dependent on the treatments with sandy soil emitting the lowest and peat soil the highest emissions overall. Coated urea reduced  $\text{N}_2\text{O}$  emissions by around 40% in the sandy loam soil compared to the conventional fertilizer, but emissions increased in the other soils during dry season. In a study that tested an NI (DCD) and coated urea on two contrasting soils, Andosol and Fluvisol, the NI only significantly reduced  $\text{N}_2\text{O}$  emissions (compared to urea) in Andosol, and nitrification was the dominant process compared to Fluvisol. For coated urea,  $\text{N}_2\text{O}$  emissions even increased in the Andosol and were ineffective in the Fluvisol. The authors concluded that varying activities in the main  $\text{N}_2\text{O}$  production processes, nitrification and denitrification, in the different soils were responsible for the contrasting results of the EEFs [45].

## 2.3. Organic amendments

The role of OAs in altering  $\text{N}_2\text{O}$  emissions is problematic [15, 20]. Organic amendments directly contribute to  $\text{N}_2\text{O}$  emissions through N transformation processes. OAs also indirectly influence  $\text{N}_2\text{O}$  emissions, e.g., through altering the soil pH or through their C:N ratio. A high C:N ratio increases soil organic matter; however, a low C:N ratio may increase  $\text{N}_2\text{O}$  emissions from soils [20–22, 47].

The results concerning  $\text{N}_2\text{O}$  emissions after OA application are contradictory and also depend on which OA is applied. Some studies report reduced or similar  $\text{N}_2\text{O}$  emissions after OA application when compared to conventional fertilizers. Ref. [19] tested the effects of composted pig manure compared to a conventional fertilizer (ammonium nitrate) on  $\text{N}_2\text{O}$  emissions.

After 7 years of applying both fertilizers, they found (14 months after the last application) that denitrification rates were higher in the pig compost treatment probably due to higher organic C contents and microbial biomass. However,  $N_2O$  emissions were lower, possibly due to high organic C contents and higher pH which favors  $N_2$  production. The authors concluded that even though denitrifier activity increased under pig compost, it is still a vital option to reduce  $N_2O$  emissions if the conditions are more favorable for  $N_2$  production.

However, OA application can also increase  $N_2O$  emissions through increased denitrification rates. The decreases in soil pH and the subsequent enhanced microbial respiration lead to a decrease in the redox potential which provides good conditions for denitrifiers [20, 21]. Other factors favoring denitrification are increased soil moisture (which leads to decreasing  $O_2$  concentrations) and using residues with a high N content and low C/N ratios. In a 28 day study by [21], different residues (leguminous species and ryegrass) were incorporated into loamy sand soil with different soil moisture levels. The authors found that  $N_2O$  emissions mainly derived from denitrification and were stimulated after residue application in all treatments. However, the level of emissions strongly depended on soil moisture and residue quality. The incorporation of legumes, which are characterized by high N contents and low C/N ratios, induced faster and greater emissions than ryegrass and control soil. Thus, higher soil moisture and residues with a low C/N ratio like lettuce or clover can lead to higher  $N_2O$  emissions [21, 23].

Especially when applied to soils with low C content, animal manure and slurry tend to increase  $N_2O$  emissions because of their large readily available C and N concentrations. The newly available C leads to a sudden rise in microbial activity and  $O_2$  consumption which creates anaerobic conditions favorable for denitrification [20].

A meta-study that analyzed crop residue effects on  $N_2O$  emissions found no statistically significant effect on  $N_2O$  emissions when averaged across all studies [22]. They concluded that the quantity of  $N_2O$  emissions from OAs like residues depends on many factors including synthetic N fertilizer application, residue type, and application method, as well as land use type. For example, compared to controls,  $N_2O$  emissions were decreased by 12% when applied together with synthetic fertilizers but increased by 42% if only residues were applied. The combination of chemical fertilizer with crop residues seems to inhibit  $N_2O$  emissions through decreased dissolved organic carbon (DOC) in the soil, thus decreasing denitrification rates.  $N_2O$  emissions highly depended on land use type and were decreased by 27% in paddy fields but increased by 93 and 24% in fallows and uplands, respectively. For upland soil, the application of residues led to favorable (increased) water and soil temperature conditions for microbes related to  $N_2O$  emissions. The application method can also influence  $N_2O$  emissions. For example, mulching of crop residues, which seems to enhance microbial activity, increased emissions by 63%, while ditch mulching, burying, and burning all decreased emissions by around 27%. Also, lettuce and bean residues enhanced  $N_2O$  emissions by 123 and 138%, respectively, probably due to their low C/N ratios of 7.5 and 12, respectively [22]. An incubation study that assessed the effects on  $N_2O$  emissions of a wide range of C/N ratios of plant residues with or without urea also found that lower C/N ratios led to higher DOC concentrations which increased  $N_2O$  emissions. They also found that the residue treatments increased, while residues + urea decreased DOC which affected  $N_2O$  emissions [47].



More studies are necessary to evaluate the effectiveness of OAs in reducing  $N_2O$  emissions. OA application mainly affects soil parameters like moisture, pH,  $O_2$  concentration, and substrate availability; however, these factors are the main influencers of nitrification and denitrification processes. Possibilities to influence and mitigate  $N_2O$  emissions after OA application mainly arise from changing the management practices, e.g., cultivation practices and application rates. To avoid  $NH_3$  volatilization, OAs should be incorporated into the soil to avoid contact with the atmosphere; however, this might increase  $N_2O$  emissions due to higher N availability in the soil [20].

A possible option to mitigate  $N_2O$  emissions from OAs is to combine them with EEFs. In combination with NIs,  $N_2O$  emissions from liquid manure like cattle slurry or pig manure can be greatly reduced [15, 48–50]. [48] tested the effect of the NI DMPP in reducing  $N_2O$  emissions from grassland after cattle slurry application. They found that DMPP reduced cumulative  $N_2O$  emissions by 69 and 48% in autumn and spring, respectively. In another study using pig manure on irrigated rice in a Mediterranean environment, DMPP also reduced  $N_2O$  emissions [50]. But so far, studies on the combination of OAs with NIs are scarce compared to the single treatments.

In summary, OAs have the potential to be environmental-friendly if soil parameters like moisture and pH are carefully evaluated, and the best management practices, e.g., no tillage or split application, are applied. In addition, careful assessment of optimal OA rates, improved timing of OA application, and crop N demand or using a combination of OAs and stabilized fertilizers are some of the options to decrease  $N_2O$  emissions after OA application [20].

### 3. Conclusion and recommendations

Overall, the N budget has to be understood first to estimate the potential benefit of EEF on  $N_2O$  emissions.  $N_2O$  emission peaks and the annual contribution of different periods (e.g., sowing, after harvest, rainy season) have to be assessed to determine the use of EEF effectively. Also, the contribution of nitrification, denitrification, and other processes concerning N turnover needs to be assessed in more detail. Especially, microbes, the drivers of these processes, need to be addressed in terms of changes in their activity, community structure, and abundance after EEF application and the subsequent changes in N turnover processes. In summary, more studies are necessary to assess the overall effectiveness of EEFs since their power in mitigating  $N_2O$  emissions varies with many factors. An individual fertilizer plan and type which is optimized for the prevalent climate conditions, soil type, management practice, etc. would be optimal in order to effectively reduce  $N_2O$  emissions. The use of EEFs has to be combined with the assessment of an N balance approach to fully exploit their potential.

### Conflict of interest

The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other



equity interests; and expert testimony or patent-licensing arrangements) or nonfinancial interest (such as personal or professional relationships, affiliations, knowledge, or beliefs) in the subject matter or materials discussed in this manuscript.

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## References

- [1] Erisman JW, Sutton MA, Galloway J, et al. How a century of ammonia synthesis changed the world. *Nature Geoscience*. 2008;**1**:636-639
- [2] Allito B, Nana E-M, Alemneh A. Rhizobia strain and legume genome interaction effects on nitrogen fixation and yield of grain legume: A review. *Molecular Soil Biology*. 2015;**6**:1-12
- [3] Ferguson BJ, Mens C, Hastwell AH, et al. Legume nodulation: The host controls the party. *Plant, Cell & Environment*. 2018:1-11
- [4] Timilsena YP, Adhikari R, Casey P, et al. Enhanced efficiency fertilisers: A review of formulation and nutrient release patterns. *Journal of the Science of Food and Agriculture*. 2015;**95**:1131-1142
- [5] Galloway JN, Townsend AR, Erisman JW, et al. Transformation of the nitrogen cycle. *Science*. 2008;**320**:889-892
- [6] Galloway JN, Dentener FJ, Capone DG, et al. Nitrogen Cycles: Past, Present, and Future. *Biogeochemistry*. 2004;**70**(2):153-226. DOI: 10.1007/s10533-004-0370-0
- [7] Inselsbacher E, Hinko-Najera Umana N, Stange FC, et al. Short-term competition between crop plants and soil microbes for inorganic N fertilizer. *Soil Biology and Biochemistry*. 2010;**42**:360-372
- [8] Trenkel ME. Slow and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Use Efficiency in Agriculture. Paris: International Fertilizer Industry Association (IFA); 2010. DOI: 10.1017/CBO9781107415324.004. [Epub ahead of print]
- [9] Halvorson AD, Snyder CS, Blaylock AD, et al. Enhanced-efficiency nitrogen fertilizers: Potential role in nitrous oxide emission mitigation. *Agronomy Journal*. 2014;**106**:715-722
- [10] Azeem B, Kushaari K, Man ZB, et al. Review on materials & methods to produce controlled release coated urea fertilizer. *Journal of Controlled Release*. 2014;**181**:11-21

- [11] Li X, Li Q, Xu X, et al. Characterization, swelling and slow-release properties of a new controlled release fertilizer based on wheat straw cellulose hydrogel. *Journal of the Taiwan Institute of Chemical Engineers*. 2016;**60**:564-572
- [12] Hatfield JL, Venterea RT. Enhanced efficiency fertilizers: A multi-site comparison of the effects on nitrous oxide emissions and agronomic performance. *Agronomy Journal*. 2014;**106**:679-680
- [13] Burton DL, Li X, Grant CA. Influence of fertilizer nitrogen source and management practice on N<sub>2</sub>O emissions from two black Chernozemic soils. *Canadian Journal of Soil Science*. 2008;**88**:219-227
- [14] Akiyama H, Yan X, Yagi K. Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N<sub>2</sub>O and NO emissions from agricultural soils: Meta-analysis. *Global Change Biology*. 2010;**16**:1837-1846
- [15] Ruser R, Schulz R. The effect of nitrification inhibitors on the nitrous oxide (N<sub>2</sub>O) release from agricultural soils—A review. *Journal of Plant Nutrition and Soil Science*. 2015;**178**:171-188
- [16] Martins MR, Sant'Anna SAC, Zaman M, et al. Strategies for the use of urease and nitrification inhibitors with urea: Impact on N<sub>2</sub>O and NH<sub>3</sub> emissions, fertilizer-<sup>15</sup>N recovery and maize yield in a tropical soil. *Agriculture, Ecosystems and Environment*. 2017;**247**:54-62
- [17] Naz MY, Sulaiman SA. Slow release coating remedy for nitrogen loss from conventional urea: A review. *Journal of Controlled Release*. 2016;**225**:109-120
- [18] Yamamoto CF, Pereira EI, Mattoso LHC, et al. Slow release fertilizers based on urea/urea-formaldehyde polymer nanocomposites. *Chemical Engineering Journal*. 2016;**287**:390-397
- [19] Dambreville C, Hallet S, Nguyen C, et al. Structure and activity of the denitrifying community in a maize-cropped field fertilized with composted pig manure or ammonium nitrate. *FEMS Microbiology Ecology*. 2006;**56**:119-131
- [20] Thangarajan R, Bolan NS, Tian G, et al. Role of organic amendment application on greenhouse gas emission from soil. *Science of the Total Environment*. 2013;**465**:72-96
- [21] Li X, Sørensen P, Olesen JE, et al. Evidence for denitrification as main source of N<sub>2</sub>O emission from residue-amended soil. *Soil Biology and Biochemistry*. 2016;**92**:153-160
- [22] Shan J, Yan X. Effects of crop residue returning on nitrous oxide emissions in agricultural soils. *Atmospheric Environment*. 2013;**71**:170-175
- [23] Baggs EM, Rees RM, Smith KA, et al. Nitrous oxide emission from soils after incorporating crop residues. *Soil Use and Management*. 2000;**16**:82-87
- [24] Forster P, Ramaswamy V, Artaxo P, et al. Changes in atmospheric constituents and in radiative forcing (IPCC 2007). In: Solomon S, Qin D, Manning M, et al., editors.

Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press; 2007. pp. 130-234

- [25] Syakila A, Kroeze C. The global nitrous oxide budget revisited. *Greenhouse Gas Measurement and Management*. 2011;**1**(1):17-26
- [26] Bouwman AF, Boumans LJM, Batjes NH. Emissions of N<sub>2</sub>O and NO from fertilized fields: Summary of available measurement data. *Global Biogeochem Cycles*. 2002;**16**: 6-1-6-113
- [27] Snyder CS, Bruulsema TW, Jensen TL, et al. Review of greenhouse gas emissions from crop production systems and fertilizer management effects. *Agriculture, Ecosystems and Environment*. 2009;**133**:247-266
- [28] Ravishankara AR, Daniel JS, Portmann RW. Nitrous oxide (N<sub>2</sub>O): The dominant ozone-depleting substance emitted in the 21st century. *Science*. 2009;**326**:123-125
- [29] IPCC. Climate Change 2014: Mitigation of Climate Change. Cambridge, England: Cambridge University Press; 2015
- [30] Reay DS, Davidson EA, Smith KA, et al. Global agriculture and nitrous oxide emissions. *Nature Climate Change*. 2012;**2**:410-416
- [31] Van Kessel MAHJ, Speth DR, Albertsen M, et al. Complete nitrification by a single microorganism. *Nature*. 2015;**528**:555-559
- [32] Qiao C, Liu L, Hu S, et al. How inhibiting nitrification affects nitrogen cycle and reduces environmental impacts of anthropogenic nitrogen input. *Global Change Biology*. 2015;**21**:1249-1257
- [33] Wrage-Mönnig N, Horn MA, Well R, et al. The role of nitrifier denitrification in the production of nitrous oxide revisited. *Soil Biology and Biochemistry*. 2018;**123**:A3-A16
- [34] Shcherbak I, Millar N, Robertson GP. Global metaanalysis of the nonlinear response of soil nitrous oxide (N<sub>2</sub>O) emissions to fertilizer nitrogen. *Proceedings of the National Academy of Sciences of the United States of America*. 2014;**111**:9199-9204
- [35] EPA. Global anthropogenic non-CO<sub>2</sub> greenhouse gas emissions: 1990-2030. How to obtain copies how to obtain the data for further information. Off Atmos Programs Clim Chang Div US Environ Prot Agency: 1990-2030; 2011
- [36] Yamamoto A, Uchida Y, Akiyama H, et al. Continuous and unattended measurements of the site preference of nitrous oxide emitted from an agricultural soil using quantum cascade laser spectrometry with intercomparison with isotope ratio mass spectrometry. *Rapid Communications in Mass Spectrometry*. 2014;**28**:1444-1452
- [37] Baggs EM. A review of stable isotope techniques for N<sub>2</sub>O source partitioning in soils: Recent progress, remaining challenges and future considerations. *Rapid Communications in Mass Spectrometry*. 2008;**22**:1664-1672

- [38] Shim JH, Powers HH, Meyer CW, et al. Hydrologic control of the oxygen isotope ratio of ecosystem respiration in a semi-arid woodland. *Biogeosciences Discussions*. 2013;**10**:1-48
- [39] Di HJ, Cameron KC. How does the application of different nitrification inhibitors affect nitrous oxide emissions and nitrate leaching from cow urine in grazed pastures? *Soil Use and Management*. 2012;**28**:54-61
- [40] Cui M, Sun X, Hu C, et al. Effective mitigation of nitrate leaching and nitrous oxide emissions in intensive vegetable production systems using a nitrification inhibitor, dicyandiamide. *Journal of Soils and Sediments*. 2011;**11**:722-730
- [41] Zhang M, Fan CH, Li QL, et al. A 2 year field assessment of the effects of chemical and biological nitrification inhibitors on nitrous oxide emissions and nitrogen use efficiency in an intensively managed vegetable cropping system. *Agriculture, Ecosystems and Environment*. 2015;**201**:43-50
- [42] Lam SK, Suter H, Mosier AR, et al. Using nitrification inhibitors to mitigate agricultural N<sub>2</sub>O emission: A double-edged sword? *Global Change Biology*. 2017;**23**:485-489
- [43] Rose TJ, Wood RH, Rose MT, et al. A re-evaluation of the agronomic effectiveness of the nitrification inhibitors DCD and DMPP and the urease inhibitor NBPT. *Agriculture, Ecosystems and Environment*. 2018;**252**:69-73
- [44] Uchida Y, von Rein I, Akiyama H, et al. Contribution of nitrification and denitrification to nitrous oxide emissions in Andosol and from Fluvisol after coated urea application. *Soil Science & Plant Nutrition*. 2013;**59**:46-55
- [45] Akiyama H, Uchida Y, Tago K, et al. Effect of dicyandiamide and polymer coated urea applications on N<sub>2</sub>O, NO and CH<sub>4</sub> fluxes from Andosol and Fluvisol fields. *Soil Science & Plant Nutrition*. 2015;**61**:541-551
- [46] Sakata R, Shimada S, Arai H, et al. Effect of soil types and nitrogen fertilizer on nitrous oxide and carbon dioxide emissions in oil palm plantations. *Soil Science & Plant Nutrition*. 2015;**61**:48-60
- [47] Huang Y, Zou J, Zheng X, et al. Nitrous oxide emissions as influenced by amendment of plant residues with different C:N ratios. *Soil Biology and Biochemistry*. 2004;**36**:973-981
- [48] Merino P, Merino P, Menéndez S, et al. 3,4-Dimethylpyrazole phosphate reduces nitrous oxide emissions from grassland after slurry application. *Soil Use and Management*. 2005;**21**:53-57
- [49] Misselbrook TH, Cardenas LM, Camp V, et al. An assessment of nitrification inhibitors to reduce nitrous oxide emissions from UK agriculture. *Environmental Research Letters*; 2014;**9**. DOI: 10.1088/1748-9326/9/11/115006. [Epub ahead of print]
- [50] Guardia G, Cangani MT, Sanz-Cobena A, et al. Management of pig manure to mitigate NO and yield-scaled N<sub>2</sub>O emissions in an irrigated Mediterranean crop. *Agriculture, Ecosystems and Environment*. 2017;**238**:55-66