REVIEW ARTICLE

Nitrous oxide emissions in agricultural soils: a review[1]

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RESUMO

Emissões de óxido nitroso em solos agrícolas: uma revisão

A concentração atmosférica de gases do efeito estufa tem aumentado de forma significativa, desde o início da Revolução Industrial. Dentre os principais gases estão o CO_2, CH_4 e N_2O, sendo que o CH_4 e N_2O apresentam 25 e 298 vezes maior potencial de aquecimento global que o CO_2. Grande parte das emissões de N_2O ocorre nos solos e está relacionada a atividades agrícolas. Neste sentido, esta revisão objetivou apresentar os mecanismos de formação e emissão de N_2O em solos agrícolas e reunir e discutir informações sobre como as práticas de manejo do solo podem ser usadas para reduzir tais emissões. A formação de N_2O no solo se dá, principalmente, pelos processos de nitrificação e desnitrificação, que são influenciados por fatores como umidade, temperatura, presença de oxigênio, teores disponíveis de carbono orgânico e de nitrogênio e relação C/N do solo. Dentre estes fatores, aqueles relacionados ao solo podem facilmente ser alterados por práticas de manejo. Portanto, conhecer os processos de formação do N_2O nos solos e compreender os fatores que alteram as emissões é fundamental para que sejam desenvolvidas medidas eficientes de redução das emissões de N_2O em solos agrícolas.

PALAVRAS-CHAVE: Emissão de gases do efeito estufa; nitrificação; desnitrificação.

ABSTRACT

The greenhouse gases concentration in the atmosphere have significantly increased since the beginning of the Industrial Revolution. The most important greenhouse gases are CO_2, CH_4 and N_2O, with CH_4 and N_2O presenting global warming potentials 25 and 298 times higher than CO_2, respectively. Most of the N_2O emissions take place in soils and are related with agricultural activities. So, this review article aimed at presenting the mechanisms of N_2O formation and emission in agricultural soils, as well as gathering and discussing information on how soil management practices may be used to reduce such emissions. The N_2O formation in the soil occurs mainly through nitrification and denitrification processes, which are influenced by soil moisture, temperature, oxygen concentration, amount of available organic carbon and nitrogen and soil C/N ratio. Among these factors, those related to soil could be easily altered by management practices. Therefore, understanding the processes of N_2O formation in soils and the factors influencing these emissions is fundamental to develop efficient strategies to reduce N_2O emissions in agricultural soils.

KEY-WORDS: Greenhouse gases emission; nitrification; denitrification.

INTRODUCTION

Life on Earth depends on a temperature range controlled by the greenhouse effect. Changes in the concentration of greenhouse gases (GHG), mainly carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), have occurred in the past years and have been related to the increase in global temperature. Among those gases, N_2O is of great importance because it can stand in the atmosphere for more than 114 years and has a warming potential 298 times greater than CO_2.

Global N_2O emissions reach about 17.7 Tg of N per year, being 6.7 Tg (37.8%) from anthropic sources. Agricultural soils share 2.8 Tg of N per year, i.e., 15.3% of the total amount of emissions, or 41.8% of anthropic emissions (Denman et al. 2007). According to the second Brazilian GHG inventory, N_2O emissions were about 576 Gg, in 2005, i.e., 7.7% of the national emissions, which reached 2,200 Tg of CO_2-eq (Brasil 2010). The agriculture sector was responsible for about 87.2% of N_2O emissions, mainly from animal waste management and agricultural soils (Cerri et al. 2009).

If we consider the importance of N_2O as a GHG and how much agricultural soils contribute to originate it, the development of strategies to decrease N_2O in the atmosphere should necessarily include agricultural practices. So, this review article aimed at presenting the mechanisms of N_2O formation and emission in agricultural soils, as well as gathering and discussing information on how soil management practices may be used to reduce such emissions.

ATMOSPHERE AND GREENHOUSE EFFECT

The Earth's atmosphere is basically composed by nitrogen (N_2) (78%) and oxygen (O_2) (21%) (Le Treut et al. 2007). One third of the solar radiation that intercepts the outer atmosphere is bounced back to space. The remaining two thirds pass through the atmosphere and are absorbed by the Earth's surface and by the atmosphere itself. Then, the surface emits back longwave radiation in the form of infrared rays. A great amount of this energy is absorbed by the atmosphere and re-emitted to the Earth's surface. This process is known as greenhouse effect and, without this mechanism, the Earth's surface temperature would be below the water freezing point and life as we know would not exist (Le Treut et al. 2007).

Water vapor and CO_2 are the most important GHG, but other gases such as CH_4, N_2O, ozone, halocarbons and aerosol can also increase the atmosphere temperature (Le Treut et al. 2007). Although water vapor is the main GHG in the atmosphere, it is little affected by human activities (Forster et al. 2007), while CO_2, CH_4 and N_2O are greatly influenced by them. Thus, these three gases are considered the most important ones related to the greenhouse effect.

Each GHG absorbs the infrared radiation and re-emits it as heat, increasing the atmosphere temperature, what is called global warming potential (GWP). The GWP is characteristic of each gas (Snyder et al. 2009) and is assigned as a function of its life time in the atmosphere and rated in relation to CO_2, since this is the most abundant GHG in the atmosphere. Therefore, considering a time horizon of 100 years, CH_4 has a life time of 12 years and a GWP of 25 and N_2O has a life time of 114 years and a GWP of 298 (Forster et al. 2007).

The atmospheric CO_2 concentration was about 280 ppm (parts per million), until 1750 (Industrial Revolution), and increased to 380 ppm, in 2005. This increase was mainly caused by fossil fuels burning,

cement industry and deforestation. Emissions of CH_4 result from fossil fuel combustion, biomass burning, paddy fields, landfill and cattle breeding (Denman et al. 2007, Forster et al. 2007). The concentration of CH_4 in the atmosphere has ranged between 400 ppb (parts per billion), during glacial periods, and 700 ppb, during interglacial periods, while present day concentrations reach 1,774 ppb (Denman et al. 2007, Forster et al. 2007).

The N_2O concentration in the atmosphere increased (Denman et al. 2007, Forster et al. 2007, Le Treut et al. 2007) from 270 ppb, during the pre-industrial period, up to 319 ppb, in 2005 (IPCC 2007). The main sources of N_2O are the application of N-fertilizers on soil, fossil fuel combustion and some natural mechanisms that occur in terrestrial and aquatic ecosystems. The annual increase rate varies from 0.2% to 0.3%.

Table 1 shows the main sources of N_2O in the world, during the 1990 decade, discriminating anthropic and natural sources. Almost 38% of the global emissions were related to anthropic sources, and agriculture is the main component, with 15.82% of global emissions. In Brazil, N_2O emissions from agricultural soils were estimated in 457 Gg, in 2005 (Brasil 2010). Thus, any strategy that aims at decreasing the GHG atmospheric concentration has to focus on the agricultural sector, because this is the main source of N_2O. Moreover, the reduction of N lost to the atmosphere as N_2O can increase the N use efficiency, as it increases the amount of N available to plants, increasing crop yields.

NITROUS OXIDE

The nitrogen cycle is presented in Figure 1. Atmospheric N_2 is fixed into ammonia (NH_3) by free-living and symbiotic bacteria and archaea (diazotrophs), using the nitrogenase enzyme, the universal catalyst, to break the N_2 triple bond. In soil, NH_3 can be converted into ammonium ion (NH_4^+), which can be oxidized to nitrate ion (NO_3^-), in a three-step process called nitrification. Nitrite (NO_2^-) and NO_3^- ions are generated during nitrification and they may be reduced during the denitrification process, that is the stepwise reduction of NO_3^- to N_2 by four enzymes, generating intermediate products: NO_2^-, NO and N_2O. During the NO_3^- ammonification to NH_4^+, via NO_2^-, it can also occur NO_3^- reduction, thus producing N_2O (Thomson et al. 2012).

Table 1. Main sources of N_2O to the atmosphere.

| Source	N-N_2O (Tg N year^{-1})		
	World (1990)*	Brazil (1990)**	Brazil (2005)**
Anthropic			
Fossil fuel combustion and industrial processes	0.700	0.009	0.020
Agriculture	2.800	0.210	0.310
Land use change and forests	-	0.009	0.010
Others	3.200	0.006	0.009
Total anthropic sources	6.700	0.230	0.350
Natural			
Soils under native vegetation	6.600		
Oceans	3.800		
Lightning bolts	-		
Atmospheric chemistry	0.600		
Total natural sources	11.000		
Total	17.700		

* Denman et al. (2007); ** Brasil (2010).
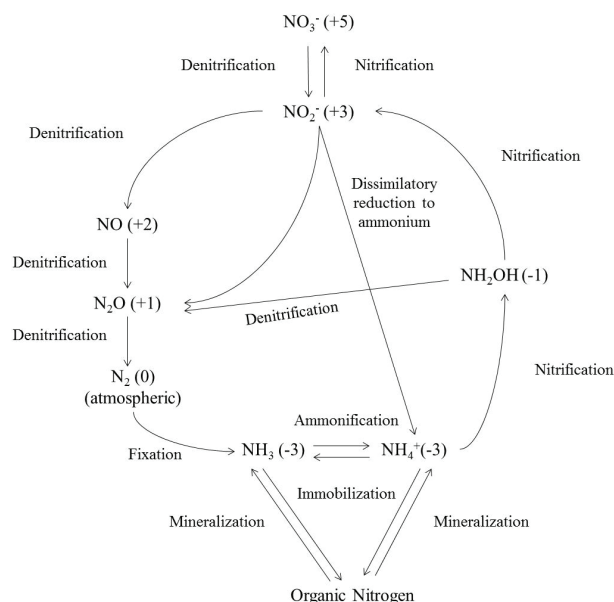
Figure 1. Nitrogen cycle. The oxidation states of N are given in parentheses and the name of processes are indicated.

SYNTHESIS OF N_2O IN THE SOIL

Several concurrent processes are responsible for nitrogen gases emissions in agricultural soils (Bockman & Olfs 1998, Stevens & Laughlin 1998). Most of the N_2O is produced through the biological processes of nitrification and denitrification. Autotrophic aerobic nitrification (by ammonia-oxidizing bacteria and nitrite-oxidizing bacteria) and anaerobic denitrification, mediated by denitrifying bacteria, are the main microbial processes in the nitrogen cycle in the soil. Other microorganisms are involved in nitrification and denitrification processes: anammox bacteria can convert NH_4^+ and NO_2^- into N_2, under anaerobic conditions, while some fungi can produce N_2 and N_2O by denitrification and codenitrification, and archeae mediate nitrification in marine ecosystems and are capable of promoting denitrification in soils (Hayatsu et al. 2008)

A small fraction of N_2O is produced in non-biological processes: the chemical decom-position of nitrite (chemidenitrification) and hydroxylamine oxidation (NH_2OH) (Bremner 1997). Chemidenitrification is the decomposition of NO_2^- that occurs in neutral and acidic soils, causing volatilization and fixation of NO_2^- in the soil organic matter (Bremner et al. 1980, Bremner 1997). The amount of N_2O produced this way is almost negligible (Bremner et al. 1980, Bremner 1997). Hydroxylamine is an intermediate compound in the oxidation of NH_4^+ to NO_3^- that can produce much more N_2O than the chemidenitrification process (Bremner 1997). In neutral and acidic soils, N_2O is the main product of the NH_2OH oxidation, due to its reaction with Mn and Fe, while in calcareous soils (pH from 7.8 to 8.2) the NH_2OH reacts with $CaCO_3$ and the main product is N_2 (Bremner et al. 1980).

Nitrification and denitrification processes are further discussed, since they are the most important ones to the N_2O formation in soils. Nitrification is the aerobic oxidation of NH_4^+ to NO_3^- caused by chemoautotrophic bacteria in two stages: nitritation, in which the NH_4^+ is oxidized

to NO_2^- by *Nitrosomonas* sp., *Nitrosospira* sp. and *Nitrosococcus* sp.; and nitratation, in which the NO_2^- is oxidized to NO_3^- by *Nitrobacter* sp., *Nitrosospira* sp. and *Nitrococcus* sp. (Moreira & Siqueira 2006). In general, nitrification can be summarized by the following reactions: nitritation: $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + H_2O + 4H^+ + energy$; nitratation: $2NO_2^- + O_2 \rightarrow 2NO_3^- + energy$. During this process, the NO_2^- concentration increases as NH_4^+ is being oxidized and then decreases as NO_3^- is being formed.

Denitrification is the reduction process of NO_3^- to N_2, mediated by facultative anaerobic bacteria, which correspond to 0.1-5.0% of the total bacteria population in the soil (Moreira & Siqueira 2006). This process can be complete, resulting in N_2, or can be incomplete, and a variable fraction of N can be emitted as NO and N_2O (Figure 1).

Despite denitrification is responsible for the most part of the N_2O produced in the soil, nitrification can also produce N_2O, when O_2 is limited. Bremner (1997) presented results from many researches which showed that nitrifying microorganisms can significantly contribute to N_2O emissions from soils. According to this author, the N_2O production during nitrification is increased when the soil pH and organic matter content increase and with increase in soil moisture (from air dried to field capacity) and in soil temperature (5-40ºC), by addition of nitrifiable N forms, animal manures and plant residues. N_2O produced by nitrification can be decreased when nitrification inhibitors are used.

Under anaerobic condition, the concentration of NO_2^-, which is a toxic compost, increases in the soil (Khalil et al. 2004), and it may be alternatively used by the nitrifying microorganisms as an electron final acceptor, resulting in N_2O and NO during nitrification (Snyder et al. 2009), as it follows:

$$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$$
$$\downarrow$$
$$NO \rightarrow N_2O \rightarrow N_2$$
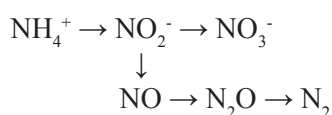
Synthesis and emission of N_2O by microbial processes result from complexes interactions among several factors, such as soil temperature, texture, structure and pH, availability of N, decomposable organic material and water (Bockman & Olfs 1998). Crop rotation, soil mobilization, N sources and rates, time and depth of N application interact and significantly influence the N_2O emission by

the soil (Liu et al. 2006, Tan et al. 2009, Signor et al. 2013).

FACTORS INFLUENCING N_2O PRODUCTION BY NITRIFICATION AND DENITRIFICATION

Despite the importance of N (NH_4^+ and NO_3^-) to nitrification and denitrification reactions, these processes are also influenced by soil characteristics, such as aeration, compaction, temperature, moisture, pH, organic matter, available N, C/N ratio, texture and also by soil management and crop rotation (Bremner 1997, Brentrup et al. 2000, Snyder et al. 2009). The main factors influencing emissions of N_2O from nitrification are temperature and soil density (Davidson & Swank 1986). On the other hand, emissions of N_2O from denitrification are mainly influenced by the amount of water filled pores space (WFPS).

Nitrification is strictly aerobic: NH_4^+ and NO_2^- oxidation are strongly diminished when the O_2 concentration is low (Khalil et al. 2004). Although denitrification is an anaerobic process, Khalil et al. (2004) observed that it can occur even at high O_2 pressure, because anaerobic conditions intra-aggregates are common in arable soils, what reduces the nitrification rate and increases the share of N emitted as N_2O. In general, under aerobic or semi-aerobic conditions, N_2O is produced by nitrifying microorganisms, while under anaerobic conditions it is produced by denitrifying microorganisms (Bremner 1997, Stevens et al. 1997, Khalil et al. 2004).

Akiyama et al. (2000) observed a decrease in the amount of NH_4^+ and increase in NO_3^- in the soil, during the N_2O peak of emission. As NO_3^- is being produced while NH_4^+ is being consumed, then the nitrification process is occurring and thus it was the main source of N_2O. Khalil et al. (2004) observed that N_2O emissions achieved a steady state when the nitrification also kept steady and NO_3^- concentration was minimal.

Temperature, moisture and aeration

Temperature and moisture are of great importance for nitrification and denitrification, because they determine the activity of microorganisms. Moreover, soil temperature and moisture strongly influence not only the N_2O production but also its diffusion to the atmosphere (Davidson & Swank

1986). Under mild temperatures, the rate of nitrogen conversion is small, increasing as temperature increases (Akiyama et al. 2000, Brentrup et al. 2000, Hao et al. 2001). However, in a wider range, N_2O emissions exponentially increase with increasing soil temperatures (0-50ºC) (Liu et al. 2011). This explains the existence of a close relationship among seasonal variation of N_2O flux and soil and air temperatures (Wolf & Brumme 2002, Zhang & Han 2008). It is important to highlight the positive feedback between temperature and denitrification rate: increasing soil temperatures stimulate soil respiration (microbial activity), also increasing anaerobic sites in which denitrification can take place.

In general, the greater the soil moisture, the greater will be the N_2O emission (Baggs et al. 2000, Giacomini et al. 2006), because both the nitrification and denitrification processes are influenced by moisture (Davidson & Swank 1986). However, under very high moisture contents, the N_2O production decreases, but when there are moisture alternations, with successive moist and dry periods, the N_2O emissions increase (Brentrup et al. 2000). This occurs because the soil water content increases microbial activity, but, under very high moistures, the microbial activity is inhibited.

Liu et al. (2011) showed that N_2O emissions initially increased and then decreased with increasing soil moisture. Perdomo et al. (2009) observed the largest N_2O flux after rain or during periods of high soil temperature. Liu et al. (2006) related large emissions of N_2O to rain or irrigation events and affirmed that the N_2O diffusion from soil to the atmosphere markedly increased just after rain, going back to normal after three days.

The expression of the genes encoding the enzymes that produce and consume N_2O is regulated by environmental signals, typically by low oxygen concentrations (Thomson et al. 2012). According to Brentrup et al. (2000), when the soil aeration is lower, N_2 is the main nitrogen gas emitted to the atmosphere. Soil aeration has a close relationship with soil moisture. The greater the WFPS, the smaller the number of soil pores filled with air, enhancing N_2O produced by denitrification. The amount of WFPS is also positively correlated with available carbon, nitrification potential and mineralization potential, confirming the importance of moisture to microbial activities and to reactions that produce N_2O in the soil (Davidson & Swank 1986). However,

very high water content in the soil decreases N_2O emissions (Liu et al. 2011). A general assumption is that the formation of N_2O in soils is benefited when the WFPS reaches approximately 80% (Bockman & Olfs 1998, Denmead et al. 2010).

Denitrification is the main source of N_2O in WFPS higher than 70%, but nitrification is the main process when the WFPS decreases to 60% (Ruser et al. 2006). Nevertheless, it is important to highlight that being the main process is not the same thing as having the higher emission rates.

Relief position

N_2O emissions may be influenced also by the relief position, since it affects other factors involved in the N_2O emissions, such as moisture dispersion, C organic content and soil fertility. The low relief areas tend to be more humid and to have greater organic matter content, when compared to higher lands. Therefore, microorganism respiration and oxygen consumption are potentially greater, influencing the N_2O production in low lands (Davidson & Swank 1986).

Soil characteristics

The proportion of N_2O in the total flux of N gases emitted from soils is also influenced by soil type (Stevens & Laughlin 1998). Clayey soils tend to show greater N_2O emissions than sandy soils (Brentrup et al. 2000), and N management may increase the emission of N_2O, particularly in soils of fine texture and without mobilization before seeding (Chen et al. 2008, Tan et al. 2009).

N_2O emissions induced by soil management practices and by rain were four times greater in a clay loam soil than in a loamy sand (Tan et al. 2009). In the clayey soil, the small amount of macropores would increase anaerobic microsites, also increasing N_2O emissions. Neill et al. (2005) reported that emissions in sandy soils occur with greater soil moisture than that necessary for similar emissions in a clayey soil.

Denitrification enzymes require a variety of metal cofactors, including Mo, Fe, Cu and Zn. The absolute requirement of nitrous oxide redutase (enzyme that reduces N_2O to N_2) for Cu accounts to the critical role of this element in denitrification. This is an important aspect, with agricultural and environmental implications (Thomson et al. 2012).

Soil pH is another important factor influencing N_2O emissions, because nitrous oxide redutase is inhibited by low pH and in the presence of O_2. Generally, if denitrification is the main source of N_2O, higher pH values decrease the soil N_2O emissions, but if nitrification is the main process of N_2O production, then an increase in the soil pH stimulates the N_2O production.

According to Bremner (1997), the production of N_2O by denitrification is favored by high concentrations of NO_3^- and low pH in incubated soils. For low pH values, the emission of N_2O would be greater, because a small amount of this gas would be reduced to N_2 (Chapuis-Lardy et al. 2007). Knowles (1982) affirmed that in soils with pH of 4.0, N_2O is the main product of denitrification. The increase in one unit of pH may decrease 0.2 units in the molar fraction of the N_2O emitted (Stevens & Laughlin 1998). Thus, the continuing acidification of agricultural soils through excessive use of nitrogen fertilizers could drastically enhance N_2O emissions, while the careful adjustment of soil pH by liming would reduce emissions (Thomson et al. 2012). The nitrification process (aerobic) tends to reduce the soil pH, while the denitrification (anaerobic) can increase the soil pH (Khalil et al. 2004).

Available carbon

Increasing the soil organic C content can increase the N_2O production (Brentrup et al. 2000). Furthermore, the soil moisture and soluble C content show a significant correlation with N_2O emissions, during residue decomposition (Ciampitti et al. 2008). Available C influences nitrification and denitrification reactions (Bremner 1997), because it can stimulate microbial growth and activity, and also provide the organic carbon needed by soil denitrifiers (Cameron et al. 2013). Additionally, microbial growth increases the consumption of O_2 and generates anaerobic conditions necessary for denitrification.

In Amazonian soils, peaks of N_2O emission occurred after the input of plant residues (Passianoto et al. 2003) and after the addition of labile carbon (dextrose) to soil (Carmo et al. 2005). However, the effect of organic matter depends on the degree of anaerobic conditions created by microbial metabolism (Stevens & Laughlin 1998). When moisture and N availability are not limiting to N_2O production, greater fluxes are observed in soils with high amounts of available organic carbon (Ruser et al. 2006).

C/N ratio

Nitrogen transformations in soils include two important biological processes: immobilization (or assimilation), that is the uptake of nitrogen by microorganisms and its conversion into organic nitrogen, and mineralization (or ammonification), that is the conversion of organic nitrogen to NH_3 (Figure 1). The balance between mineralization and immobilization depends on the soil C/N ratio and cultural residues added. Soil and residues with a small C/N ratio (lower than 30/1) present a dominance of mineralization over the immobilization, and the available N can be absorbed by plants or used in microbial processes.

The presence of straw with high C/N ratio on the soil surface may increase the immobilization of the N fertilizer applied (Baggs et al. 2000), and thus decrease the denitrification reactions and N_2O emissions. When no straw, or straw with a small C/N ratio, is present in the soil surface, the N immobilization probably will not occur, more N will be available for nitrification and denitrification processes and higher N_2O emissions may occur (Baggs et al. 2000).

Interaction of factors to explain N_2O emissions in soils

The model proposed by Firestone & Davidson (1989) satisfactorily represents the interactions and the control level of many factors involved in N_2O emissions in the soil. Also known as "hole-in-the-pipe", the model summarizes the influence of microbiological and ecological factors on NO and N_2O emissions by soils (Figure 2), suggesting that the production of NO and N_2O are related to available N in the soil.

The rate of N flowing through the pipe is the first level of control of NO and N_2O emissions and roughly represents the N cycling in the system. Amounts of NO and N_2O lost by the holes in the pipe are the second level of emission control, and are mainly related to soil moisture. The emissions of such gases depend on the balance among production, consumption and diffusive transport in soils.

In dry and well aerated soils, nitrification is the dominant process and the gas diffusion is greater,
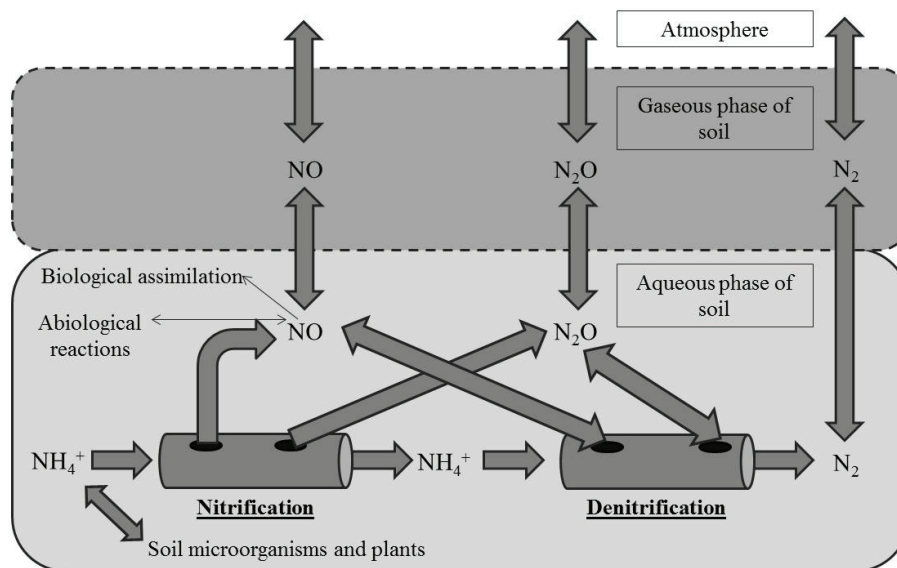
Figure 2. "Hole-in-the-pipe" model. Adapted from Davidson et al. (2000).

allowing a greater emission of the more oxidized form (NO), before it would be consumed in other processes. In moist soils, the rate of gas diffusion and aeration are smaller, and greater amount of NO would react before being released to the atmosphere. In such condition, the more reduced oxide (N_2O) would be the final dominant product released to the atmosphere. Under supersaturation conditions (anaerobic soil), most part of the N_2O is reduced to N_2, before being released to the atmosphere (Davidson et al. 2000).

SOIL AS A SINK OF N_2O

In spite of these reports on production and emission of N_2O, soils can sink N_2O from the atmosphere. This phenomenon is still poorly understood, but it can be extremely important in agricultural systems. Factors influencing the consumption of N_2O by soils are still unclear, but negative fluxes have been reported in a wide range of conditions frequently (but not always) associated to low availability of N and O_2 in soils, i.e., favorable conditions to reduce N_2O to N_2. The consumption of N_2O also depends on soil properties, water content, soil temperature, pH and availability of labile organic C and N. Such variety of conditions suggests that a great number of processes should be related to this phenomenon. The longer the N_2O remains in the soil, whether because it was produced in deeper layers or due to slow diffusion to the atmosphere, the greater

amounts of N_2O will be used as electron acceptor and greater will be the emissions of N_2 (Chapuis-Lardy et al. 2007).

MANAGEMENT FACTORS AFFECTING N_2O FORMATION

Despite the influence of climatic conditions on the N_2O production, soil management practices affecting factors previously described and benefiting microbial activity can also influence the N_2O production. Among them, soil tillage, recycling N from crop residues and the application of N-fertilizers (mineral or organic) are of great importance. However, there are considerable shortcomings in the current state of knowledge on how dynamic factors can control denitrification, and much of this is due to the high spatial and temporal variability of denitrification rates in the field (Groffman et al. 2009) and to the failure to include functional differences in the microbial composition, in models that estimate N_2O emissions (Cavigelli & Robertson 2001).

Soil tillage

The effects of soil tillage practices on N_2O emissions result from changes in the soil structure, soil aeration, microbial activity, rate of residue decomposition and rate of N mineralization, as well as soil temperature and moisture. No-tillage (NT)

have been reported as a soil management system that increases N_2O emissions, when compared to conventional tillage (CT) (Liu et al. 2006, Rochette 2008, Carvalho et al. 2009). In a subtropical Oxisol, in Brazil, N_2O emissions after harvest were three times higher in NT than in CT (Escobar et al. 2010). This can be explained by the greater population of denitrifier microorganisms in the NT than in the CT system (Linn & Doran 1984), the greater density of non-mobilized soils (Ball et al. 1999) and the maintenance of greater water content in NT soils (Baggs et al. 2003, 2006).

The higher soil moisture, due to the crop residue in NT (Baggs et al. 2006), can increase microbial activity near the soil surface, consuming the available O_2 and creating anaerobic microsites. Liu et al. (2011) studied N_2O emissions in a crop rotation system, in China, and showed that the incorporation of maize and wheat straw significantly increased the soil temperature, due to their heat-retaining property. This higher temperature could have stimulated the enzymatic activity of nitrifiers and denitrifiers, enhancing the microbial N_2O production. In the CT system, such mechanism would be dissipated by the tillage in the upper soil layer, which increases the O_2 concentration in soil and consequently decreases the N_2O emission, in spite of the greater mineralization rate of crop residue and organic matter promoted by soil tillage (Baggs et al. 2003, 2006). According to Baggs et al. (2000), most of N_2O emissions induced by residues incorporation occur in the first two weeks after this event.

Nevertheless, not all reports agree with greater emissions in NT. Metay et al. (2007) and Jantalia et al. (2008) did not observe differences in N_2O emissions between CT and NT, in the Brazilian Savannah and in South of Brazil. This was also reported by Liu et al. (2005), for an irrigated corn field in northeastern Colorado. N_2O emissions in NT areas with 12 and 22 years old, in Paraná State (Brazil), were similar and influenced by the crop rotation system (Siqueira Neto et al. 2009a). Perdomo et al. (2009) observed emissions four times greater in CT, as compared to NT, in Uruguay. Passianoto et al. (2003) estimated N_2O emissions during pasture restoration in the Amazon region and observed greater emissions in CT than in NT. Laboratory experiments conducted by Huang et al. (2004) have shown that soil tillage and plant residue mixed into soil increased N_2O and CO_2 emissions.

Six et al. (2004) affirm that areas with recent adoption of NT (up to 10 years old) show N_2O emissions higher than CT. In older NT areas, the behavior is different: NT in humid areas with 20 years old have lower emissions than CT, while, in dry areas, NT and CT have similar N_2O emissions. Van Kessen et al. (2013) also showed that NT in humid areas increases N_2O emissions in early years and then reduces them, in comparison to CT (NT for more than 10 years old). Omonode et al. (2011) showed that 30 years old NT areas presented N_2O emissions lower than CT. This occurs because, in areas with early NT system, the soil moisture is changed, favoring the denitrification process and thus causing N loss and inducing N deficiency in plants, reducing the crop production (Six et al. 2004). Many of these conclusions were drawn for temperate climate regions, but we believe that similar responses would be observed in tropical regions. Thus, in studies comparing different soil tillages, it is important to take into account the time since NT has been introduced.

Residues quality

The biochemical composition of plant residues added to the soil is responsible for higher or lower N_2O emissions (Gomes et al. 2009), because the maintenance of straw on the soil surface affects the N mobilization and immobilization and, consequently, the N availability in the soil, and also the nitrification and denitrification processes.

Liu et al. (2011) reported that wheat straw incorporation increased N_2O emissions in the subsequent maize season, while the incorporation of maize straw did not influence the emissions. Toma & Hatano (2007) observed greater N_2O emissions in plots receiving low C/N ratio residues, possibly because these residues are easily decomposable. In a NT crop system, in southern Brazil, soil N_2O emissions were lower after maize (higher C/N ratio) than after soybean harvest (lower C/N ratio) (Escobar et al. 2010).

Siqueira Neto et al. (2009b) measured greater N_2O emissions in areas cultivated with corn-wheat than in areas cultivated with soybean-wheat. They explained this by the high amount of N applied to the corn field, in contrast to the biological N (via microorganism fixation) used as N source by the soybean crop. Jantalia et al. (2008) reported that by

using N-fixing in legume crops, N_2O emissions were not altered in subsequent crops. In agreement with such finding, Siqueira Neto et al. (2009a) suggested that legume crops could be used as N source in agricultural systems, with the advantage of decreasing N_2O emissions, in comparison to N-fertilizers.

An interaction between straw C/N ratio and mineral N-fertilizer addition may occur, increasing nitrification and denitrification rates and, therefore, increasing the N_2O production and emission in agricultural soils. Liu et al. (2011) reported that the addition of wheat straw (C/N = 78.7) slightly decreased the mineral N content in the soil, due to the high C/N ratio, while the application of N-fertilizer in plots with this straw resulted in higher N_2O emissions than in plots without wheat straw. In this case, in plots with straw, the high C and N contents did not limit the N_2O biological production, while in plots without straw the C content limited the microbial activity and, thus, the N_2O production was lower.

N_2O emissions also depend on the phenological stage of the crop, or decomposition state of the residue, because this is related to the C/N rate. For soybean, N_2O emissions increased during the growing and maturity processes, comprising 68% of the total emissions of N_2O, during the crop cycle. Pastures with 4 and 10 years old had N_2O emissions similar or slightly smaller than in forest areas, while in pastures older than 10 years emissions were smaller than in forests (Neill et al. 2005). Fernandes Cruvinel et al. (2011) reported higher nitrate availability and N_2O fluxes during the senescence of bean and soybean and the post-harvest phase of cotton, which could be related to root mortality and N release from roots and nodules.

Nitrogen fertilization

Before 1950, less than 50% of N_2O emissions was caused directly or indirectly by the use of N-fertilizers in agriculture, being most of the emissions associated to animal breeding. As a result of the increase in food production and the consequent use of N-fertilizers, two thirds of the N_2O emissions were related to crop production, in 1996 (Mosier 2001).

Once the N_2O emissions by nitrification and denitrification depend on the N content in the soil (Akiyama et al. 2000), the rate of N_2O emissions is also related to the N-fertilizer applied

in the soil (Passianoto et al. 2003, Chen et al. 2008, Zanatta et al. 2010, Signor et al. 2013). The use of N-fertilizers influences directly the amount of NH_4^+ or NO_3^- available in the soil. The greater the amount of $N-NH_4^+$ in the fertilizer, the greater will be the nitrification process (Mosier 2001, Khalil et al. 2004, Liu et al. 2005). As a consequence, the loss of N_2O can also increase, because the NO_2^- formed during the nitrification process can be used as electron acceptor, if O_2 is limited, and also because the denitrification can occur after the nitrification, when soil conditions are favorable. Emissions of N_2O will also be greater when NO_3^- in the soil is high (Carmo et al. 2005, Ruser et al. 2006, Zanatta et al. 2010). When the NO_3^- availability decreases, N_2O emissions will also decrease, because denitrification is reduced (Hellebrand et al. 2008). On the other hand, N-fertilization implies a higher plant biomass production, and then more crop residues (and carbon sources) would be available in the soil, what could increase N_2O emissions for a long period, after the N-fertilizer application (Hellebrand et al. 2008).

A mathematical relationship between accumulated N_2O emission and amount of N applied as fertilizer is not well defined. Chen et al. (2008) and Zhang & Han (2008) affirm that this relation is linear and can be used to estimate N_2O emissions by soil, whereas Ma et al. (2010) presented results of N_2O emissions exponentially related to N-fertilization rates in maize crop fields, in Canada. Signor et al. (2013) showed that N_2O emissions in sugarcane fields increase as ammonium nitrate rates applied to the soil increase (exponential or linear relation), while N_2O emissions induced by urea reach a point of maximum that occurs around 114 kg N ha^{-1}.

In addition, the type of fertilizer also influences the behavior of N_2O emissions. In general, ammoniacal fertilizers increase N_2O emissions slower than nitric fertilizers, because nitric sources can be denitrified immediately, while ammonia sources still have to be nitrified before the denitrification.

Abbasi & Adams (2000) measured emissions three to eight times greater in soils treated with KNO_3, as compared to those receiving ammoniacal fertilizers. From 60% to 100% of N applied as fertilizer disappeared (by plant uptake or denitrification losses) seven days after the application of KNO_3, while the same effect was observed only 28 days after the application of ammoniacal N. Carmo et al. (2005) also observed that the application of

N-NO$_3$ in Amazonian soils increased N$_2$O emissions more than the N-NH$_4$ application. The use of N-NO$_3$ fertilizer increased N$_2$O emissions in 56%, while the use of N-NH$_4$ promoted an increase of only 15% (Delaune et al. 1998). Zanatta et al. (2010) studied the application of different N-fertilizers and N$_2$O emissions in southern Brazil and showed that nitric fertilizers induce larger N$_2$O emissions than amidic (urea) or ammonium fertilizers. Signor et al. (2013) studied N fertilization in two sugarcane fields, in Brazil, and showed that N$_2$O emissions induced by ammonium nitrate were more intense and faster than emissions induced by urea.

Velthof & Mosquera (2011) observed lower emissions from animal slurry than from calcium ammonium nitrate, for grassland, and attributed this to the uptake of ammonium present in the slurry, before it can be nitrified, reducing the N available for denitrification in the soil. Shimizu et al. (2013), studying N$_2$O emissions induced by mineral N-fertilizer and manure in five grassland areas, during six years, showed that the N$_2$O emission factor (proportion of applied N that is lost to the atmosphere as N$_2$O) of manure is lower than that of mineral fertilizer.

Pelster et al. (2012) evaluated N$_2$O emissions in two soil types (silty clay and sandy loam), for two years. They compared emissions induced by calcium ammonium nitrate, poultry manure, liquid cattle manure and liquid swine manure and suggested that the manure application only increases N$_2$O emissions in soils with low C content, i.e., in soils where C was limiting the biological production of N$_2$O. Nevertheless, there are some reports of no differences in N$_2$O emissions induced by different N sources.

Bergstrom et al. (2001) observed no differences in N$_2$O emissions induced by urea, ammonium sulfate and calcium nitrate. However, during 24 days of evaluation, these authors carried out just eight samplings. They also highlighted the limited number of measurements in each sampling day and the spatial variability on soil N$_2$O emissions to explain why they did not detect differences between N sources.

N$_2$O emissions induced by N-fertilizers are concentrated in some weeks after the fertilizer application. The largest N$_2$O fluxes occur during the first two weeks after the fertilizer application (Bergstrom et al. 2001, Liu et al. 2005, Liu et al. 2006, Schils et al. 2008), while the N effect on N$_2$O emissions disappear in two months after

the application (Zhang & Han 2008). Therefore, researches should give priority to measurements of N$_2$O emissions during the first two weeks after fertilization (Schils et al. 2008), with more interspaced measurements after this period.

N$_2$O emissions are reduced in cases of small availability of N in the soil (Yang & Cai 2007) and when small precipitations occur after the N application (Perdomo et al. 2009). In conditions of soil saturation (but not soaked), the split application of KNO$_3$ decreased the emission of N$_2$O, as compared to a single application (Ciarlo et al. 2008). However, if a single dose of N-fertilizer at seeding is followed by rain, it can produce elevated N$_2$O emissions (Tan et al. 2009). Splitting the doses of N-fertilizers increases their efficiency and reduces losses by leaching and denitrification, implying in benefits for reducing GHG emissions and ensuring natural resources preservation (Tan et al. 2009). Splitting N rates is also important to supply N during the crop cycle, mainly in periods in which it is more requested, ensuring a higher crop yield.

The fertilizer application depth also influences the N$_2$O emission (Liu et al. 2006). Van Kessen et al. (2013), in a meta-analysis study, showed that the application of N-fertilizer at more than 5.0 cm depth can decrease N$_2$O emissions, particularly in humid climates. Emissions are smaller when the N-fertilizer is deposited at 10.0 cm depth, as compared to the deposition at the soil surface or at 5.0 cm depth. The application at 10.0 cm depth increases the residence time of N$_2$O in the soil, also increasing the chance of its reduction to N$_2$ (Chapuis-Lardy et al. 2007).

However, Velthof & Mosquera (2011) showed that the application of cattle slurry by shallow or deep injection on grassland or maize land increased N$_2$O emissions, as compared to surface application. In this case, slurry applications in inner soil layers are indicated to reduce NH$_3$ volatilization and increase the amount of mineral N entering the soil. Moreover, the slurry injection increases the available C concentration in the soil and thus the microbial activity that also enhances the O$_2$ consumption and stimulates denitrification (Velthof & Mosquera 2011).

The interactions of N-fertilizers and other factors influencing N$_2$O emissions should also be highlighted. Fertilizer applications during dry weather result in small emissions of N$_2$O than the application under moist conditions (Smith et al. 1998, Schils et al. 2008, Zhang & Han 2008). Metay

et al. (2007) observed the greatest emission of N_2O when the application of fertilizer was concurrent to precipitation events, and Passianoto et al. (2003) reported intense emissions of N_2O induced by fertilizer associated to the first rain after the N application. However, with small N availability, even in conditions of high moisture content, emissions will be reduced (Denmead et al. 2010).

The use of slow releasing fertilizers is an important strategy to reduce N_2O emissions induced by N-fertilizers, because they are involved in slower nutrient release, despite the fact that the rate, patterns and duration of the release are not well controlled (Shaviv 2001). The use of controlled release N-fertilizer in southern Brazil promoted lower N_2O emissions, in comparison to ammonium nitrate, calcium nitrate, ammonium sulphate and uran (Zanatta et al. 2010).

Slow release fertilizers are classified in three groups: (i) organic-N low-solubility compounds, that include biologically and chemically decomposing products, as urea-formaldehyde and isobutyledene-diurea, respectively; (ii) fertilizers with a physical barrier, i.e., fertilizers coated with organic polymers (thermoplastic or resins) or inorganic materials (sulfur or mineral based) that can be hydrophobic or hydrophilic; (iii) inorganic low-solubility compounds, for example, metal ammonium phosphates and partially acidulated phosphates rocks (Shaviv 2001).

Jiang et al. (2010) demonstrated that N_2O emissions from coated urea (with calcium and magnesium phosphate, polymer or sulfur) were higher than from common urea emissions, especially when precipitation events occurred following basal N application. However, the application of urea-formaldehyde and urea with nitrification inhibitors (hydrochinone and dicyandiamide) reduced N_2O emissions and this was not accompanied by a decrease in the biomass production.

Moreover, N-fertilizers stabilized or bio-amended by inhibitors are classified as slow-acting nitrogen (Shaviv 2001). Nitrification inhibitors are also indicated as an important strategy to reduce N_2O emissions induced by N-fertilizers (Zanatta et al. 2010).

Di & Cameron (2012) observed that dicyandiamide (DCD) and 3,4-dimethylpyrazole phosphate (DMPP) reduced from 62% to 66% the N_2O emissions induced by urine on grazed pasture. During a two years study, Pfab et al. (2012) reported

that DMPP reduced N_2O emissions from 40% to 45%, without affecting cropping yields. DMPP reduces N_2O fluxes, but do not delay or change their temporal pattern, when compared to conventional fertilizer (Menéndez et al. 2012). The DMPP efficiency is dependent on temperature and soil water content. Menéndez et al. (2012) showed that, at 40% WFPS, the DMPP reduced emissions from 17% to 42%. However, at 80% WFPS, the DMPP efficiency decreased from 45% to 23%.

DCD and DMPP can also significantly increase the soil organic N, shift the main form of N in the soil (from NO_3^- to NH_4^+), increase the soil dissolved organic carbon, crop yield, aboveground biomass, C and N uptake by plants (Liu et al. 2013). However, the use of DCD for seven years, in three pasture soils, did not change the soil microbial C and N, protease and deaminase activities, and had no negative impact on the abundance of archea and bacteria in the soils, indicating the DCD as an effective N_2O mitigation technology (Guo et al. 2013). Despite the fact that slow release fertilizers and nitrification inhibitors may reduce N_2O emissions, they are more expensive than conventional fertilizers and have not been widely used (Cameron et al. 2013).

The International Panel on Climate Change (IPCC) suggests a methodology to estimate soil N_2O emissions, according to mineral and organic fertilizers, and also for the mineralization of N from crop residues added to soil. In these cases, it may be considered that 1% (uncertainty range from 0.3% to 3%) of the N added is converted into N_2O (IPCC 2006). This value, known as emission factor, was suggested to simplify the calculation in the life cycle study of agricultural crops (Brentrup et al. 2000).

Table 2 presents the emission factors reported in several papers, for many crops, where values vary from 0.03% to 21%. Schils et al. (2008) and Zhang & Han (2008) attribute the small emission factors they observed to the low soil water content. The high emission factor value reported by Denmead et al. (2010) (21%) was related to the combination of high concentration of organic carbon and frequent rain, causing many events of pore saturation and increasing the N_2O emission.

The emission factor seems to be directly influenced by the N dose. Chen et al. (2008) observed that the N_2O emission increased linearly with the increase of N rates. However, the largest emission factor occurred for the smallest N dose

Table 2. Crops and N₂O emission factors reported by several authors around the world.

Crop	N$_2$O emission factor (%)	Location	Reference
Rapeseed, corn and sugarcane	3.00-5.00	Based on average data from literature	(Crutzen et al. 2008)
Soybean	0.55-1.97	Argentina	(Ciampitti et al. 2008)
Pasture for bale	0.28-0.62	Scotland	(Smith et al. 1998)
Potato	0.86-1.90	Scotland	(Smith et al. 1998)
Winter wheat	0.17	Scotland	(Smith et al. 1998)
Spring barley	0.67	Scotland	(Smith et al. 1998)
Winter wheat	1.68	China	(Chen et al. 2008)
Forest	0.10-0.03	USA	(Delaune et al. 1998)
No-till	2.80	Brazil	(Passianoto et al. 2003)
Conventional till	0.90	Brazil	(Passianoto et al. 2003)
Pasture (mineral fertilizer)	0.17	Netherlands	(Schils et al. 2008)
Pasture (mineral fertilizer and cow manure)	0.29	Netherlands	(Schils et al. 2008)
Pasture	0.35	China	(Zhang & Han 2008)
Abandoned agriculture area	0.52	China	(Zhang & Han 2008)
Sugarcane (acid drainage soil)	21.00	Australia	(Denmead et al. 2010)
Sugarcane (silt-clayey soil)	2.80	Australia	(Denmead et al. 2010)
No-till	0.20	Brazil	(Giacomini et al. 2006)
Reduced till	0.25	Brazil	(Giacomini et al. 2006)
No-till and conventional till in the Brazilian Savannah	0.03	Brazil	(Metay et al. 2007)
Pasture in the Amazon	2.80	Brazil	(Neill et al. 2005)
Meta-analysis study	0.70-1.20	-	(Bouwman & Boumans 2002)
Meta-analysis study	0.17-2.90	-	(Novoa & Tejeda 2006)

applied to the soil. Velthof & Mosquera (2011) reported that increasing the N application rate on maize field also increased the emission factor, independently of the N source (calcium ammonium nitrate, injected cattle slurry or injected pig slurry). Thus, a fixed emission factor does not reflect the effect of the N application rate on N₂O emissions (Velthof & Mosquera 2011).

The use of an emission factor proposed by the IPCC is very simplistic and do not reflect variations in management activities, climate and ecosystems (Rees & Ball 2010). The proposed value does not take into account the soil type and the fact that the climate within a region is not always adequate to describe the spatial and temporal variability of N₂O emissions (Rees & Ball 2010), as well as the crops to which the fertilizer is applied (Flynn et al. 2005). Although there are not enough long-term datasets to provide the information needed to design emission factors for different climate zones or soil types, the use of specific emission factors that reflect regional variability in climate, soil type and management is a requirement to improve greenhouse gases inventories (Thomson et al. 2012).

SUMMARIZING N₂O MITIGATION PRACTICES

Considering the previous comments and observations made by Thomson et al. (2012), it is possible to highlight some present and future strategies that can be adopted to reduce soil N₂O emissions:

(i) Prioritizing the use of low N₂O emission fertilizers: in general, $N\text{-}NH_4^+$ fertilizers emit less N₂O than $N\text{-}NO_3^-$. So, it is interesting to use manure or organic fertilizers as N source when it is possible, because their N₂O emissions are lower than for mineral N-fertilizers;

(ii) Managing the N-fertilizer application: N₂O emissions from soils are reduced when N-fertilizers are depth applied, instead of surface application. Moreover, it reduces the N available in the soil, especially when heavy rains are expected, and decrease the proportion of N lost as N₂O. So, splitting the rate of N-fertilizer recommended to the crop and applying the fertilizers to the inner soil layers can be used to reduce N₂O emissions;

(iii) Managing the soil chemistry and microbiology: understanding the enzymology and microbiology of denitrification is important. For

example, when Cu concentration in the soil is low and pH values are below 7.0, denitrification is incomplete, producing N_2O instead of N_2. Then, using liming to reduce soil acidity and adjusting micronutrients, specially Cu contents, can reduce N_2O emissions;

(iv) Plant breeding: reducing the dependence on fertilizers through engineering crop plants to fix nitrogen by themselves, or by capitalizing C-N interactions in the rhizosphere, can be useful to reduce emissions. The composition of plant-derived C flow or N uptake demand can be changed to avoid N losses to the atmosphere as N_2O. Moreover, the release of biological nitrification inhibitors could be promoted by plant breeding;

(v) Promoting sustainable agricultural intensification: this could be done by using crop varieties and livestock breeds with high yield, avoiding unnecessary external inputs, improving the fertilizer use efficiency, using lime to increase the soil pH, using nitrification inhibitor technology, adopting agroecological practices, quantifying and minimizing the impact of management systems. In order to increase sustainability, it is important to understand how agricultural inputs can positively or negatively affect the biological process and ecosystem services that support agriculture.

FINAL CONSIDERATIONS AND FUTURE DIRECTIONS

Nitrous oxide is an important greenhouse gas, due to its high global warming potential (298 times higher than CO_2). Agricultural soils are the main N_2O source to the atmosphere, and the key processes affecting its production (nitrification and denitrification) are influenced by various factors that can be modified by agricultural management practices. The available N in the soil is the most important of these factors and is directly related to the N-fertilizers application. Therefore, if, on one hand, the use of N-fertilizer is important to provide that plants reach a desirable yield, on the other hand, a portion of this added N can be lost to the atmosphere as N_2O, enhancing the greenhouse effect.

Despite the importance of N-fertilizers to nitrous oxide emissions, many questions about it remain unclear. The behavior of N_2O emissions from different N sources, different responses according to the crop the fertilizer is applied to, influence of native soil organic matter content and quality, interactions

between N and other nutrients, as well as the real influence of micronutrients on N_2O emissions should be better explored in future researches. Another important point is to explore the N plant demands and N_2O emissions, trying to find management practices to maximize plant yield and minimize N_2O emissions, also considering splitting the N recommended dose.

Information on how differently N-fertilizers induce N_2O emissions is useful in GHG inventories and contributes to reliable final values in these studies. However, nowadays, N_2O emissions in agricultural soils are estimated by using a default emission factor that was not necessarily obtained in the place for which the estimative is being done, and do not taking into account the environmental specific characteristics where the fertilizer is applied (soil type and characteristics, crop, type and quantity of N added to the area), what can generate unreliable GHG inventories.

In Brazil, there are few studies available about this theme. When elaborating Brazilian GHG inventories or life-cycle assessments, it is important to use information generated under specific climate and soil conditions, and for crops planted in the country. So, it is necessary to develop long term studies, comprising different N sources and rates, evaluating N_2O emissions during all the crop cycle and also taking into account the influence of crop residues on these emissions. It is also important to repeat these measurements in different regions, in order to obtain consistent values that will really contribute to the national GHG estimatives.

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