

*Review*

# Methane and nitrous oxide emission from pastures and crop fields

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The AgriGES project is a Concerted Research Action lead by Gembloux Agro-Bio Tech, aiming to quantify methane and nitrous oxide emission from pastures and crop fields, respectively. Besides quantification, a second important goal of the AgriGES project is to study the flux dynamics and to gain a better understanding of the biophysical processes coming into play. We focus here on N<sub>2</sub>O fluxes and first propose an overview of the current modelling efforts. Two main weaknesses of these models have been identified, and potential new developments are suggested to mitigate these issues, with an emphasis on the denitrification process. Secondly, we propose a review of the current knowledge on the main environmental factors influencing nitrous oxide emission. Several mitigation options are also explored.

**Key words:** Nitrous oxide emission, environmental factors, modeling.

## INTRODUCTION

According to the Intergovernmental Panel on Climate Change (IPCC) 5<sup>th</sup> assessment report (Stocker et al., 2013b), nitrous oxide (N<sub>2</sub>O) concentration in the atmosphere was 324 ppb in 2011, being 20% higher than in the pre-industrial period. This greenhouse gas (GHG) concentration is still increasing at an

approximately constant rate of 0.8 ppb/year since the 1980s. N<sub>2</sub>O concentrations are far below other GHG concentrations, e.g. CO<sub>2</sub> but it has a global warming potential 298 times higher than CO<sub>2</sub> over 100 years. N<sub>2</sub>O is thought to be responsible for around 7.5% of the total radiative forcing induced by GHG (Stocker et al., 2013b). Nitrous oxide emissions caused by human activities represent more than two thirds of the total emissions. N<sub>2</sub>O emitted from agricultural soil is known to be a major source (about 60%) of these

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anthropogenic emissions (Mosier et al., 1998; Syakila and Kroeze, 2011).

The physical and biological processes responsible for nitrous oxide production in soil and its emission to the atmosphere lead to an extreme spatial and temporal variability of fluxes. Concerning the latter, it is commonly assumed that N<sub>2</sub>O emission is composed of a background flux mainly due to the nitrification process, while high emission peaks occur due to denitrification in times of anaerobiosis e.g. after a rainfall. On an annual basis, these peaks generally account for about 50% of the total N<sub>2</sub>O emissions, while representing only a minor part (about 10%) of the time (Groffman et al., 2009; Molodovskaya et al., 2012). The occurrence and magnitude of these peaks are also dependent on other variables influenced by human activities (mainly N-availability) enhanced by fertilization practices.

In this context, more and more attention is being given to the identification of the main environmental factors driving nitrous oxide emission, as well as to mitigation strategies to be applied in agriculture. Any mitigation options proposed to farmers need to be based on scientific evidence. This includes experimental tests at field scale, but this may also be done via the soil system modelling, provided that the model has been validated on experimental data.

Several models have been developed to predict N<sub>2</sub>O emissions from soils. This paper first aims to identify why so many models have been proposed. Secondly, special attention will be paid to denitrification (NO<sub>3</sub>-reduction to N<sub>2</sub>) as it is the main biogeochemical process responsible for nitrous oxide emission from soils. Finally, a review of the current knowledge on environmental factors (soil pH, moisture, temperature, nitrogen (N) and carbon (C) content) and, to a lesser extent, a review of the explored mitigation strategies (e.g. reduced tillage, cover crop, lower fertilizer input) is also proposed.

Two main bottlenecks have been identified in current modelling: competition between the different steps of denitrification is never taken into account; and soil physics - particularly gaseous transports in soils - is poorly represented in most of the models. Some models assume direct emission of the produced gases to the atmosphere, thus bypassing all other reactions that may occur during the gas transport. Implementing new developments would be a great contribution to improving existing models.

## PROPOSED MODELS

Despite the existence of well-known concurrent models (Blagodatsky and Smith, 2012) such as (this list is non-exhaustive) DNDC (Li et al., 1992a, b), ECOSYS (Grant et al., 1993a, b), STICS (Brisson et al., 2003, 1998,

2002), and DAYCENT (Parton et al., 1998, 2001), many different groups continue to develop new ones (e.g. MiCNiT (Blagodatsky et al., 2011), TOUGHREACT-N (Maggi et al., 2008)) or try to refine existing approaches, such as NLOSS which is based on DNDC (Riley and Matson, 2000).

There are several reasons for this:

1. From a historical point of view, some models have been designed for specific goals (e.g. DAYCENT for CO<sub>2</sub> emissions, STICS for crop yield), and later applied to other subsidiary outputs such as N<sub>2</sub>O emissions.
2. A lack of cooperation between research groups attached to different research fields such as soil biology, soil physics, or agronomy (Blagodatsky and Smith, 2012; Sutton et al., 2011). The multidisciplinary nature of process-based approaches makes communication between researchers difficult. They may use different terminologies to refer to a same process or event, e.g. “dissimilatory nitrate reduction to ammonia” and “nitrate ammonification”.
3. A lack of modular implementation, which makes it difficult to insert new developments into old models. Rubol et al. (2013), for instance, have implemented a new model to take nitrate ammonification into account because of growing experimental evidence of the importance of this process.
4. The need for models applicable to a wide range of temporal and spatial scales (Manzoni and Porporato, 2009). The scale of models ranges from days to decades and from experimental plots to the whole planet. At large regional or national scales, simple experimental models with few parameters are preferable to more complex mechanistic ones, because the number of parameters tends to increase with the model complexity. Lots of these parameters in mechanistic models are site and climate specific (Saggar et al., 2013), and need to be initialized from experimental measurements.

The up-scaling of process-based models is still problematic, but they nevertheless have a great advantage over simpler ones in that their modelling scheme is closer to reality, thus giving the opportunity for a deeper understanding of the biophysical processes influencing N<sub>2</sub>O emissions, and a better simulation of mitigation options at the farm scale.

Heinen (2006) makes a distinction between two different types of process-based models: microbial growth models and soil structural models. The former models focus on the dynamics of the microbial organisms for the N-cycling processes and often assume immediate transfer of the produced gases from the soil to the atmosphere. The latter consider gaseous transport in soils in more detail, simulating the anoxic fraction of the pore volumes in which denitrification occurs (Blagodatsky and Smith, 2012). Meanwhile,

### NITROGEN DYNAMICS IN CROPS AND PASTURE (adapted from Saggar et al, 2013)

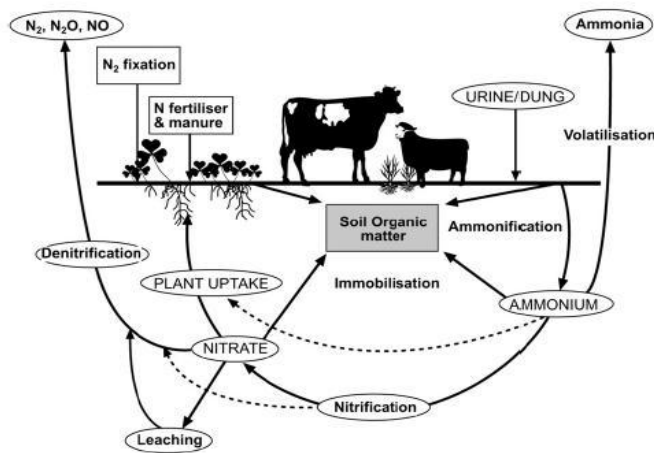


Figure 1. Basic N-cycle.

### REACTION STEPS OF DENITRIFICATION (adapted from Saggar et al, 2013)

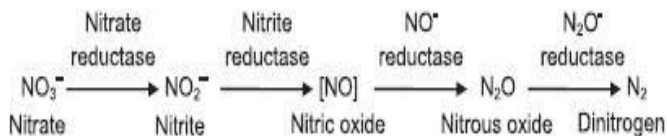


Figure 2. Reaction steps of denitrification.

most models consider simple dependencies of environmental variables (temperature, moisture) on the production of gases, and completely neglect the microbial nature of the C and N cycles.

Chen et al. (2008) provided a very comprehensive comparison of the most widely used models. The vast majority of these models are to be classified as microbial growth models (e.g. DNDC, DAYCENT, STICS). Most of the soil structural models have been tested in laboratory experiments, such as that of Arah and Vinten (1995), while a few attempts to up-scale them are worth noting (Langeveld and Leffelaar, 2002). There is probably a huge knowledge gap to fill, that is coupling a microbial growth model and a soil structural model into one. Since both mechanisms occur over the same timescale, their interaction cannot be neglected (Blagodatsky and Smith, 2012). This would be difficult to insert into the implementation of older models,

justifying some new attempts such as MiCNit (Blagodatsky et al., 2011) and PASTIS-CANTIS (Cannavo et al., 2006) to combine these two aspects.

### DENITRIFICATION

Denitrification is a natural microbial process and is an essential part of the nitrogen cycle, briefly illustrated in Figure 1. Denitrification is the stepwise reduction of nitrate ( $\text{NO}_3^-$ ) to nitrogen ( $\text{N}_2$ ) via nitrite ( $\text{NO}_2^-$ ), nitric oxide ( $\text{NO}$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ) (Figure 2). Denitrification is performed by facultative anaerobic bacteria. In conditions of oxygen ( $\text{O}_2$ ) depletion, these bacteria use nitrate as a substitute electron acceptor for adenosine triphosphate (ATP) generation, which is the energy source for cell processes. Each of the four steps of denitrification is catalyzed by a specific enzyme (nitrate reductase: Nar; nitrite reductase: Nir; nitric oxide reductase: Nor; nitrous oxide reductase: Nos). Since  $\text{NO}$  is highly cytotoxic, all denitrifiers have the gene to code Nor. On the other hand, some denitrifiers lack the gene to code Nos, therefore  $\text{N}_2\text{O}$  is their final product of denitrification. The complete denitrification cycle is mainly a symbiotic process, with bacteria coding Nos performing the last step.

There is growing evidence for competition among the different steps of denitrification. The experiment from Pan et al. (2013a) strongly suggests that this competition plays on the available electron donors (labile carbon). Whereas it is commonly thought that this competition only occurs under carbon-limiting conditions, their results tend to prove that it also occurs with high available carbon content.

According to them, the limiting step that triggers the competition is that the Nir, Nor and Nos use the same pathway to receive electrons, that is they all use the cytochrome c550 coenzyme, while Nar uses the ubiquinone/ubiquinol pool. This may explain their observations, showing a greater competition between Nir and Nos than between Nar and Nos or Nar and Nir. Under carbon-limiting conditions, Nir is highly favoured over Nos, leading to high nitrous oxide emissions.

Other experimental studies have indicated that an increasing nitrate concentration tends to enhance  $\text{N}_2\text{O}$  emission, provided that there is enough available labile carbon (Senbayram et al., 2012). Other molecules are also known to regulate enzyme activity and production, including intermediates from denitrification. Indeed, an increase in  $\text{NO}$  concentration favours  $\text{NO}$ -reductase production (Thomson et al., 2012; Zumft, 1997). This makes great sense in terms of biological evolution, since bacteria produce this enzyme to reduce a lethal component ( $\text{NO}$ ) in response to its increase in concentration. It is also worth noting that  $\text{N}_2\text{O}$  reduction to  $\text{N}_2$  is energetically less favourable compared to the other steps in denitrification (Senbayram et al., 2012),

which may also explain why bacteria tend to favour the previous steps in denitrification, resulting in greater N<sub>2</sub>O emission and comparatively less N<sub>2</sub> produced.

Denitrification can also be performed by some fungi. The mechanisms and the relative importance of fungal denitrification have not yet been fully addressed, even though a few authors have found experimental evidence that fungi comprise the majority of denitrifying organisms in grassland soils (Laughlin and Stevens, 2002). The reaction steps are quite similar to bacterial denitrification, but the enzymes involved are different and are not inhibited by O<sub>2</sub>. Another important difference is that none of these fungi have the gene to code N<sub>2</sub>O-reductase.

An overview by Heinen (2006) assesses more than fifty simplified denitrification models. The majority of these models are to be used at a regional scale. Denitrification is considered as a first order decay process, which is inadequate to explain observed non-linearities in soil N-dynamics (e.g. non-linear response of N<sub>2</sub>O emission on quantity of N-fertilizer input (Kim et al., 2013).

Following the pioneering work of Leffelaar and Wessel (1988), most process-based models (e.g. DNDC and TOUGHREACT-N) consider denitrification as a 4-step chain reaction, each step being independent of the others, except that the product of a previous reaction is the reactant of the next one. It is assumed that each reaction follows Michaelis-Menten kinetics. In this regard, STICS constitutes an exception by using a simplified sub-model of denitrification, namely NOE (Bessou et al., 2010; Henault et al., 2005). Very few attempts have been made so far to model the competition between the different reaction steps. As another example of the multidisciplinary nature of this topic, efforts have been made by researchers in waste water treatment, where denitrification is a crucial process.

Based on their previous experimental results (2013a), Pan et al. (2013b) have proposed a new model in which denitrification steps are thought to be mediated by electron carriers going through cell membranes, and competition among the different steps is modelled as a competition for these electron carriers. Each reaction rate is multiplied by a Michaelis-Menten term regarding the carrier concentration, with different affinity constants for each reaction. This seems to be a promising approach to account for the inhibition of nitrous oxide reduction by nitrite and nitrate.

## A MODEL OF SOIL STRUCTURE

Directly representing the soil pore space structure in current models might be a tricky task, because it would involve a review of all simulated processes, changing their implementation to make them fit in to the geometric structure. Moreover, including a 3-

dimensional (3D) representation of the soil structure in a model is likely to incur time and computer memory consumption issues (Blagodatsky and Smith, 2012).

Another approach involves using soil structural models as a pre-process tool to provide pedotransfer functions to be later used in a more generic model. In this regard, the pore-solid-fractal approach (PSF) derived by Perrier et al. (1999) has proved to be a powerful tool that is able to account for a wide variety of soil physical properties (Ghanbarian-Alavijeh et al., 2011; Perfect and Kay, 1995), such as the theoretical water retention curve derived by Wang and Zhang (2011).

Rappoldt and Crawford (1999) used the 3D-soil space resulting from the PSF model in order to solve the oxygen diffusion-respiration equation in soils. In relation to denitrification, their results can be used to simulate the soil anoxic fraction as a function of its water content in a given depth layer. This, together with a model of denitrification rate as a function of the soil depth (most likely decreasing with depth because of the decrease of the microbial community), may potentially lead to a better simulation of the N<sub>2</sub>O emission peak dynamics, both in magnitude and temporal occurrence.

## MAIN DRIVERS

Several environmental factors are known to play a key role in greenhouse gas emission from soils. In general, complete denitrification is favoured by high water content, neutral to slightly basic pH, high temperature, low O<sub>2</sub> diffusion, and labile C availability. While each individual influence is quite well researched, there is still a lack of complete comprehension of some mechanisms by which these factors (e.g. pH) act on emissions, and a fully comprehensive scheme of their interactions is thought to be unrealistic (Butterbach-Bahl et al., 2013). Several authors have provided reviews of the current knowledge on these driving factors. Of particular interest are: Butterbach-Bahl et al. (2013), Giles et al. (2012), and Saggari et al. (2013).

The timescales at which these factors influence N<sub>2</sub>O emission from soils vary in a very wide range, from hours to decades. For instance, water content is known to regulate the anoxic volume of soils in a very direct way, while soil pH may have a long-term effect via microbial community adaptation. Long-term feedback effects are also reported, e.g. the increase of soil temperature due to the global warming will probably enhance greenhouse gas emission from soils in the coming decades.

### Soil pH

Soil pH is known to be a key variable in soil biogeochemical processes, although its influence is not

yet well understood (Liu et al., 2010; Simek and Cooper, 2002; Van den Heuvel et al., 2011). Regarding nitrous oxide emissions, it is globally accepted that acidic conditions (lower pH) tend to increase  $\text{N}_2\text{O}:\text{N}_2$  emission ratio while decreasing total  $\text{N}_2\text{O}$  and  $\text{N}_2$  emission (Liu et al., 2010). To minimize  $\text{N}_2\text{O}$  emission, a neutral to slightly alkaline soil pH seems to be optimal (Giles et al., 2012), dependent on other soil characteristics.

Soil pH affects denitrification in many different ways. Both direct and indirect effects of pH on denitrification rates, denitrification end product, and denitrifier community have been reported. Liu et al. (2010) have shown that a pH-dependent effect on denitrification enzyme activity occurs at a post-transcriptional level. They suggested that pH may disable the protein assembly, or influence its shape, leading to unusable active site. Bakken et al. (2012) working with a specific bacteria (*Paracoccus denitrificans*), observed that at pH 7, nearly no  $\text{N}_2\text{O}$  was emitted from batch cultures, while at pH 6,  $\text{N}_2\text{O}$ -reductase activity was drastically reduced, leading to high  $\text{N}_2\text{O}$  emissions.

Indirect effects of soil pH on denitrification may include changes in organic carbon availability and nitrogen mineralization rates (Simek and Cooper, 2002). These two variables tend to decrease under acidic conditions, leading to a smaller microbial community, which in turn leads to lower denitrification rates in soils (Van den Heuvel et al., 2011). Meanwhile, this effect could be counterbalanced by a long term adaptation of the microbial community.

### Soil moisture and oxygen availability

Soil water content may influence gaseous emissions from soils in many different ways. For instance, water presence in soil is necessary for plant and microbial growth, which in turn can influence biochemical reaction rates and enhance nitrate uptake by crops. However, soil water content is particularly studied for its key role in the development of anaerobic conditions in soils. Indeed, most of the models (e.g. DNDC) use the water filled pore space (WFPS) of soils as a proxy to define periods of activation and inhibition of the denitrification process.

Several experimental studies, e.g. Bateman and Baggs (2005), have shown the existence of a WFPS threshold value above which denitrification rates increase sharply with soil water content, and under which denitrification rates are low and seem unrelated to WFPS. DNDC uses a threshold value of 60%, and this value differs according to soil type. After reaching a maximum around 70 to 80% WFPS, nitrous oxide emission generally tends to decrease. This is thought to be caused by a lower gas diffusion into soils, thus giving more time for denitrifiers to reduce  $\text{N}_2\text{O}$  (Smith et

al., 2003).

De Klein and Van Logtestijn (1996) suggest that the WFPS threshold value is equivalent to or slightly higher than field capacity. This makes sense in several ways: at field capacity, micro-pores are still filled with water; whereas these pores are also thought to be the privileged location of microorganisms (including denitrifiers) in soils (Or et al., 2007). In addition, Saggari et al. (2013) report a duration of 24 to 48 h after a rainfall for  $\text{N}_2\text{O}$  emissions to return to their background level. The experimental definition of the field capacity is indeed the soil water content 48 h after its saturation.

This threshold value may also be related to several models describing the anoxic fraction of soils as a function of its water content (Arah and Vinten, 1995; Rappoldt and Crawford, 1999; Schurgers et al., 2006). These models show a highly non-linear response of soil anoxic fraction to soil WFPS, with the anoxic fraction notably increasing above a certain threshold value which may be compared to the observed threshold value for the denitrification activity. The threshold values computed by Rappoldt and Crawford (1999) and Schurgers et al. (2006) are in accordance with the WFPS threshold range given by Bateman and Baggs (2005).

### Soil temperature

Soil temperature most significantly influences gas emission via its role in microbial growth and activity (Braker et al., 2010). Denitrification occurs across a wide temperature range (near 0 to 75°C), and is limited by water availability (freezing below 0°C) and microbial death at too high a temperature (Saggari et al., 2013). Optimal temperatures for denitrification rates have been reported from 25 to 30°C (Braker et al., 2010).

Of particular interest are fluctuations of temperature around 0°C, which lead to freeze-thaw cycles with high emission peaks reported in numerous studies, e.g. (Mørkved et al., 2006). Several explanations have been proposed for these peaks (de Bruijn et al., 2009).  $\text{N}_2\text{O}$  may accumulate in frozen phases due to lower gas diffusion and be released on thawing. It has also been suggested that substrate availability may be more important in winter because of low plant uptake during this period.

Increasing temperature may also cause higher oxygen consumption, thus leading to an increase in the anoxic fraction of the soil pores as less oxygen is available (Smith et al., 2003).

At a seasonal scale, Wolf and Brumme (2002) reported a linear relation between temperature and nitrous oxide emission on a bare soil with WFPS kept constant at field capacity. On a larger time scale, global warming (and consequent soil warming) is likely to have an important positive feedback on  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$

emission from soils in the coming decades (Arneeth et al., 2010; Stocker et al., 2013a; van Groenigen et al., 2011), mainly resulting from an enhanced microbial activity.

### Soil carbon and nitrogen content

As electron donors and electron acceptors for denitrification respectively, both labile organic carbon and nitrate play a key role in nitrous oxide emissions. Besides the direct effect of providing supplies for the denitrifiers, other indirect effects have also been reported (Giles et al., 2012). For instance, the presence of carbon stimulates heterotrophic respiration, hence favouring anaerobic conditions in soils.

Several studies focus on the C:N ratio of fertilizers as well as on the applied rate to reach maximum crop yield while limiting N<sub>2</sub>O emission. In their meta-analysis, Van Groenigen et al. (2010) reported a sharp increase in nitrous oxide emission when the N-fertilizer input leads to nitrogen saturation (excess of N compared to plant and microbial maximum demand) of soils, which may indicate that a precise control of N-input is a straightforward and effective option to reduce nitrous oxide emission.

The incubation experiment led by Senbayram et al. (2012) found that, for soils with low nitrate content, the nitrous oxide emission can be substantially lowered by the addition of organic matter with high content of labile C, by promoting the reduction of N<sub>2</sub>O to N<sub>2</sub>. Alternatively, for soils with high nitrate content, labile organic C enhanced nitrous oxide emission, most likely due to an inhibitory effect of NO<sub>3</sub><sup>-</sup> on the N<sub>2</sub>O-reductase.

### Explored mitigation options

Strategies to reduce greenhouse gas emissions from agriculture mainly rely on our knowledge of the main drivers, with the aim to influence these factors (e.g. pH and liming, soil carbon and nitrogen content and fertilization practices) in order to decrease the emission levels as much as possible. These strategies have to be placed in a wider context, considering other constraints that best management practice assessments should also acknowledge:

1. Productivity must be kept at a sustainable level in order to ensure food security.
2. Avoidance of nitrate leaching to maintain water quality. Moreover, this nitrate will eventually end in waste water treatment plants where denitrifiers are used to remove it from water, also leading to nitrous oxide emissions (Cui et al., 2014; Pan et al., 2013b).

3. The greenhouse gas budget of an agricultural farm should also take into account GHG emission from agricultural machinery, GHG emission for the production and transport of inputs (pesticides, fertilizers, lime, etc.). Promoting less intensive crop systems and reducing inputs to the field results in the saving of a considerable amount of GHG emissions upstream of the cropping itself (Smith et al., 2008).

4. The need to compute greenhouse gas emissions for a complete sequence of crops, which is more relevant than for a single crop as a previous crop affects the following one because of its influence on soil nutrients (Lehuger et al., 2011).

Several mitigation options for direct nitrous oxide emissions from the field are discussed hereafter. It is most likely that the best way to reduce these emissions involve a mix of these different practices, as they influence each other.

### Fertilizers

As shown experimentally by Van Groenigen et al. (2010), nitrous oxide emission increases exponentially with excess N-fertilizer compared to plant demand. According to their study, lowering N-input to match the crop demand would be a straightforward and effective way to reduce N<sub>2</sub>O emission per crop yield. Once this is done, if soil nitrate content remains at a relatively low level, addition of labile organic carbon may also be a way to enhance reduction of N<sub>2</sub>O to N<sub>2</sub>, thus also leading to a reduction of nitrous oxide emission. In this regard, combining both organic and synthetic fertilizers would be an efficient mitigation option (Senbayram et al., 2012).

Changing spatial and temporal location of N-input may also be an important factor in improving their efficiency. For instance, in the UK, avoiding manure application during autumn and early spring may be an effective way to reduce yearly emissions, since it often rains a lot during these periods leading to high denitrification rates in soils. This mitigation scenario has been tested with DNDC and shows promising results.

Technical progress has (Cardenas et al., 2013) also been made in the manufacture of slow- (or “controlled-”) release fertilizers, that is, fertilizers which decompose more slowly than traditional ones, thus providing nutrients more homogeneously over time (Azeem et al., 2014). The use of slow-release fertilizers seems to be a promising way to increase N-use efficiency, but their cost remains prohibitive.

### Enzymatic regulations

While all of the enzymes involved in the denitrification process are influenced by environmental factors,

explored mitigation options focus mainly on the  $\text{N}_2\text{O}$ -reductase. Enhancing  $\text{N}_2\text{O}$ -reductase activity is expected to decrease the  $\text{N}_2\text{O}:\text{N}_2$  ratio. Liming of acidic soil is a way to achieve this, but it also leads to higher total  $\text{N}_2\text{O}+\text{N}_2$  emission (Bakken et al., 2012).

Meanwhile, this additional direct loss of N-input is thought to be largely compensated by the decrease of nitrate leaching, since nitrate is consumed by denitrifiers. Another key variable for the  $\text{N}_2\text{O}$ -reductase enzyme is the soil copper content. Indeed, copper (Cu) is a mandatory and irreplaceable cofactor in order for this enzyme to be active. Thus, addition of Cu in copper-poor soil may also decrease  $\text{N}_2\text{O}:\text{N}_2$  ratio, without disturbing the total  $\text{N}_2\text{O}+\text{N}_2$  emission (Richardson et al., 2009; Thomson et al., 2012)

Regarding other biogeochemical processes, the use of nitrification (oxidation of ammonia to nitrate) inhibitors together with ammonium-based fertilizers has also been addressed (Liu et al., 2013). Inhibiting nitrification is expected to reduce nitrate losses by leaching and denitrification, while still leaving a usable form of N (that is, ammonium) for plant uptake. Liu et al. (2013) reported an increase of crop yield, and a better nitrogen use efficiency, as well as a reduction of  $\text{N}_2\text{O}$  emissions. Meanwhile, a phytotoxic effect associated with excessive inhibitor application rates was also reported, as well as a subsequent yield reduction.

Moreover, several key points have not been addressed yet concerning the use of nitrification inhibitors, e.g. the GHG emission resulting from their manufacture and their long-term impact on the soil microbial community.

### Cover crops

Cover crops, also known as catch crops, are mainly used during winter to avoid soil erosion by the structural effect of roots preventing soil loss, and nitrate leaching by plant uptake. N sequestered by cover crops is then made available for the main crops during the growth season, which enhances the yearly N-use efficiency of the crop rotation. Given this dual effect, cover crops are often considered as a win-win practice for N-management (Constantin et al., 2010), and their use is thought to reduce reliance on fertilizer input. In drier lands the positive impact of cover crops is less pronounced, since there is naturally less nitrate leaching in winter in these areas.

There are also concerns about water and nitrogen stress induced by cover crops, resulting in yield reduction issues for the main crop (Celette and Gary, 2013; Celette et al., 2008).

### Conservation tillage

It is widely thought that conventional tillage is the primary cause of the decrease in soil organic carbon

content. Many soils have lost up to 40% of the C they contained before cultivation (Baker et al., 2007). The first intent of reduced or no-till practices is to promote soil C sequestration, thus allowing soils to refill in order to act as a reservoir. In addition to this potential for sequestration, an increased soil C content can also promote the reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$ , provided that soil nitrate remains at a relatively low level. In order to control nitrate content, conservation tillage is often used in combination with other management practices, such as lower N-fertilizer application rates and the use of winter cover crops (Constantin et al., 2010; Petersen et al., 2011). A higher soil organic carbon content is also thought to enhance plant uptake, but this effect may be counterbalanced by a greater soil compaction, leading to a difficult root growth.

Nevertheless, a few authors have pointed out that evidence of soil C sequestration induced by reduced tillage is not that obvious. Baker et al. (2007) argued that the sampling depth in most of the experimental studies is not deep enough. Conservation tillage may change the C distribution in soils, thus increasing the C content in the first 30 cm layer, but at deeper depths some studies show a decrease in soil C content.

## CONCLUSIONS AND PERSPECTIVES

In this paper, the current knowledge on the main driving factors influencing nitrous oxide emissions from cultivated fields has been reviewed. While many environmental factors have been studied (such as soil pH, water content, temperature), there is still progress to be made to gain a complete comprehension of the influence of soil physical properties on GHG production and emission.

In this regard, a fractal model of soils seems a promising approach to give a consistent theoretical basis that is able to account for a wide variety of soil physical properties (Ghanbarian-Alavijeh et al., 2011; Perfect and Kay, 1995). In particular, the pore-solid-fractal approach (Perrier et al., 1999) allows derivation of a theoretical water retention curve (Wang and Zhang, 2011) and provides a 3D-space in which to simulate several key processes, including the temporal dynamics of the anoxic fraction of the pore volume (Rappoldt and Crawford, 1999).

Another key process which is not taken into account in current modelling efforts is the competition among the different steps of denitrification. The approach from Pan et al. (2013b) seems promising, but needs to be tested in a wider range of anaerobic conditions.

These potential developments need to be incorporated in a more general process-based model of soil C and N cycles which will need to be chosen from the different existing models, based on their current performance in agricultural and meteorological conditions encountered in our region.

**Abbreviations:** ATP, adenine triphosphate; C, carbon; CANTIS, carbon and nitrogen transport in soil; CH<sub>4</sub>, methane; CO<sub>2</sub>, carbon dioxide; Cu, copper; DNDC, denitrification-decomposition; GHG, greenhouse gas; IPCC, intergovernmental panel on climate change; MiC-NiT, microbial carbon and nitrogen turnover; N, nitrogen; N<sub>2</sub>, dinitrogen; Nar, nitrate reductase; Nir, nitrite reductase; N<sub>2</sub>O, nitrous oxide; NO<sub>2</sub><sup>-</sup>, nitric oxide; NO<sub>3</sub><sup>-</sup>, nitrate; NOE, nitrous oxide emissions; Nor, nitric oxide reductase; Nos, nitrous oxide reductase; PASTIS, predicting agricultural solute transport in soils; PSF, pore-solid-fractal; STICS, simulateur multidisciplinaire pour les cultures standard ; UK, United Kingdom; WFPS, water filled pore space.

### Conflict of Interest

The authors have not declared any conflict of interest.

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### REFERENCES

- Arah JRM, Vinten AJA (1995). Simplified model of anoxia in aggregated soils. *Eur. J. Soil Sci.* 46:507-517.
- Arneeth A, Harrison SP, Zaehle S, Tsigaridis K, Menon S, Bartlein PJ, Feichter J, Korhola A, Kulmala M, O'Donnell D, Schurgers G, Sorvari S, Vesala T (2010). Terrestrial biogeochemical feedbacks in the climate system. *Nature Geosci.* 3:525-532.
- Azeem B, Kussaari K, Man ZB, Basit A, Thanh TH (2014). Review on materials & methods to produce controlled release coated urea fertilizer. *J Control Release* 181C:11-21.
- Baker JM, Ochsner TE, Venterea RT, Griffis TJ (2007). Tillage and soil carbon sequestration-What do we really know? *Agric. Ecosystems Environ.* 118:1-5.
- Bakken LR, Bergaust L, Liu B, Frostegard A (2012). Regulation of denitrification at the cellular level: A clue to the understanding of N<sub>2</sub>O emissions from soils. *Philos. Trans. R Soc. Lond. B Biol. Sci.* 367:1226-34.
- Bateman EJ, Baggs EM (2005). Contributions of nitrification and denitrification to N<sub>2</sub>O emissions from soils at different water-filled pore space. *Biology Fertil. Soils* 41:379-388.
- Bessou C, Mary B, Léonard J, Roussel M, Gréhan E, Gabrielle B (2010). Modelling soil compaction impacts on nitrous oxide emissions in arable fields. *Eur. J. Soil Sci.* 61:348-363.
- Blagodatsky S, Grote R, Kiese R, Werner C, Butterbach-Bahl K (2011). Modelling of microbial carbon and nitrogen turnover in soil with special emphasis on N-trace gases emission. *Plant Soil* 346:297-330.
- Blagodatsky S, Smith P (2012). Soil physics meets soil biology: Towards better mechanistic prediction of greenhouse gas Emissions from soil. *Soil Biol. Biochem.* 47:78-92.
- Braker G, Schwarz J, Conrad R (2010). Influence of temperature on the composition and activity of denitrifying soil communities. *FEMS Microbiol. Ecol.* 73:134-48.
- Brisson N, Gary C, Justes E, Roche R, Mary B., Ripoche D, Zimmer D, Sierra J, Bertuzzi P, Burger P (2003). An overview of the crop model STICS. *Eur. J. Agron.* 18:309-332.
- Brisson N, Mary B, Ripoche D, Jeuffroy MH (1998). STICS: a generic model for the simulation of crops and their water and nitrogen balances. I. Theory and parameterization applied to wheat and corn. *Agronomie* 18:311-346.
- Brisson, N, Ruget F, Gate, P, Lorgeou, J (2002). STICS: A generic model for simulating crops and their water and nitrogen balances. II. Model validation for wheat and maize. *Agronomie* 22:69-92.
- Butterbach-Bahl K, Baggs EM, Dannenmann M, Kiese R, Zechmeister-Boltenstern S (2013). Nitrous oxide emissions from soil: how well do we understand the processes and their controls? *Philos Trans. R Soc. Lond. B Biol. Sci.* P. 368.
- Cannavo P, Lafolie F, Nicolardot B, Renault P (2006). Modeling seasonal variations in carbon dioxide and nitrous oxide in the Vadose Zone. *Vadose Zone J.* 5 990.
- Cardenas LM, Gooday R, Brown L, Scholefield D, Cuttle S, Gilhespy S, Matthews R, Misselbrook T, Wang J, Li C, Hughes G, Lord E (2013). Towards an improved inventory of N<sub>2</sub>O from agriculture: Model evaluation of N<sub>2</sub>O emission factors and N fraction leached from different sources in UK agriculture. *Atmospheric Environ.* 79:340-348.
- Celette F, Gary C (2013). Dynamics of water and nitrogen stress along the grapevine cycle as affected by cover cropping. *Eur. J. Agron.* 45:142-152.
- Celette F, Gaudin R, Gary C (2008). Spatial and temporal changes to the water regime of a Mediterranean vineyard due to the adoption of cover cropping. *Eur. J. Agron.* 29:153-162.
- Chen D, Li Y, Grace P, Mosier AR (2008). N<sub>2</sub>O emissions from agricultural lands: A synthesis of simulation approaches. *Plant Soil* 309:169-189.
- Constantin J, Mary B, Laurent F, Aubrion G, Fontaine A, Kerveillant P, Beaudoin N (2010). Effects of catch crops, no till and reduced nitrogen fertilization on nitrogen leaching and balance in three long-term experiments. *Agric. Ecosystems Environ.* 135:268-278.
- Cui F, Zheng X, Wang K, Zhou Z, Deng J (2014). Assessing biogeochemical effects and best management practice for a wheat-maize cropping system using the DNDC model. *Biogeosciences* 11:91-107.
- de Bruijn AMG, Butterbach-Bahl K, Blagodatsky S, Grote R (2009). Model evaluation of different mechanisms driving freeze-thaw N<sub>2</sub>O emissions. *Agric. Ecosystems Environ.* 133:196-207.
- De Klein CAM, Van Logtestijn RSP (1996). Denitrification in grassland soils in the Netherlands in relation to irrigation, N-application rate, soil water content and soil temperature. *Soil Biol. Biochem.* 28:231-237.
- Ghanbarian-Alavijeh B, Millán H, Huang G (2011). A review of fractal, prefractal and pore-solid-fractal models for parameterizing the soil water retention curve. *Canadian J. Soil Sci.* 91:1-14.
- Giles M, Morley N, Baggs EM, Daniell TJ (2012). Soil nitrate reducing processes - drivers, mechanisms for spatial variation, and significance for nitrous oxide production. *Front Microbiol.* 3:407.
- Grant RF, Nyborg M, Laidlaw JW (1993a). Evolution of nitrous oxide from soils: I. Model development. *Soil Sci.* 156:259-265.
- Grant RF, Nyborg ., Laidlaw JW (1993b). Evolution of nitrous oxide from soils: II. Experimental results and model testing. *Soil Sci.* 156:266-277.
- Groffman PM, Butterbach-Bahl K, Fulweiler RW, Gold AJ, Morse JL, Stander EK, Tague C, Tonitto C, Vidon P (2009). Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. *Biogeochemistry* 93:49-77.
- Heinen M (2006). Simplified denitrification models: Overview and properties. *Geoderma* 133:444-463.
- Henault C, Bizouard F, Laville P, Gabrielle B, Nicoulaud B, Germon JC, Cellier P (2005). Predicting in situ soil N<sub>2</sub>O emission using NOE algorithm and soil database. *Global Change Biol.* 11:115-127.
- Kim DG, Hernandez-Ramirez G, Giltrap D (2013). Linear and nonlinear dependency of direct nitrous oxide emissions on fertilizer nitrogen input: A meta-analysis. *Agric. Ecosystems Environ.* 168:53-65.
- Langeveld CA, Leffelaar PA (2002). Modelling belowground processes to explain field-scale emissions of nitrous oxide. *Ecolog. Modelling* 149:97-112.



- Laughlin RJ, Stevens JR (2002). Evidence for fungal dominance of denitrification and codenitrification in a grassland soil. *Soil Sci. Soc. Am. J.* 66: 1540-1548.
- Leffelaar PA, Wessel WW (1988). Denitrification in a homogeneous, closed system: Experiments and simulation. *Soil Sci.* 146:335-349.
- Lehuger S, Gabrielle B, Laville P, Lamboni M, Loubet B, Cellier P (2011). Predicting and mitigating the net greenhouse gas emissions of crop rotations in Western Europe. *Agric. Forest Meteorol.* 151:1654-1671.
- Li C, Frolking S, Frolking TD (1992a). A model of nitrous oxide evolution from soil driven by rainfall events: 1. model structure and sensitivity. *J. Geophys. Res.* 97:9759-9776.
- Li C, Frolking S, Frolking TD (1992b). A model of nitrous oxide evolution from soil driven by rainfall events: 2. Model applications. *J. Geophys. Res.* 97:9777-9783.
- Liu B, Morkved PT, Frostegard A, Bakken L R (2010). Denitrification gene pools, transcription and kinetics of NO, N<sub>2</sub>O and N<sub>2</sub> production as affected by soil pH. *FEMS Microbiol. Ecol.* 72:407-17.
- Liu C, Wang K, Zheng X (2013). Effects of nitrification inhibitors (DCD and DMPP) on nitrous oxide emission, crop yield and nitrogen uptake in a wheat-maize cropping system. *Biogeosciences* 10:2427-2437.
- Maggi F, Gu C, Riley WJ, Hornberger GM, Venterea RT, Xu T, Spycher N, Steefel C, Miller NL, Oldenburg CM (2008). A mechanistic treatment of the dominant soil nitrogen cycling processes: Model development, testing, and application. *J. Geophys. Res.* P. 113.
- Manzoni S, Porporato A (2009). Soil carbon and nitrogen mineralization: Theory and models across scales. *Soil Bio. Biochem.* 41:1355-1379.
- Molodovskaya M, Singurindy O, Richards BK, Warland J, Johnson MS, Steenhuis TS (2012). Temporal variability of nitrous oxide from fertilized croplands: Hot moment analysis. *Soil Sci. Soc. Am.* 76:1728-1740.
- Mørkved PT, Dörsch P, Henriksen TM, Bakken LR (2006). N<sub>2</sub>O emissions and product ratios of nitrification and denitrification as affected by freezing and thawing. *Soil Biol. Biochem.* 38:3411-3420.
- Mosier AR, Kroeze C, Nevison C, Oenema O, Seitzinger S, Van Cleemput O (1998). Closing the global N<sub>2</sub>O budget: Nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient Cycling in Agroecosystems* 52:225-248.
- Or D, Smets BF, Wraith JM, Dechesne A, Friedman SP (2007). Physical constraints affecting bacterial habitats and activity in unsaturated porous media – a review. *Adv. Water Res.* 30:1505-1527.
- Pan Y, Ni BJ, Bond PL, Ye L, Yuan Z (2013a). Electron competition among nitrogen oxides reduction during methanol-utilizing denitrification in wastewater treatment. *Water Res.* 47:3273-3281.
- Pan Y, Ni B J, Yuan Z (2013b). Modeling electron competition among nitrogen oxides reduction and N<sub>2</sub>O Accumulation in denitrification. *Environ. Sci. Technol.* 47:11083-11091.
- Parton WJ, Hartman M, Ojima D, Schimel D (1998). DAYCENT and its land surface submodel: description and testing. *Global Planetary Change* 19:35-48.
- Parton WJ, Holland EA, Del Grosso SJ, Hartman MD, Martin RE, Mosier AR., Ojima DS, Schimel DS (2001). Generalized model for NO<sub>x</sub> and N<sub>2</sub>O emissions from soils. *J. Geophys. Res.* 106:403-419.
- Perfect E, Kay BD (1995). Applications of fractals in soil and tillage research: A review. *Soil Tillage Res.* 36:1-20.
- Perrier E, Bird N, Rieu M (1999). Generalizing the fractal model of soil structure the pore solid fractal approach. *Geoderma* 88:137-164.
- Petersen SO, Mutegi JK, Hansen EM, Munkholm LJ (2011). Tillage effects on N<sub>2</sub>O emissions as influenced by a winter cover crop. *Soil Biol. Biochem.* 43:1509-1517.
- Rappoldt C, Crawford JW (1999). The distribution of anoxic volume in a fractal model of soil. *Geoderma* 88:329-347.
- Richardson DJ, Felgate H, Watmough N, Thomson AJ, Baggs EM (2009). Mitigating release of the potent greenhouse gas N<sub>2</sub>O from the nitrogen cycle – could enzymic regulation hold the key? *Trends Biotechnol.* 27:388-397.
- Riley WJ, Matson PA (2000). NLOSS: A mechanistic model of denitrified N<sub>2</sub>O and N<sub>2</sub> from soils. *Soil Sci.* 165:237-249.
- Rubol S, Manzoni S, Bellin A, Porporato A (2013). Modeling soil moisture and oxygen effects on soil biogeochemical cycles including dissimilatory nitrate reduction to ammonium (DNRA). *Adv. Water Res.* 62:106-124.
- Saggar S, Jha N, Deslippe J, Bolan NS, Luo J, Giltrap DL, Kim DG, Zaman M, Tillman RW (2013). Denitrification and N<sub>2</sub>O:N<sub>2</sub> production in temperate grasslands: processes, measurements, modelling and mitigating negative impacts. *Sci. Total Environ.* 465:173-95.
- Schurgers G, Dorsch P, Bakken L, Leffelaar P, Haugen L (2006). Modelling soil anaerobiosis from water retention characteristics and soil respiration. *Soil Biol. Biochem.* 38:2637-2644.
- Senbayram M, Chen R, Budai A, Bakken L, Dittert K (2012). N<sub>2</sub>O emission and the N<sub>2</sub>O/(N<sub>2</sub>O+N<sub>2</sub>) product ratio of denitrification as controlled by available carbon substrates and nitrate concentrations. *Agric. Ecosystems Environ.* 147:4-12.
- Simek M, Cooper JE (2002). The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *Eur. J. Soil Sci.* 53:345-354.
- Smith KA, Ball T, Conen F, Dobbie KE, Massheder J, Rey A (2003). Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *Eur. J. Soil Sci.* 54:779-791.
- Smith P, Martino D, Cai Z, Gwary D, Janzen H, Kumar P, McCarl B, Ogle S, O'Mara F, Rice C, Scholes B, Sirotenko O, Howden M, McAllister T, Pan G, Romanenko V, Schneider, U, Towprayoon S, Wattenbach M, Smith J (2008). Greenhouse gas mitigation in agriculture. *Philos Trans. R Soc. Lond. B Biol. Sci.* 363:789-813.
- Stocker BD, Roth R, Joos F, Spahni R, Steinacher M, Zaehle S, Bouwman L, Xu R, Prentice IC (2013a). Multiple greenhouse-gas feedbacks from the land biosphere under future climate change scenarios. *Nature Climate Change* 3:666-672.
- Stocker TF, Qin D, Plattner GK, Tignor M, Allen SK, Boschung J, Nauels A, Y Xia, Bex V, Midgley PM (eds.) (2013b). IPCC: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.
- Sutton MA, Howard CM, Erisman JW, Bealey WJ, Billen G, Bleeker A, Bouwman AF, Grennfelt P, Van Grinsven H, Grizzetti B (2011). European Nitrogen Assessment, chapter 5: The challenge to integrate nitrogen science and policies: The European Nitrogen Assessment approach, Cambridge University Press.
- Syakila A, Kroeze C (2011). The global nitrous oxide budget revisited. *Greenhouse Gas Meas. Manag.* 1:17-26.
- Thomson AJ, Giannopoulos G, Pretty J, Baggs EM, Richardson DJ (2012). Biological sources and sinks of nitrous oxide and strategies to mitigate emissions. *Philos Trans. R Soc. Lond. B Biol. Sci.* 367:1157-1168.
- Van den Heuvel RN, Bakker SE, Jetten MS, Hefting MM (2011). Decreased N<sub>2</sub>O reduction by low soil pH causes high N<sub>2</sub>O emissions in a riparian ecosystem. *Geobiology* 9:294-300.
- Van Groenigen JW, Velthof GL, Oenema O, Van Groenigen KJ, Van Kessel C (2010). Towards an agronomic assessment of N<sub>2</sub>O emissions: a case study for arable crops. *Eur. J. Soil Sci.* 61:903-913.
- van Groenigen KJ, Osenberg CW, Hungate BA (2011). Increased soil emissions of potent greenhouse gases under increased atmospheric CO<sub>2</sub>. *Nature* 475:214-216.
- Wang K, Zhang R (2011). Estimation of soil water retention curve: An asymmetrical pore-solid fractal model. *Wuhan University J. Nat. Sci.* 16:171-178.
- Wolf I, Brumme R (2002). Contribution of nitrification and denitrification sources for seasonal N<sub>2</sub>O emissions in an acid German forest soil. *Soil Biol. Biochem.* 34:741-744.
- Zumft WG (1997). Cell biology and molecular basis of denitrification. *Microbiol. Mol. Biol. Rev.* 61:533-616.