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Nitrous oxide emissions by agricultural soils: effect of temperature dynamics; up-scaling measurements from the plot to the landscape

Jordan Bureau

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***ÉCOLE DOCTORALE ÉNERGIE, MATÉRIAUX, SCIENCES DE LA
TERRE ET DE L'UNIVERS***

INRA, UR Science du Sol

THESIS presented by

Jordan BUREAU

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Discipline: **Environmental Sciences**

**Nitrous oxide emissions by agricultural soils: effect
of temperature dynamics; up-scaling measurements
from the plot to the landscape**

PhD directed by:

Klaus BUTTERBACH-BAHL Professor, IMK-IFU, Garmisch-Partenkirchen
Catherine HÉNAULT Research director, INRA Science du sol, Orleans

REVIEWERS:

Eric CESCHIA Senior lecturer, CESBIO, Toulouse
Bernard NICOLARDOT Professor, AgroSup, Dijon

JURY:

Klaus BUTTERBACH-BAHL Professor, IMK-IFU, Garmisch-Partenkirchen
Valéry CATOIRE Professor, University of Orléans
Eric CESCHIA Senior lecturer, CESBIO, Toulouse
Christophe FLECHARD Researcher, INRA Agrohydrologie, Rennes
Catherine HÉNAULT Research director, INRA Science du sol, Orleans
Bernard NICOLARDOT Professor, AgroSup, Dijon

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Introduction générale

Depuis sa création, la composition de l'atmosphère de la Terre n'a cessé d'évoluer. L'atmosphère primitive était composée d'eau, de dioxyde de carbone (CO_2) et de diazote (N_2), mais il n'y avait pas de dioxygène (O_2) (Zahnle 2006). Vinrent ensuite les atmosphères primaire et secondaire, avec les mêmes constituants mais une évolution de leurs proportions. Puis, apparurent les cyanobactéries qui en réalisant la photosynthèse ont produit du dioxygène. La présence d'oxygène dans l'atmosphère a conduit à la création de la couche d'ozone dans la stratosphère. Le dernier évènement majeur dans l'atmosphère terrestre est apparu il y a seulement 150 ans, avec la révolution industrielle et la libération de gaz en grandes quantités, notamment de CO_2 . En effet, depuis le début de cette nouvelle ère, les activités anthropiques s'accroissent, avec à titre d'exemple, l'intensification de l'agriculture, des activités industrielles, du transport, de la déforestation et de la production d'énergie et de déchets.

De nos jours, plusieurs sujets environnementaux soulèvent des inquiétudes, notamment du fait des changements dans la composition de l'atmosphère. Ainsi la destruction de la couche d'ozone et le réchauffement climatique, qui modifient notre environnement et les conditions de vie sur Terre, sont directement liées aux émissions gazeuses anthropiques. Parmi les gaz qui contribuent au changement climatique ou à la destruction de la couche d'ozone, on peut citer le CO_2 , le méthane (CH_4) et le protoxyde d'azote (N_2O).

Des scientifiques du monde entier travaillent actuellement à alerter la population et les politiques sur ces problèmes environnementaux afin d'en enrayer les conséquences. Des conférences et conventions telles que Genève (1979), Vienne (1985), Kyoto (1997), et les différentes conférences des Parties (COP) sont dédiées à ces thématiques. Les scientifiques doivent travailler sur les processus à l'origine des émissions de gaz à effet de serre pour

développer des méthodes d'estimation de leurs émissions les plus précises possibles ainsi que pour mettre en place des stratégies d'atténuation.

Objectifs de la thèse

Concernant les émissions de N₂O par les sols, les études présentées dans la littérature peuvent se classer en 3 catégories:

- L'étude du déterminisme des émissions de N₂O et des facteurs de contrôle qui peuvent mener à des émissions (Breuer et al. 2002; Dobbie and Smith 2001; Kurganova and de Gerenyu 2010; Stanford et al. 1975; Zhang et al. 2016).

- Les méthodes de mesure directes *in situ*, sur des surfaces variées (cultures, prairies, forêts), pendant des périodes spécifiques, s'appuyant sur différents principes et équipements de mesure (Beauchamp 1997; Desjardins et al. 2010; Flechard et al. 2007; Phillips et al. 2007; Stehfest and Bouwman 2006).

- La modélisation, à partir de données collectées au champ ou au laboratoire, combinant des éléments issus des mesures et des études de déterminisme. Les modèles peuvent avoir des applications prédictives ou d'identification des sources (Gilhespy et al. 2014; Gu et al. 2016; Langensiepen et al. 2008; Riley and Matson 2000; Wolf et al. 2012).

Ces 3 types d'études sont liés. L'objectif de la thèse a été de travailler sur chacune de ces approches complémentaires, en étudiant l'effet de la température sur les émissions de N₂O (déterminisme), en mesurant les émissions de N₂O à l'aide de différentes méthodes (mesures) mais aussi en développement des méthodes d'attribution des flux, c'est-à-dire pour retrouver les sources d'émissions, et ainsi reconstituer la variabilité spatiale des émissions de N₂O (modélisation).

Par ailleurs, le N_2O est produit à l'échelle microscopique mais ses effets se manifestent à l'échelle globale. Le changement d'échelle (Figure 1) peut s'appréhender de façon graduelle. Les 3 approches d'étude proposées peuvent se développer aux différentes échelles : (1) les études de déterminisme plus spécifiquement de la micro-échelle à l'échelle du paysage, (2) les mesures de flux *in situ*, plus spécifiquement de l'échelle de la parcelle et du petit paysage et enfin à l'échelle globale, (3) la modélisation parfois à micro-échelle mais permettant surtout le changement d'échelle vers celles régionale, nationale et globale.

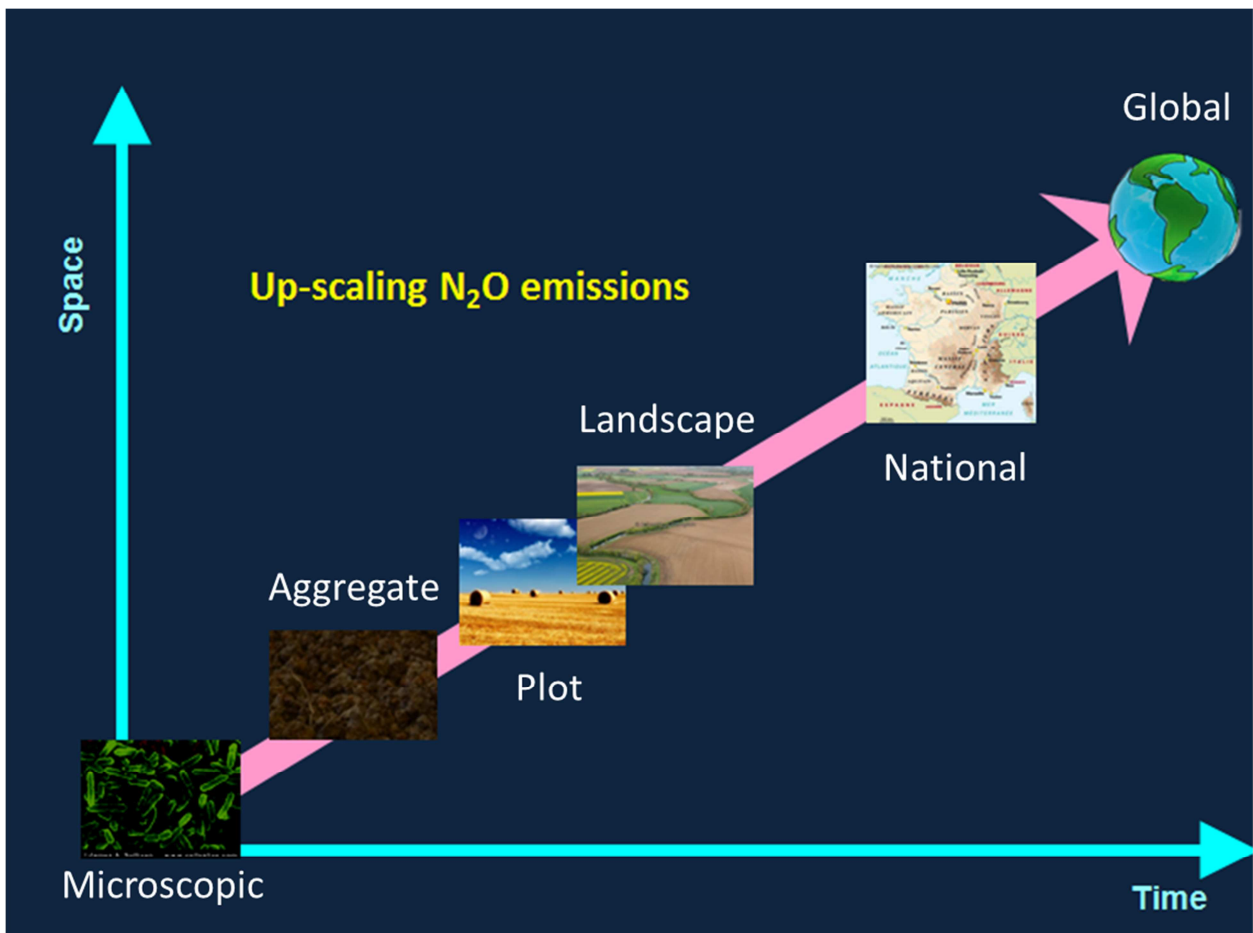


Figure 1: Différentes échelles dans lesquelles le N_2O peut être étudié.

Nous avons combiné les expérimentations en laboratoire, les expérimentations sur le terrain, et la modélisation pour progresser sur la quantification des flux de N_2O , à l'échelle de la parcelle et du paysage. Les objectifs de notre travail étaient (i) de progresser sur le déterminisme des émissions de N_2O et d'améliorer les outils de quantification indirecte par les modèles, avec un travail spécifique sur l'effet de la variation de température sur les émissions de N_2O , pour être intégré dans les modèles, (ii) de progresser sur la réalisation de mesures directes à l'échelle de la parcelle et du paysage, avec l'application de techniques de mesure intégratives dans le temps et le développement d'un dispositif de mesures intégratives dans le temps et l'espace, et, (iii) de progresser dans l'attribution des sources des émissions de N_2O , par le développement d'approches d'attribution de flux à partir des données collectées pendant la campagne de mesures.

Plusieurs questions scientifiques ont été levées sur l'effet des variations de température sur les émissions de N_2O , sur la campagne de mesures, et sur le développement d'une méthode d'attribution de flux.

Concernant l'effet de la température sur les émissions de N_2O :

- Est-ce que les émissions de N_2O sont plus fortes lorsque la température augmente au cours du temps ?
- Qu'en est-il de la régulation par la température du processus de dénitrification et plus particulièrement du processus de réduction du N_2O ?
- Est-ce que les modèles prennent correctement en compte l'effet de la température ?

Concernant la campagne de mesures :

- Est-ce que les mesures faites à partir de 3 méthodes différentes et à différentes échelles peuvent fournir des valeurs comparables ?
- Est-ce que la variabilité spatio-temporelle peut être totalement couverte ?

- Quel type de culture et pratique culturale émet le plus de N₂O ?

Concernant le développement d'une méthode d'attribution de flux :

- Est-ce que les origines des flux de N₂O peuvent être retrouvées à partir de mesures locales et intégratives ?
- Quelle méthode serait la meilleure pour cela et comment estimer sa validité et ses incertitudes ?
- Quelle est la variabilité spatiale des flux de N₂O sur un paysage d'un rayon de 1 km, occupé par un mélange de cultures et de forêts ?

Les résultats de ce travail sont présentés en 6 parties :

- La première partie est une synthèse bibliographique dont le but est de rappeler les problématiques environnementale et scientifique de ce travail, de décrire les émissions de N₂O, les processus impliqués ainsi que l'effet des conditions environnementales. De plus, cette partie introduit les différentes méthodes de quantification pour évaluer les émissions de N₂O.

- La deuxième partie présente le site expérimental à partir duquel du sol a été prélevé pour une expérimentation en laboratoire et sur lequel une campagne de mesures de 2 mois a été réalisée. Elle présente également des études précédentes réalisées sur ce site expérimental.

- La troisième partie porte sur une expérimentation en laboratoire sur l'effet du changement journalier de température sur les émissions de N₂O par un sol agricole.

- La quatrième partie présente la campagne de mesures qui a eu lieu pendant 2 mois au printemps 2015, avec 3 types de mesures réalisés à l'échelle de la parcelle et du paysage, avec

l'utilisation de chambres automatiques, d'une chambre manuelle, et d'un système d'eddy covariance.

- La cinquième partie présente 2 approches d'attribution de flux de N_2O , développées à partir des résultats trouvés pendant la campagne de mesures par les différentes méthodes, et leur validation.

- Enfin, la dernière partie présente les conclusions de cette thèse et les perspectives de ce travail.

General introduction

Since the creation of Earth, its atmospheric composition never stopped to evolve. It began with the primitive atmosphere made of water (H₂O), carbon dioxide (CO₂), dinitrogen (N₂) but no dioxygen (O₂) (Zahnle 2006). There were then the primary and secondary atmospheres with the same constituents but with an evolution of the proportion. After that, came the first cyanobacteria which realized photosynthesis and consequently produced dioxygen. The presence of oxygen in the atmosphere leads to the creation of the ozone layer in the stratosphere. The last big event in the terrestrial atmosphere occurred 150 years ago, with the human industrial revolution and the liberation of huge amount of gases, especially CO₂. Indeed, since the beginning of this new era, anthropogenic activities never stopped to increase with for example the intensification of agriculture, industrial activities, transportation, deforestation, production of energy and waste.

Nowadays, several environmental subjects are under concern, and many of them are due to the change of the terrestrial atmosphere. Indeed, the ozone layer depletion and the global warming, which are threatening our environment, our lives, are directly caused by the anthropogenic emissions. Amongst gases which contribute the most to the climate change and the ozone layer depletion, there are CO₂, methane (CH₄), and nitrous oxide (N₂O).

Scientists all over the world are now working on warning people and politics about these environmental problems to limit consequences. Conferences and conventions such as in Geneva (1979), Vienna (1985), Kyoto (1997), and the different COP (Conference Of Parties) took place to discuss these matters and find solutions. Research groups are asked to work on the processes leading to greenhouse gas emissions to develop estimation methods with uncertainties as low as possible and then propose mitigation strategies.

Objectives of this PhD

When talking about N₂O emissions by soils, 3 types of study are presented in the literature:

- The study of the N₂O emissions determinism and the control factors which can lead or not to emissions (Breuer et al. 2002; Dobbie and Smith 2001; Kurganova and de Gerenyu 2010; Stanford et al. 1975; Zhang et al. 2016).

- Direct N₂O emission measurements on the field, on a specific area (arable land, grassland, forest), during a specific period. These measurements can be done using different types of method (Beauchamp 1997; Desjardins et al. 2010; Flechard et al. 2007; Phillips et al. 2007; Stehfest and Bouwman 2006).

- Modeling, done from data collected on the field or in a laboratory and combining both determinism and measurements. Models will then allow predicting N₂O emissions or retrieving sources of emissions (Gilhespy et al. 2014; Gu et al. 2016; Langensiepen et al. 2008; Riley and Matson 2000; Wolf et al. 2012).

All of these types of study are linked. The aim of this PhD was to develop specific studies on each of these 3 complementary types, by studying the effect of temperature on N₂O emissions (determinism), by measuring N₂O emissions on several sites using different methods (measurements), and at last, by developing 2 flux attribution methods, i.e. to retrieve emission sources and then recreate the spatial variability of emissions at the landscape scale (modeling).

N₂O is produced at the microscale, but its effects are visible at the global scale. The up-scaling (Figure 1) is gradual. Each of the 3 types of study proposed can be developed at different scales: (1) determinism studies more specifically at the microscale to the landscape scale, (2) field flux measurements more specifically at the plot and landscape scale but also at

the global scale, (3) the modeling, sometimes at the microscale but allowing the up-scaling to regional, national and global scales.

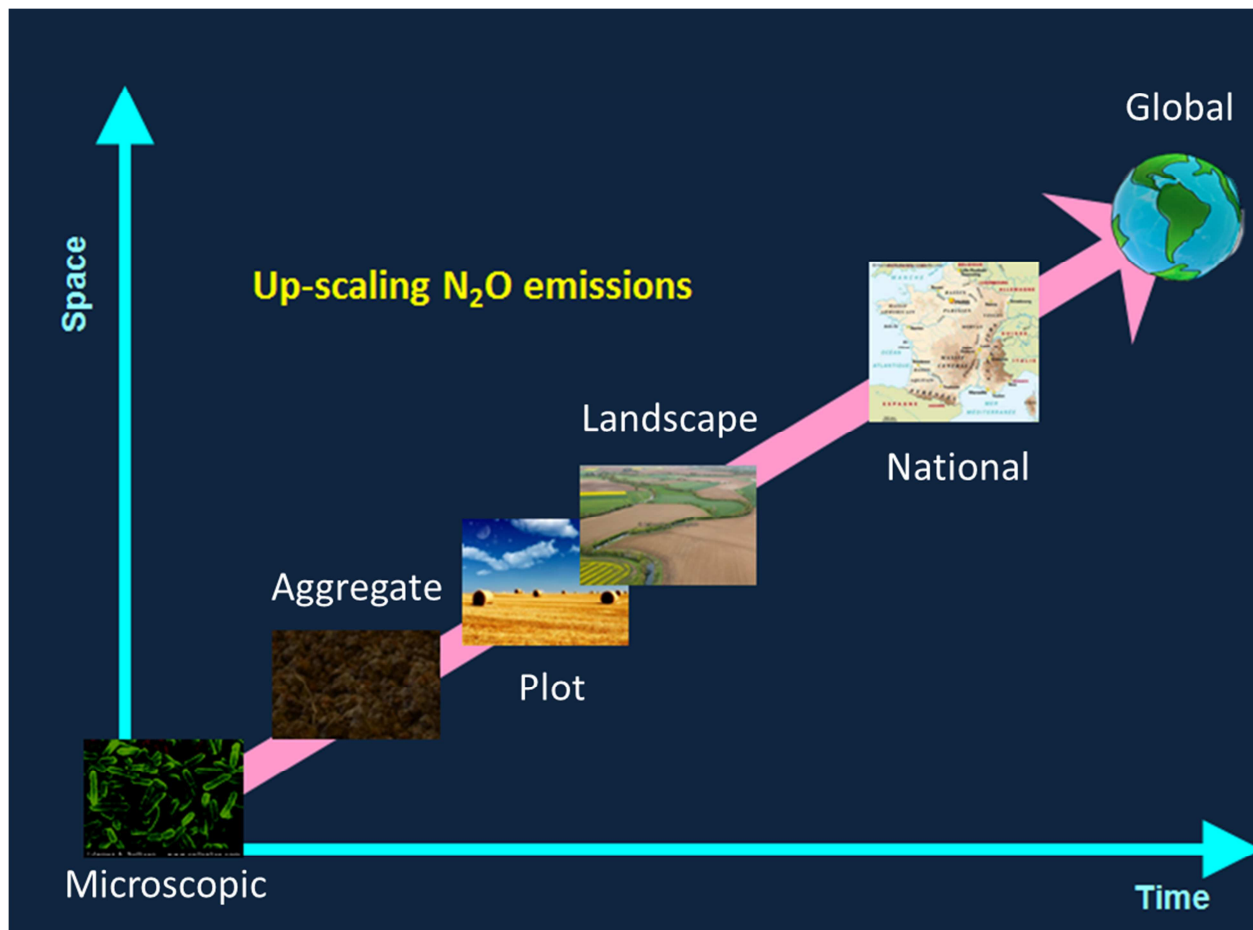


Figure 1: Different scale in which N₂O can be studied.

We combined laboratory experiments, field experiments and modeling to progress on the quantification of N₂O fluxes, at the plot and landscape scale. The objectives of our work were (i) to progress on the determinism of N₂O emissions and to improve indirect quantification tools with modeling, with a specific work about the effect of a varying temperature on N₂O emissions to be integrated in models, (ii) to progress on the realization of direct measurements at the plot and landscape scale with the application of integrative

measurement techniques over time and the development of integrative measurement layout in time and space, and, (iii) to progress on the source attributions of N₂O emissions with the development of flux attribution approaches from data collected during a measurement campaign.

Several scientific questions were raised about the effect of temperature variations on N₂O emissions, the measurement campaign and the development of a flux attribution method.

Concerning the effect of temperature on N₂O emissions:

- Are N₂O emissions higher when temperature increases over time?
- What about the temperature regulation of the total denitrification processes and particularly on the N₂O reduction process?
- Do N₂O emission models correctly take into account the effect of temperature?

Concerning the measurement campaign:

- Can measurements made with 3 different methods and at different scale provide comparable values?
- Can the spatial and temporal variability be totally covered?
- Which type of crop and cultural practices emitted the most?

Concerning the development of a flux attribution method:

- Can the origin of the N₂O fluxes be retrieved from the integrated and local measurements?
- Which method would be the best for that, and how to estimate its validity and its uncertainty?
- What is the spatial variability of the N₂O flux over a 1 km radius landscape occupied by a mix of croplands and forests?

Results of this work are presented in 6 parts:

- The first part is a bibliographic synthesis whose goal is to remind the environmental and scientific issues of this work, to describe N₂O emissions, which processes are involved and what are the effects of the environmental properties on them. Also it introduces the different quantification methods to assess N₂O emissions.

- The second part presents the experimental site where soil has been sampled for a laboratory experiment and where a 2-month measurement campaign has been carried out. It also presents previous studies performed on this experimental site.

- The third part presents a laboratory experiment on the effect of daily temperature variations on N₂O emitted by arable soils.

- The fourth part presents the measurement campaign that has taken place during 2 months on the spring of 2015, with 3 types of measurements made at the plot and landscape scale, using automatic chambers, a manual chamber, and an eddy covariance system.

- The fifth part presents 2 flux attribution approaches of N₂O emissions, developed from results found during the measurement campaign by the different methods, and their validation.

- Finally, the last part presents the conclusions of this PhD and the overviews of this work.

Chapter 1: Bibliographic synthesis

I. N₂O impacts on the environment

1. N₂O and the greenhouse effect

1.1. Greenhouse effect

The sun emits radiations due to its surface temperature of about 6000°K. These radiations wavelength are comprised between 0.2 μm (Ultraviolet (UV)) and 4 μm (Infrared (IR)). The mean solar flux reaching the high layers of the atmosphere is currently equal to 342 W m⁻². Because of the Earth mean albedo (the reflecting power), around 30% of those radiations are directly reflected by clouds, aerosols and the Earth surface. The remaining radiations are either absorbed by the Earth-Atmosphere system as heat (Figure 2) (IPCC 2007) or reach the space.

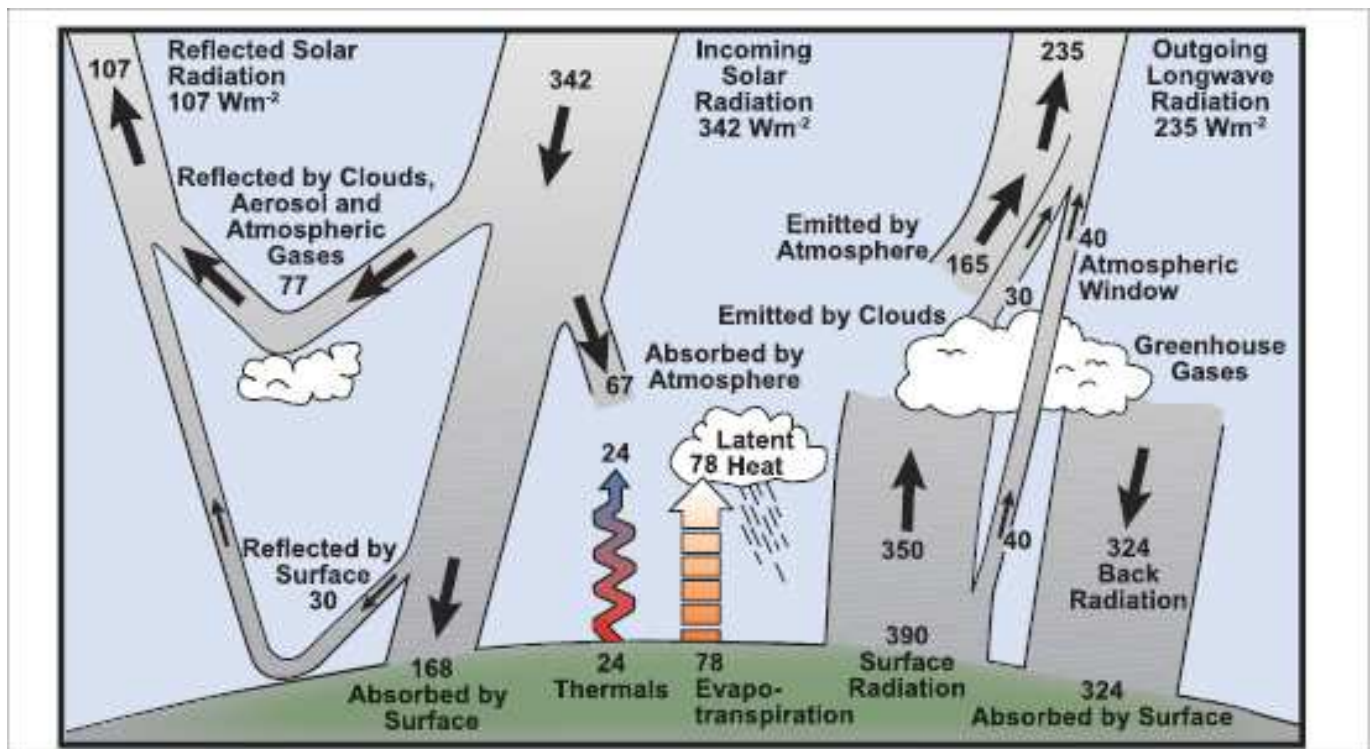


Figure 2: Global energy gain and loss in the Earth system (W m⁻²) (IPCC 2007).

The radiative balance of the Earth-atmosphere system is ensured by the energy exchange between the atmosphere, the Earth and space. The Earth mean surface temperature being 290 K, a part of the received energy is emitted as IR radiation. The remaining energy is absorbed by the water vapor and the greenhouse gases and then are reemitted toward space and the Earth surface (Figure 3). This reemission leads to an increase of the Earth surface temperature of 33°C. This is the greenhouse effect. Without this greenhouse effect, the mean Earth surface temperature would be of -18°C instead of the current +15°C.

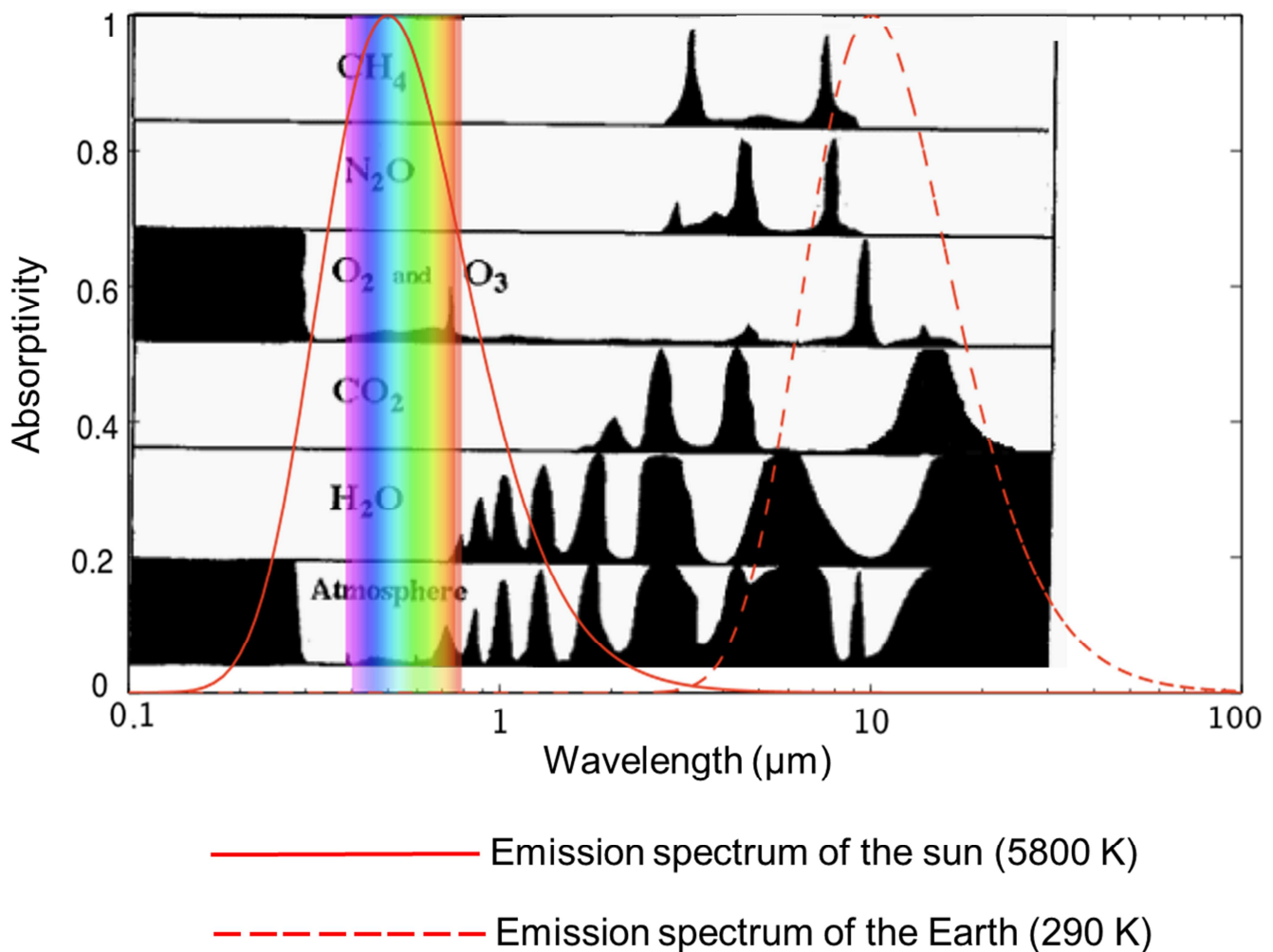


Figure 3: Emission spectrum intensity and wavelength of the Sun and the Earth, and absorption intensity and wavelength of the atmosphere and different gas (Henault and Grossel 2011).

A change in the intensity of the incoming solar radiation, in the terrestrial albedo, or in the capacity of the atmosphere to partially absorb the terrestrial IR radiation, is a natural or anthropogenic radiative forcing of the Earth system. This radiative forcing can be negative if it leads to a decrease of the Earth surface and atmosphere temperatures, or positive if it leads to an increase. Among the anthropogenic radiative forcing, the anthropogenic emissions leading to an increase of the greenhouse gases leads to a positive forcing.

1.2. N₂O and other greenhouse gases

Some atmospheric constituents are defined as greenhouse gases because they absorb IR radiations emitted by soil. The water vapor is the first gas responsible of the natural greenhouse effect. Among the other gases, many are influenced by anthropogenic activities. According to the last report of the IPCC (2014), around 60% of the anthropogenic radiative forcing comes from CO₂. With an increase of 0.4% of its concentration per year, CO₂ is one of the main actors of the radiative forcing. The rest of the radiative forcing comes from other gases such as methane (CH₄), nitrous oxide (N₂O), chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), carbon tetrafluoride (CF₄) and other trace gases.

Several parameters are to be taken into account to assess the environmental impact of a greenhouse gas: the annual increase of its concentration, its molar radiative power (capacity to heat the atmosphere up), its lifetime in the atmosphere, and its interaction with other gases. Calculation of the global warming potential is an indication that takes these parameters into account. The global warming potential is calculated by evaluating the contribution of 1 kg of a gas compared to the same quantity of CO₂ over 100 years. For N₂O, its global warming potential is around 300 times higher than CO₂ (IPCC 2014).

The current mean concentration of N₂O in the atmosphere is 329 ppb (<https://www.esrl.noaa.gov/gmd/aggi/aggi.html>) with an annual increase of 0.73 ± 0.03 ppb y⁻¹ over the last three decades (IPCC 2014). Its concentration is uniform in the atmosphere at

the global scale. It is a chemically unreactive gas with a mean lifetime in the atmosphere of about 120 years. Its long lifetime implies that first, N₂O emitted accumulates in the atmosphere for decades and thus the major part of the N₂O naturally or anthropogenically emitted is still in the atmosphere. Secondly, even if we stop the N₂O emissions right away, it will take more than a century to completely eliminate the anthropogenic N₂O. The increase of N₂O emissions since decades has an impact on the environment. Indeed, this increase is one of the causes for the increase of greenhouse gas effect in the atmosphere, thus the climate perturbation, mainly due to its very high global warming potential. Currently, N₂O is estimated to contribute to 6.2% of the additional greenhouse effect at the global scale (IPCC, 2014).

2. N₂O and the ozone layer depletion

2.1 Ozone layer depletion

The ozone layer depletion is a phenomenon observed since the late 1970s. It is a decline of the total amount of ozone in Earth's stratosphere. During spring when temperatures are really low in the stratosphere around polar regions, large holes in the ozone layer are observed. The ozone layer depletion is caused by different compounds emitted at the surface and transported into the stratosphere by wind. These compounds are mainly anthropogenic (HCFC, CFC), or at least anthropogenic influenced (CO₂, CH₄, N₂O).

CFCs and other contributory substances are referred to as ozone-depleting substances. Since the ozone layer prevents most harmful UV B wavelengths (280-315 nm) of UV light from passing through the Earth's atmosphere, observed and projected decreases in ozone generated worldwide concern, leading to adoption of the Montreal Protocol that bans the production of CFCs, halons, and other ozone-depleting chemicals such as carbon tetrachloride and trichloroethane. It is demonstrated that a variety of biological consequences such as

increases in sunburn, skin cancer, cataract, damage to plants, and reduction of plankton populations in the ocean's photic zone may result from the increased of UV exposure due to ozone depletion.

2.2. Mechanism of ozone layer depletion by N₂O

Ozone is produced in the stratosphere by photolysis of dioxygen to give 2 oxygen (O) atoms, followed by the reaction of an O₂ molecule with an O atom. Inert in the troposphere, N₂O represents the main source of nitric oxides (NO_x) in the stratosphere, making it the first gas responsible of the ozone layer depletion since the prohibition of the CFC (Ravishankara et al. 2009).

In the stratosphere, O is produced by the photolysis of O₃ and O₂, due to the light radiation ($h\nu$):



NO_x are produced by the reaction of N₂O with an excited oxygen atom O*:



Then they react with ozone molecules:



If we sum-up these reactions:



II. Sources of N₂O

1. Anthropogenic impact on N₂O emissions

Nitrous oxide is naturally present in trace quantities in the terrestrial atmosphere, but its concentration increased since the industrialization period with the same dynamic as CO₂ (UNEP 2013) (Figure 4).

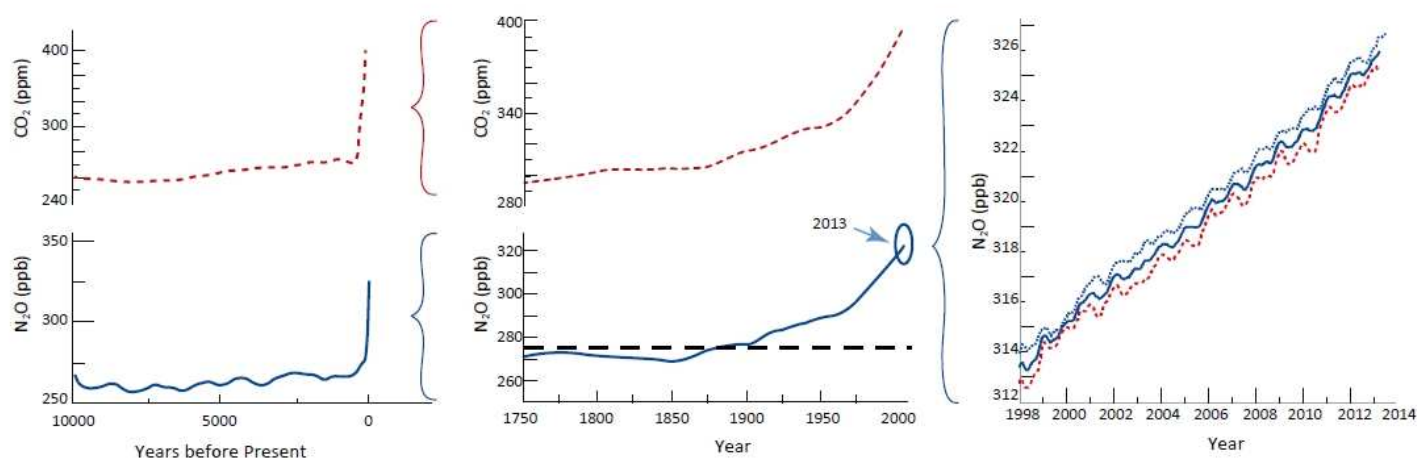


Figure 4: Increase of the N₂O concentration in the atmosphere through the age following the same dynamic as the CO₂ one (UNEP 2013).

Human activities have amplified N₂O emissions, for example, by increasing the amount of reactive nitrogen through the use of synthetic fertilizers (Driscoll et al. 2003). There are several existing N₂O sources, but agriculture appears by far to be the main anthropogenic N₂O emission source (Figure 5). 16.3 Tg N-N₂O is assessed to be emitted each year. A third comes from anthropogenic sources. 77% of the N₂O anthropogenic emissions are estimated to come from nitrogen present in mineral fertilizers and manure, and from other agricultural sources (UNEP 2013). Other important anthropogenic sources are industry and fossil fuel combustion, biomass burning, aquaculture and wastewater.

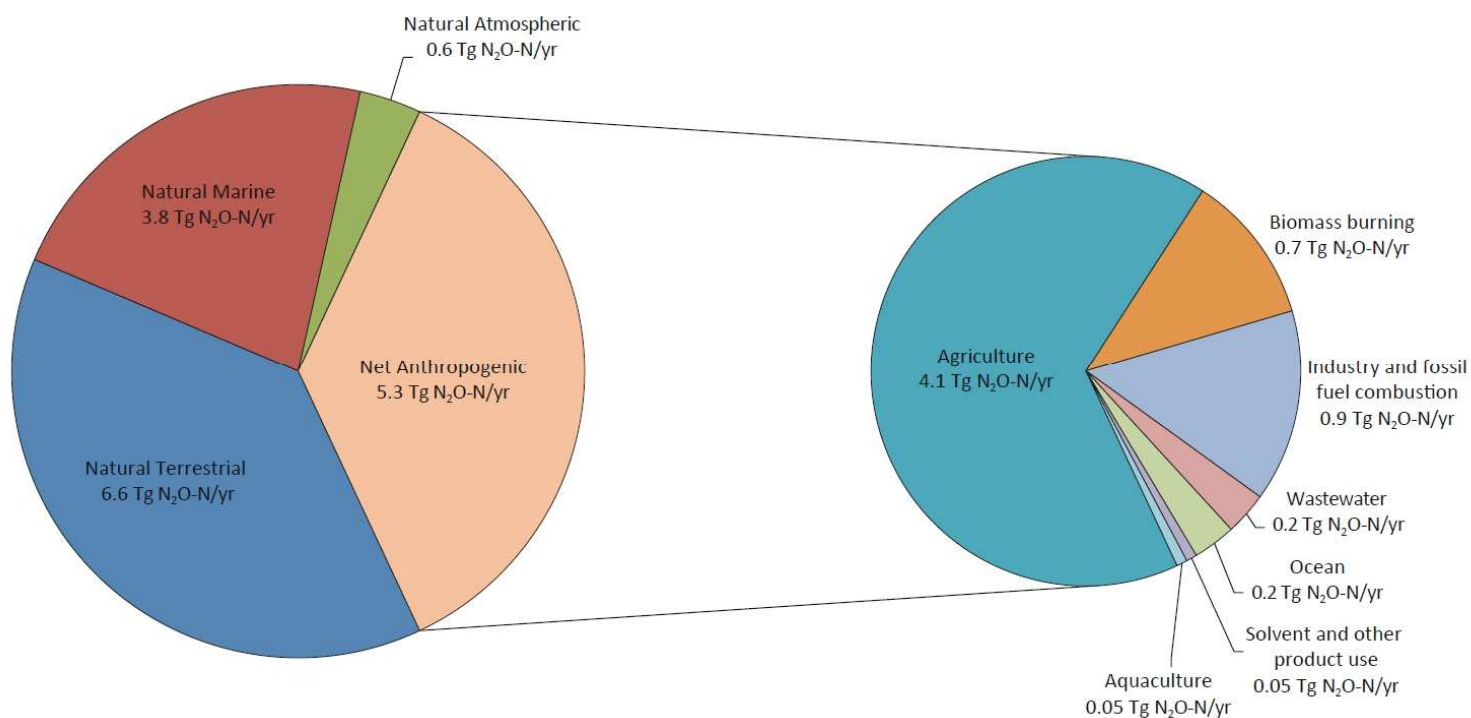


Figure 5: Main N₂O emission sources and their quantities emitted in Tg N-N₂O y⁻¹, and the detail of anthropogenic N₂O sources (UNEP 2013).

Sources are numerous, but sinks are limited. The final budget between sources and sinks is positive and represents an accumulation of N₂O in the atmosphere. However, high uncertainties remain on the estimation of N₂O emissions. That is why it is important to improve the quantification of sources and sinks in order to define economic, agronomical and political strategy to reduce N₂O emissions.

2. Mechanisms and processes of N₂O production.

2.1. N₂O emissions

N is transformed by chemical and biological process, in the water-soil-atmosphere system. In its natural cycle, N goes through these 3 compartments (Figure 6). N is present in the soil in organic and inorganic forms. N can enter the cycle by different ways, e.g. by the fixation of the atmospheric N by plants, or by N input with the use of fertilizers. Most of the plants can use N only in nitric form (N-NO₃⁻) or ammonia form (N-NH₄⁺). Nitrates (NO₃⁻), produced by nitrification or coming from the input of fertilizer on arable soils, can be assimilated by plants, immobilized by microorganisms, or leached in the drainage water or be denitrified. Ammonia (NH₄⁺) can be assimilated by plants, immobilized by microorganisms, or be nitrified. In agriculture, plants need to absorb N to grow. However, when inputs overpass plant needs, the extra N leads to losses that have an impact on the environment. Indeed, the extra N is lost as N₂O emissions in the atmosphere or nitrate leaching in groundwater for example. N₂O emissions from soils are the result of microbial activities, which have complex interactions with soil conditions, climatic conditions and land uses (Skiba and Smith 2000; Weitz et al. 2001). The variety of pedoclimatic contexts and combinations of soil agricultural practices make their impacts on N₂O emissions difficult to study in croplands (Henault et al. 2012). Moreover, with the increase in food demand and environmental concerns, agriculture is currently facing new challenges (Matson 1997; Foley, Crosson et al. 2011) which is requiring the development of more sustainable cropping systems.

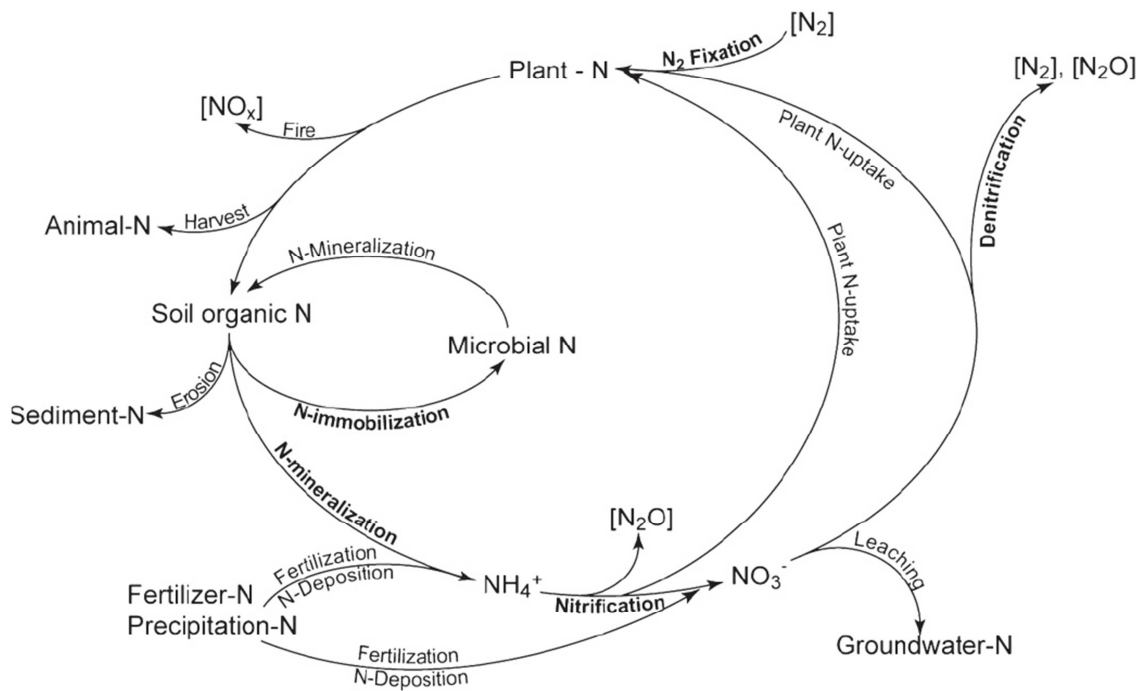


Figure 6: Nitrogen cycle in soils (Robertson and Groffman 2007).

N_2O is emitted by different biotic processes. Nitrification and denitrification, which are respectively aerobic and anaerobic processes, are the main mechanism responsible for the N_2O production (Bateman and Baggs 2005). Braker and Conrad (2011), and Syakila and Kroeze (2011) proposed that nitrification and denitrification contribute roughly to 70% of the global N_2O emissions. Indeed, the description of microbial nitrification and denitrification is a simplification, because microbial pathways provide numerous processes that produce N_2O (Figure 7) (Butterbach-Bahl et al. 2013). Moreover, there are other abiotic processes producing N_2O but they are generally limited and little studied (Robertson and Groffman 2007).

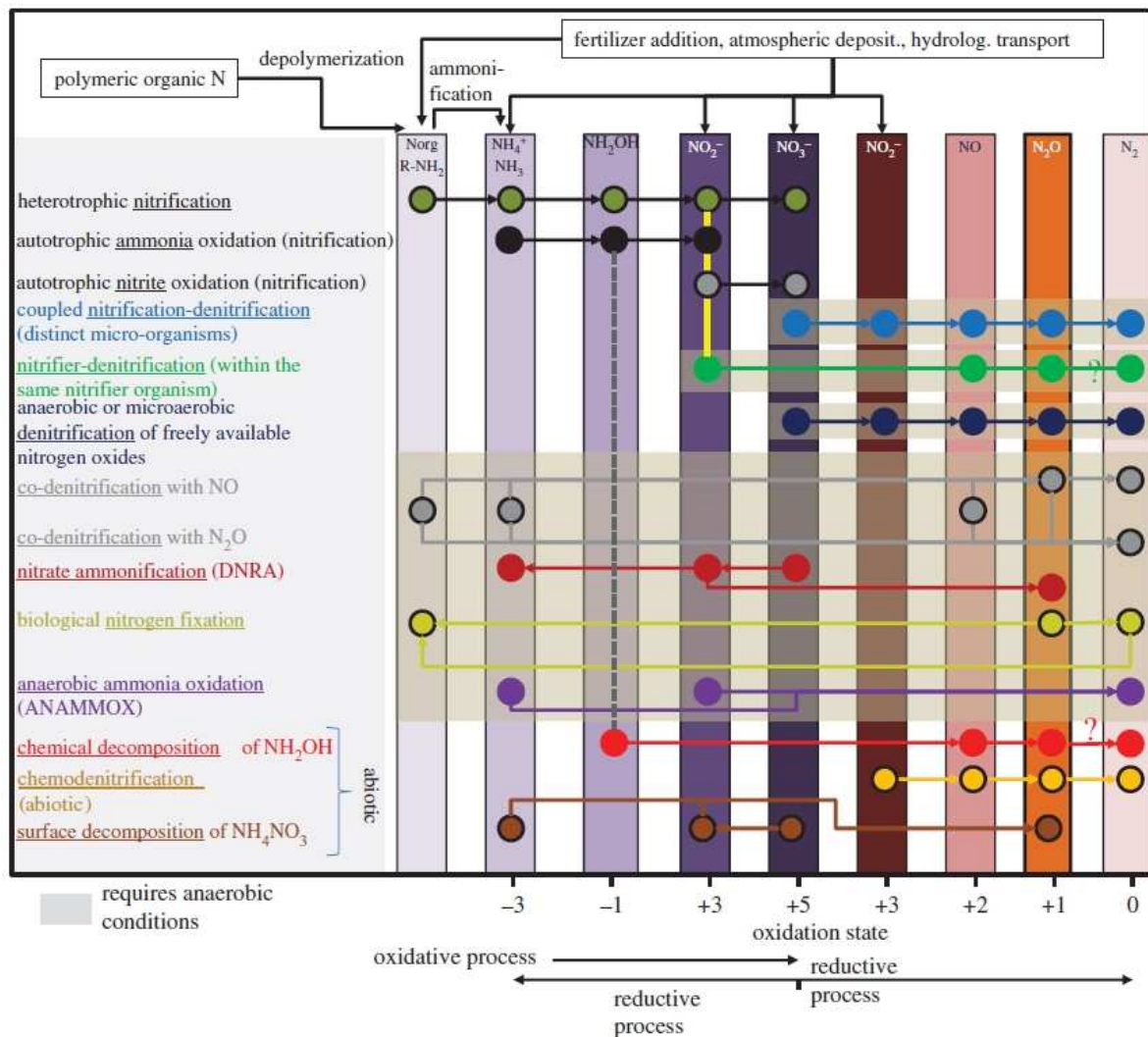
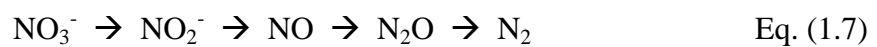


Figure 7: Biotic and abiotic processes of N₂O (Butterbach-Bahl et al. 2013).

The intensity of the N₂O emissions by soils depends on the environmental physicochemical conditions. Micro-organisms responsible for the N₂O production are sensitive to numerous parameters as the water content in soil, the oxygen quantity, the carbon and organic matter availability, the mineral nitrogen availability, and of course the pH and the temperature. These parameters influence the structure and the composition of the microbial communities responsible of the nitrification and the denitrification, the energetic microbial metabolisms (i.e aerobic respiration vs denitrification), and these processes themselves.

2.2. Denitrification

The denitrification is an anaerobic microbial respiratory process in which the oxygen of nitrogen oxides NO_3^- and NO_2^- are used as electron final acceptor. NO_3^- and NO_2^- are reduced to gaseous form: nitric oxide (NO), nitrous oxide (N_2O) and dinitrogen (N_2), catalyzed by specific enzymes respectively nitrate reductase, nitrite reductase, nitrite oxide reductase and nitrous oxide reductase. The chain reaction of denitrification can be written as follows:



Denitrification capacity concern more than 60 types of microorganisms, but mainly bacteria, of which *Pseudomonas* appears to be the most important (Williams 1992). In natural soils, denitrifying bacteria are mainly heterotrophic in aerobic or anaerobic conditions. Indeed, these microorganisms can respire using the oxygen in NO_3^- , NO_2^- or N_2O , when the level of O_2 is low. Some organisms are also capable of producing N_2O and NO by denitrification in aerobic conditions (Colliver and Stephenson 2000). The quantity of N_2O emitted by denitrification depends on the denitrification reaction rate but also on the rate of N_2O reduction. This rate depends on soils and environmental properties, such as oxygen availability, organic matter content, gas diffusion, pH, temperature, mineral nitrogen content (Figure 8) (Robertson 1989). These parameters have an influence on the activity of the 2 main enzymes implicated on the production and consumption of N_2O by denitrification in soils, NO_3^- reductase and NO_2^- reductase (Dendooven and Anderson 1994; Letey et al. 1980).

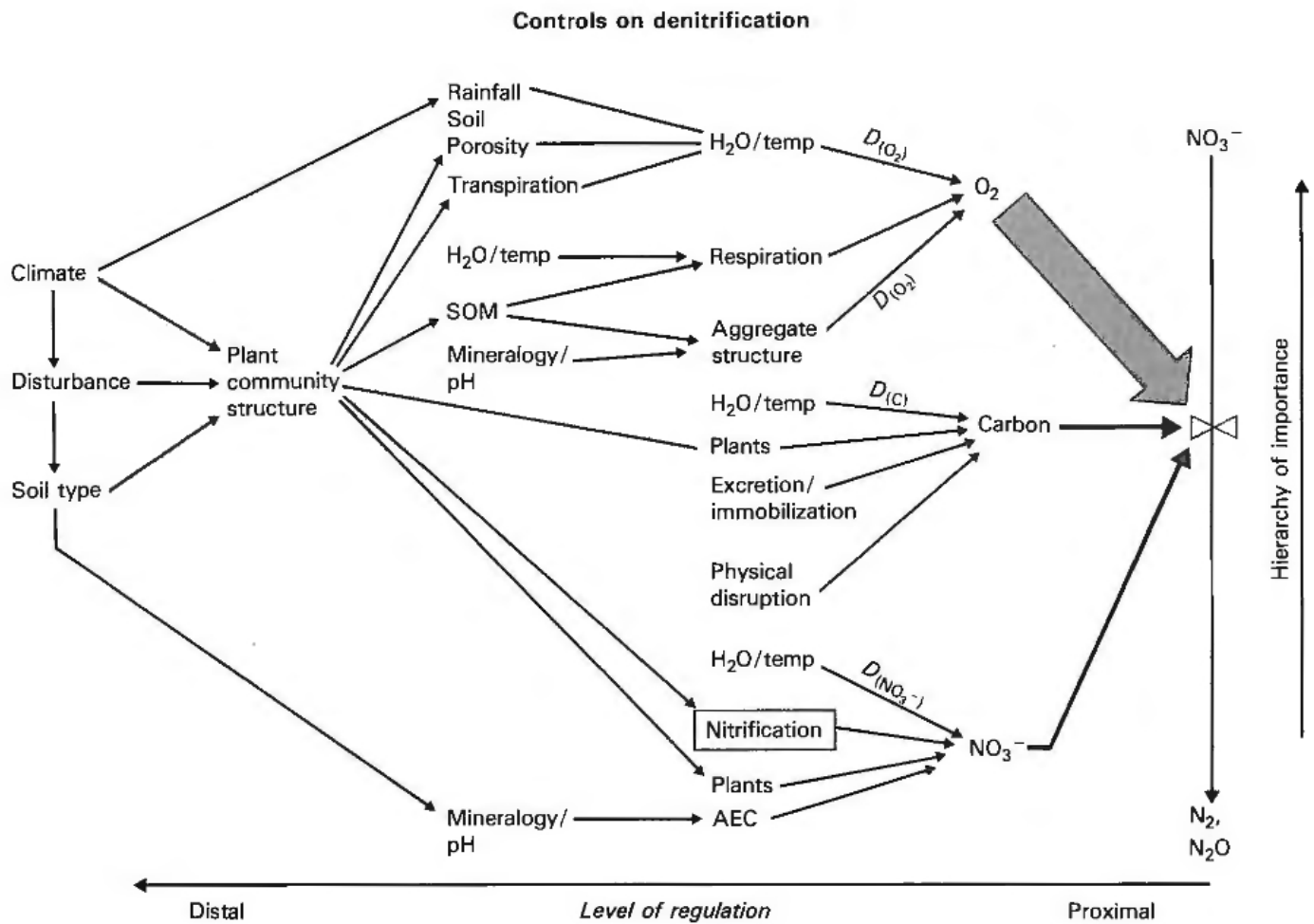
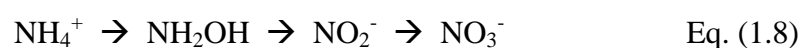


Figure 8: Major factors controlling denitrification (Robertson 1989).

2.3. Nitrification

The nitrification is an aerobic process, heterotrophic or autotrophic, leading to the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-). First the nitritation corresponding to the oxidation of NH_4^+ to NO_2^- catalyzed by ammoniac mono-oxygenase and hydroxylamine oxidoreductase enzymes. Secondly, the nitration, corresponding to the oxidation of NO_2^- to NO_3^- , catalyzed by the nitrite oxidoreductase enzyme. The chain reaction of nitrification can be written as follows:



It is performed by autotrophic bacteria, for example *Nitrosomonas* oxidize NH_4^+ to nitrite and *Nitrobacter* oxidize nitrite to nitrate (Bremner 1997). Autotrophic nitrification is the main process in arable soils while heterotrophic nitrification is the main process on acid soils in subtropical forests (Zhang et al. 2011). Nitrification also depends on soil and environmental properties, such as NH_4^+ content, oxygen availability, water content, pH, and temperature (Figure 9) (Robertson 1989).

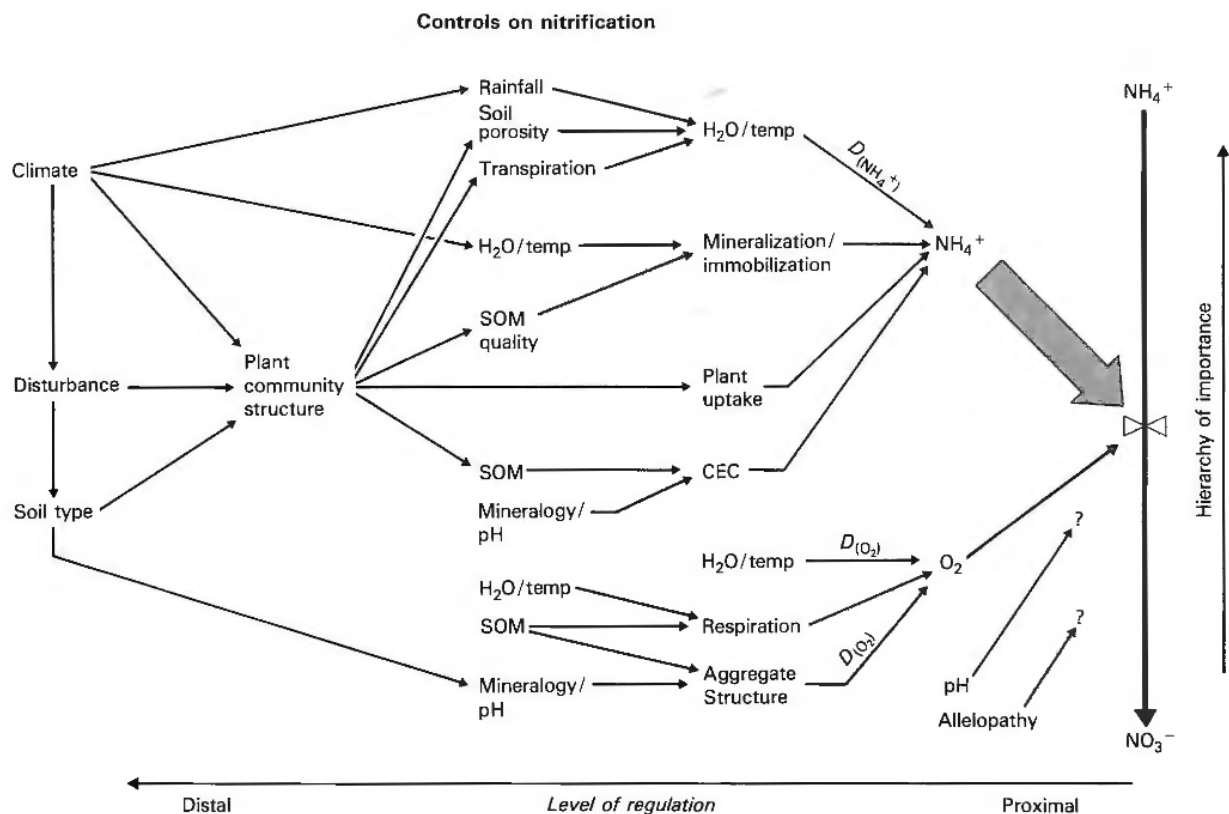


Figure 9: Major factors controlling nitrification (Robertson 1989).

2.4. Environmental factors influencing N_2O emissions

N_2O emissions by soils generally present a high temporal and spatial variability (Mathieu et al. 2006b). In the case of cultivated soils, this variability will be even greater since those environmental parameters are often altered by agricultural practices (eg tillage,

fertilization, cover crops and pesticides) (Smith and Conen 2004; Vilain et al. 2010). Robertson (1989) proposed that the factors that influence the N₂O emissions depend on the study scale. Indeed, control factors can be proximal or distal. Proximal factors are local and control the N₂O production at the micro-scale. On the other hand, distal factors are non-local and control N₂O production at a larger scale (Beauchamp 1997; Bouwman 1996; Mosier et al. 1996). Some factors appear to be favorable to the biomass bacterial activity leading to N₂O emissions.

2.4.1 Proximal factors

Stehfest and Bouwman (2006) compiled and analyzed emissions data, and they concluded that N₂O emissions will depend on the presence or absence of oxygen. The presence of oxygen is related to the water content of the environment. Indeed, the more the soils are waterlogged, the less there is oxygen available (diffusion coefficient of O₂ in water is inferior to the one in air, (Rabot et al. 2014)) and therefore denitrification as respiratory process is privileged in comparison to aerobic respiration. However, when water content is low, there is a lot of free space for gases, and therefore nitrification can prevail as a source of N₂O production due to the oxygen availability, in comparison with denitrification. There is a threshold for the WFPS at 60 %. Under this value the nitrification will be the main source of N₂O production, above this value it will be the denitrification (Linn and Doran 1984) (Figure 10). Thus, during rain events, there are generally peaks of N₂O emissions from soils, as rain led to the formation of favorable sites for anaerobic denitrification processes. In temperate climates, the annual highest emission peaks coincide with the spring rains which arrive at the same time that the use of fertilizers in cultivated land. Moreover, in a dry soil, N₂O emissions can be very limited (Bateman and Baggs 2005).

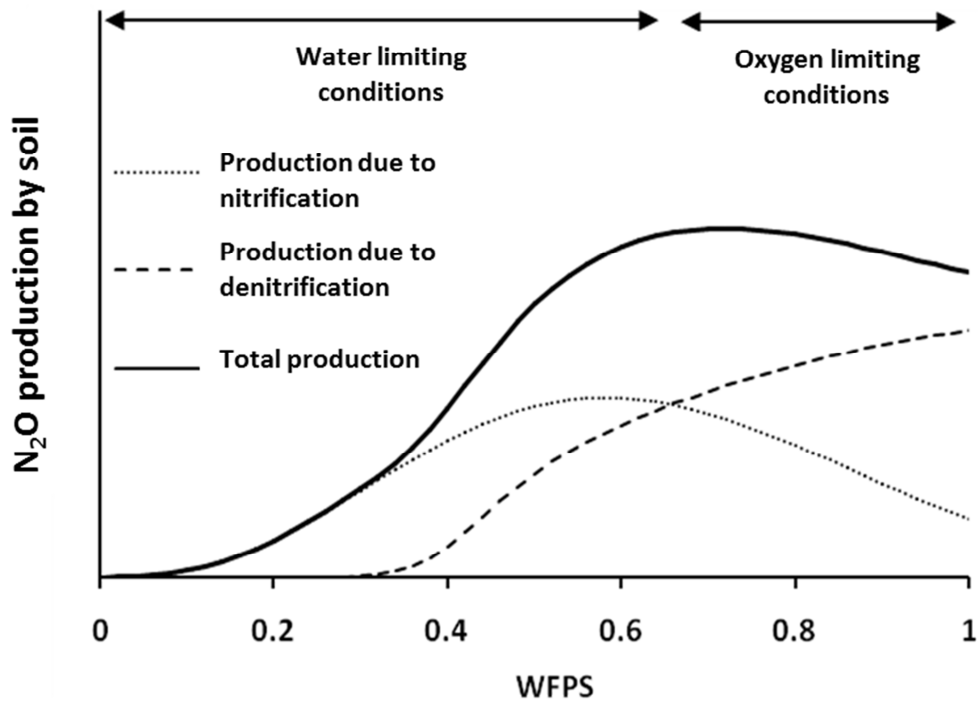


Figure 10: Major factors controlling nitrification (Henault et al. 2011)

Another factor that has an impact on the denitrification regulation is the organic carbon availability. The soil organic matter plays a direct and indirect role on denitrification as most of the denitrifying bacteria are heterotrophic. It first plays the role of the electrons donor during denitrification (Groffman et al. 2009). Moreover, organic matter globally stimulates the bacterial activity and increases the anaerobic sites formation thanks to the organisms respiration (Parkin 1987). N_2O fluxes increase with the organic carbon availability (Harrison-Kirk et al. 2013).

Another factor on the nitrification/denitrification regulation is the mineral nitrogen availability, as NH_4^+ and NO_3^- . More important N_2O emissions are observed when nitrogen fertilizers are added (Avrahami and Bohannan 2009; Kavdir et al. 2008). Input of crop residue can also stimulate microbial activity and lead to N_2O emissions (Chen et al. 2013).

pH regulates both nitrification and denitrification. As many microbial activities, the ones that lead to the N₂O emissions are sensitive to soil pH (Baath and Arnebrant 1994). Soil pH favorable to bacterial activity are neutral or slightly basic (Chen et al. 2013; Simek and Cooper 2002). Soil pH can be artificially maintained to a favorable value with liming to reduce N₂O emissions.

Temperature positively affects the functioning of microbial communities (Avrahami and Bohannan 2007; Pietikainen et al. 2005), and affects N₂O emissions. There is a positive correlation between the increase of temperature and the increase of N₂O emissions, in the range of temperature measured on the field (Smith et al 2003). Every microbial activity varies with temperature, it is negligible under a threshold temperature and increase until it reaches an optimal temperature. There are optimal temperatures for both nitrification and denitrification processes and a threshold at 11°C was proposed by Stanford (1975) under which denitrification rate sharply decrease. The denitrifying activity increase with temperature comprised between 4 and 37°C (Braker et al. 2010) while the nitrification decrease with the decrease of the temperature from 20°C to 5°C (Russell et al. 2002). However, microorganisms are able to adapt to their environment, and so it remains difficult to define a universal temperature function (Farquharson and Baldock 2008). Furthermore, it will be possible to observe significant emissions of N₂O in cold environments and during freezing and thawing periods (Morkved et al. 2006; Teepe et al. 2001).

2.4.2 Distal factors

Landscapes represent an indirect controlling factor on N₂O emissions due to their influence on the soil mineralogy, its texture and structure, on the distribution of the water, carbon and nitrogen content.

The soil use and the management practices have an impact on the N₂O production. Many studies measured N₂O emissions from the different types of soil use, and found

differences explained by the effect of the soil use on humidity, carbon and N content (Abdalla et al. 2009; Beauchamp 1997; Breuer et al. 2000; Zhang et al. 2016). Management practices (type and quantity of fertilization, tillage or ploughing, straw removal, irrigation) have an impact on N₂O emissions (Vermue et al. 2016). The application of N fertilizer have to be controlled, otherwise it can lead to huge amount of N₂O emissions. Van Groenigen et al (2010), showed the impact of N surplus and N₂O emissions (Figure 11).

Texture and soil structure define the porous system therefore the WFPS. The pore size, connectivity and tortuosity are factors controlling the period of oxygen restriction and so denitrification.

Seasonal variations of precipitations and temperature control the water content via inputs and evapotranspiration, and then control soil humidity, and the carbon and N availability (Groffman et al. 2000). Local change in precipitation can trigger change on N₂O emissions due to an increase of the soil water content.

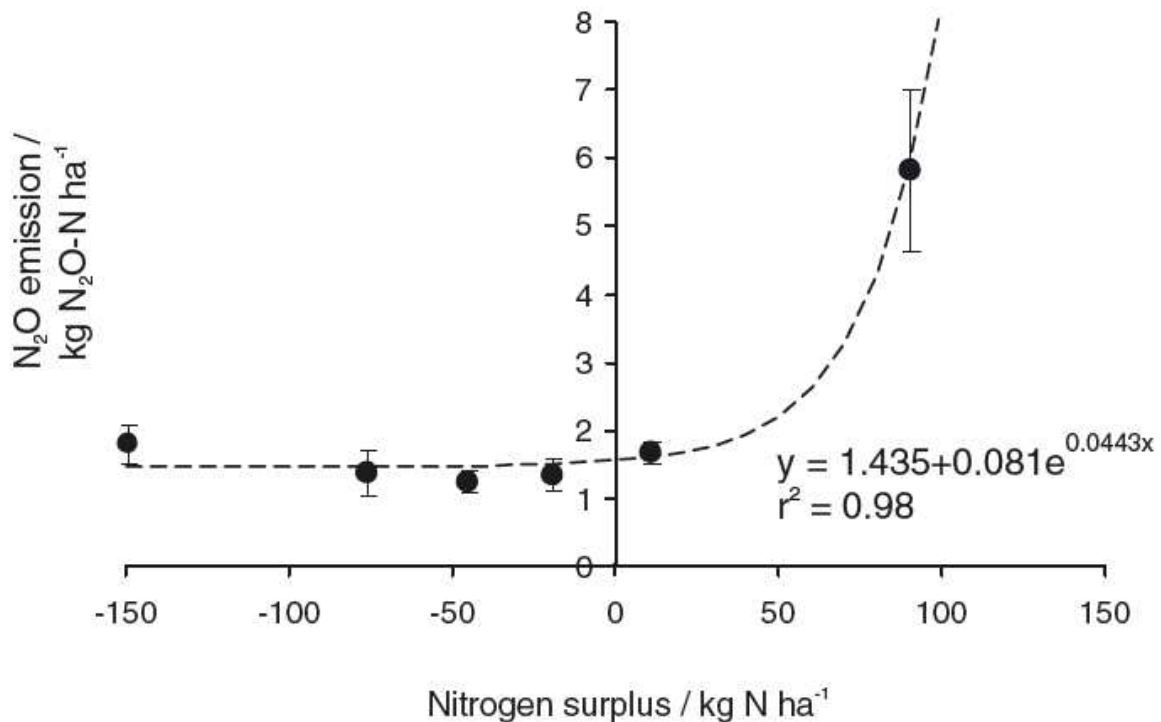


Figure 11: Impact of N surplus on N₂O emissions (Van Groenigen et al. 2010).

III. Quantification methods of N₂O emissions

Despite the importance of N₂O as a gas responsible for the global warming and the ozone layer depletion, its budget at the global scale is still not well understood and not well quantified. The difficulty to quantify N₂O emissions comes from their high temporal and spatial variability (Henault et al. 2012). However, several investigation methods have been developed in order to study N₂O emissions by soils. Some have been developed to measure N₂O emission in a laboratory, some others directly on the field. In a laboratory, measurements are generally done in soil cylinder sampled on the field and brought back to the laboratory (Dobbie and Smith 2001; Kurganova and de Gerenyu 2010; Zhang et al. 2016). In situ, the 2 main methods to quantify N₂O emissions are chambers and micrometeorological methods (Flecharde et al. 2007; Henault et al. 2012; Laville et al. 2011; Molodovskaya et al. 2011; Pattey et al. 2007). These 2 methods do not measure at the same spatial scale but they can be used together and combined (Griffis et al. 2013; Molodovskaya et al. 2011). Both methods have their own advantages and disadvantages (Denmead 2008). Analyzers to quantify N₂O emissions are generally gas chromatographs, cascade quantum lasers (QCL) or Infra-Red spectrometers.

1. Soil cylinder method

The soil cylinder method consists in taking soil samples on the field and to bring them back to the laboratory. Samples can be destructured, meaning that cylinders have been recreated afterward with a mix of the soil samples (Zhang et al. 2016). This technique is easier but it does not represent exactly the field conditions. Cylinders can also be sampled non-destructured (Dobbie and Smith 2001; Tiedje et al. 1989). To do so, cylinders have to be implanted directly on the field before brought back to the laboratory. This technique permits to be in more realistic conditions respecting the field soil structure. Once in the laboratory, all

kind of treatment can be applied to the samples, such as a change in temperature, water-filled pore space, nitrate content, organic matter content, and pH, so that factors controlling N₂O emissions can be studied. Soil cylinders are placed on closed volumes (e.g. columns, jars) with a lid placed at the top and gas samples are taken from it to be analyzed. N₂O emitted from the soil cylinders accumulates on these volumes and the increase of the N₂O concentration is measured. From this increase of gas concentration, a flux can be calculated.

2. Chamber method

The chamber method consists on placing a box on the ground in the field, enclosing a given area, and to measure the accumulation of gas inside it. This method can be used for any other gases such as CO₂ or CH₄. The flux is proportional to the rate of concentration change in the chamber over time. 2 kinds of chambers can be distinguished:

(i) The closed system for which there is no air replacement in the chamber volume during measurements. The flux of gas is calculated as:

$$F_g = \frac{V}{A} \frac{d\rho_g}{dt} \quad \text{Eq. (1.9)}$$

where F_g is the flux of gas at the surface (kg m⁻² s⁻¹), V is the volume of the head space (m³), A is the surface area covered by the chamber (m²), ρ_g is the gas concentration in the chamber (kg m⁻³), t is the time (s).

(ii) The open system for which a constant air flux is imposed inside the chamber. The flux of gas is calculated as:

$$F_g = \frac{v(\rho_{g,o} - \rho_{g,i})}{A} \quad \text{Eq. (1.10)}$$

where F_g is the flux of gas at the surface (kg m⁻² s⁻¹), v is the volume flow rate (m³ s⁻¹), $\rho_{g,o}$ is the gas concentration in the air leaving the chamber (kg m⁻³), $\rho_{g,i}$ is the gas concentration in the air entering the chamber (kg m⁻³), A is the surface area covered by the chamber (m²).

Closed system chambers are used more often than the open system chambers because they are easier to use and concentration changes are easier to detect (Denmead 2008).

Chambers can be manual meaning that measurements are done punctually (Clayton et al. 1994; Henault et al. 1998; Laville et al. 1997; Mosier et al. 1996). Chambers are placed on pre-installed frames on the field and gas accumulates during 30 min to 2 hours. Gases are sampled through a septum with a syringe and placed into vacuumed vials, then brought back to the laboratory for analysis with a gas chromatograph. Chambers always stay at the same place and several spatial repetitions are needed. Manual chambers are the most used technique to measure soil gas emissions. It is the simplest and cheapest chamber method but on the other hand, manual chambers need someone to manipulate them and so it only can be used punctually, therefore the temporal variability will not be studied very thoroughly.

The fast-box technique is a manual chamber directly connected to an analyzer on the field (Flechard et al. 2007; Grossel et al. 2014; Hensen et al. 2006). Measurements are done for a couple of minutes. The advantages are principally that measurements are done faster, only one fast-box is needed to do all the measurements, measurements can be done anywhere without any frame pre-installed on the ground, and many sites can be sampled. However, this technique needs an analyzer that can be reliable on the field.

Chambers can also be automated, meaning that they are placed on the ground and connected to an analyzer directly on the field, and are programmed to open and close (Breuer et al. 2000; ButterbachBahl et al. 1997; Christensen et al. 1996; Neftel et al. 2010). Measurements are done automatically in a closed system and the whole system can run as long as it is needed. The advantage is that no one is needed to do the measurements and they can be done all the time, during nights and weekends, so that a temporal dynamic can really be observed. On the other hand, once they are placed on a specific place, they cannot be moved to another place, and so the spatial variability cannot be studied. Furthermore, they

need power to run and so they must be placed near an electrical supplier or used with a generator and the analyzer must be stable and accurate. It is the most expensive chamber method.

Plants might need to be cut in certain case, if the chamber cannot be perfectly hermetic. This can lead to an alteration of the environment and so biases measurements. The size of the chamber is important. If the chamber is too high, the gas emissions could not be detected or misdetected due to a bad mix of the air inside the chamber. On the other hand, if chambers are too small, environmental conditions such as temperature, humidity, gas concentration, inside the chamber can be impacted and lead to a biased measurement (Hutchinson and Livingston 2001). Also chambers have to be well inserted on the soil to limit lateral gas diffusion. The deployment time also has an impact on the air and soil temperature and on humidity inside the chamber. It also impacts gas leaks, with for consequence, errors on flux estimation. That is why it is highly recommended to avoid deployment time higher than 60 minutes (Parkin and Venterea 2010) and to prefer deployment time lower than 40 minutes (Rochette and Eriksen-Hamel 2008).

Fluxes obtained with the chamber method (automated and manual) are generally associated with very large uncertainties because of the very small surface area investigated coupled to underlying various artefacts leading to alteration of the natural concentration gradient within the soil (Davidson et al. 2002) and non-linear phenomena, chamber design and flux calculations (Pihlatie et al. 2013).

3. Micrometeorological methods

Micrometeorological methods consist on estimating fluxes from wind turbulence and from gas concentrations from a mast or a tower located in the studied area. Micrometeorological methods are the most appropriate for estimating gas fluxes in situations representative of ecosystems. It is assumed that fluxes are almost constant with height and that concentrations

change vertically but not horizontally (Denmead 2008). The flux measured at a height z is the result of many sources upwind. The use of a micrometeorological mast/tower provides information on temporal variability over a wide spatial area defined by the height of the mast/tower (plot, landscape). Flux footprint is the area “seen” by the instrument at the tower. In other words, it is an area upwind from the tower, such that fluxes generated in this area are registered by the tower instruments. Another frequently used term, fetch, usually refers to the distance from the tower to the maximal upwind distance that is contribution to the flux measured by the tower. The fetch of the tower depends mainly on the height of the mast/tower. It also depends on the roughness of the field and the thermal stability (Burba and Anderson 2010).

These methods permit non-intrusive quantification of trace gases by not disturbing gas exchange between the soil and the atmosphere, they integrate fluxes over larger scale (plot, landscape) and provide continuous measurements. Fluxes obtained by micrometeorological methods are dependent on wind conditions during the measurement period. Therefore they are wind-dependent and cannot be considered as absolute values. Also the installation of such method requires a very high technical level and is quite expensive (Henault et al. 2012). Gases are analyzed by IR spectroscopy: Fourier transform IR spectroscopy (Hashmonay 2001), QCL or tunable diode laser absorption spectroscopy (De Klein et al. 1999).

The eddy Covariance is the most direct method to measure vertical turbulent fluxes of gas in the atmospheric boundary layer (Christensen et al. 1996; Flechard et al. 2007; Laville et al. 1999; Molodovskaya et al. 2011). Flux is calculated as the covariance between the fluctuations (denoted by prime and equal to the instantaneous value minus the mean value) of gas density (ρ_g in g m^{-3}) and vertical wind speed (w in m s^{-1}), and the dry mole fraction of the gas in the air (s in kg kg^{-1} of dry air) (Burba 2013).

$$F = \overline{\rho_d' w' s'} \quad \text{Eq. (1.11)}$$

This method requires state-of-the-art instruments measuring generally at frequencies of 10 Hz. The vertical wind speed w is measured with a 3-D sonic anemometer as well as the wind direction.

IV. Modeling of N₂O emissions

Estimations of direct N₂O emissions have really high uncertainties, because of their high spatial and temporal variability (Henault et al. 2012). Therefore, direct measurements of N₂O emissions by soils are expensive, long and difficult. Thereby, elaboration and development of predictive models of N₂O emissions is essential. Modeling of a process, such as N₂O emissions, has for objective to describe and predict the dynamic from mathematical functions. Several types of models exist and depend on the complexity of the process and the objective wanted. Models can be sorted following the way they are made (stochastic, empiric, mechanist) or the scale in which they work (laboratory, plot, landscape, regional, global).

The goal is to estimate emissions for a higher number of sites using simpler parameters such as temperature, humidity or nitrogen content instead of realizing direct measurements. Several models have been developed in order to simplify its use, or to integrate a new parameter compared to another model. Some are multiplicative models like NLOSS (Riley and Matson 2000) or NOE (Henault et al. 2005). They use simple mathematical formulas to express temperature, nitrate and water content effects to simulate N₂O fluxes. Formulas are calculated from field measurements. There are also ecosystem models such as DNDC (Li et al. 1992), DAYCENT (Parton et al. 2001) or CERES-EGC (Gabrielle et al. 2006). They do not simulate only N₂O emissions but the evolution of numerous parameters in the environment.

1. The IPCC approach

The IPCC approach (1997) has for objective to estimate annual anthropic N₂O emissions at the country scale. This approach introduces emission factors (EF) which are statistically evaluated from data collected on different situations and which give the quantity of N₂O emitted for a quantity of nitrogen fertilizer input. EF are defined as:

$$FE = \frac{N_{N_2O \text{ fertilized}} - N_{N_2O \text{ not fertilized}}}{N_{\text{fertilizer}}} \quad \text{Eq. (1.12)}$$

with $N_{N_2O \text{ fertilized}}$ the N₂O emissions of a fertilized plot (kg N ha⁻¹ y⁻¹), $N_{N_2O \text{ not fertilized}}$ the N₂O emissions of a non-fertilized plot (kg N ha⁻¹ y⁻¹), and $N_{\text{fertilizer}}$ the quantity of fertilizer input (kg N ha⁻¹ y⁻¹). This approach makes the simple assumption that the nitrogen input is the only regulation factor of anthropic N₂O emissions.

The current EF is 1% [0.3-3%] (IPCC 2006). Direct N₂O emissions from arable soils are calculated as:

$$N_{2O \text{ direct}} = [F_{SN} + F_{AW} + F_{CR} + F_{BN}] \times EF_1 \quad \text{Eq. (1.13)}$$

with F_{SN} the total quantity of artificial fertilizer used (kg N ha y⁻¹), F_{AW} the nitrogen quantity from manure used as fertilizer (kg N y⁻¹), F_{CR} the nitrogen quantity from crop residues which go back to soils (kg N y⁻¹), F_{BN} the nitrogen quantity coming from the crops with nitrogen fixation (kg N y⁻¹), and $EF_1 = 0.01 \text{ kg N-N}_2\text{O kg}^{-1}$ of N input².

However this method has an important uncertainty, but the purpose is to give a simple method to estimate N₂O emissions without experimentations.

2. NOE

NOE for Nitrous Oxide Emission (Henault et al. 2005) is a model simulating N₂O emissions from both denitrification and nitrification. It's a semi-mechanistic model to predict N₂O emissions at the plot scale. Simulated N₂O emissions is the sum of 2 fluxes simulated by 2 sub-models. These sub-models simulate both denitrification and nitrification from physico-chemical parameters taken into account: NO₃⁻ content, NH₄⁺ content, WFPS and soil temperature.

N₂O emissions from denitrification are estimated as follow:

$$N_2O_{denit} = r_{max} D_A \quad \text{Eq. (1.14)}$$

with

$$D_A = D_P F_N F_W F_T \quad \text{Eq. (1.15)}$$

and r_{max} , the capacity of the soil to reduce N₂O, D_P the potential denitrification, F_N , F_W and F_T functions taking into account respectively the nitrate content, the water content, and the soil temperature.

This model also considers that N₂O from nitrification is proportional to the nitrification rate which depends on the hydric potential. N₂O emissions from nitrification are estimated as follow:

$$N_2O_{nit} = z N_A, \quad \text{WFPS} < 0.62$$

$$N_2O_{nit} = r_{max} z N_A, \quad \text{WFPS} \geq 0.62$$

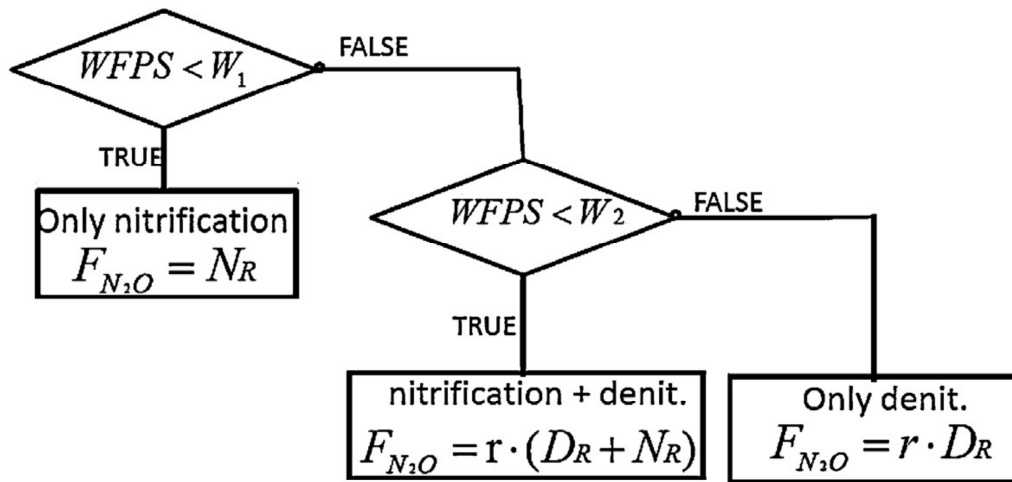
with

$$N_A = 0, \quad \text{WFPS} > 0.8$$

$$N_A = N_W N_{NH_4} N_T, \quad WFPS \geq 0.62$$

and z the proportion of nitrified N emitted as N_2O , N_W , N_{NH_4} and N_T functions taking into account respectively the water content, the ammonia content and the soil temperature.

The basic principle of the NOE model is presented Figure 12. Specific parametrization at each studied site permit to simulate realistic fluxes over different pedoclimatic contexts (Gabrielle et al. 2006; Gu et al. 2016; Hergoualc'h et al. 2009).



Where:

$$N_R = z_N \cdot N_T(T) \cdot N_N(NH_4) \cdot N_W(WFPS)$$

Nitrification rate

$$D_R = D_p \cdot F_T(T) \cdot F_N(NO_3) \cdot F_W(WFPS)$$

Denitrification rate

Figure 12: Basic principle of the NOE model (Grossel et al. 2014).

3. Ecosystem models

Ecosystem models, such as DNDC (Li et al. 1992) or CERES-EGC (Gabrielle et al. 2006), do not only simulate N_2O emissions but everything in the ecosystem. These models need input data measured on the field and will then simulate evolution of these parameters at a daily time step. Input data are (i) physical soil properties (depth, texture, density), (ii)

chemical soil properties (pH, organic carbon and nitrogen, total nitrogen), (iii) hydric soil properties (hydraulic conductivity, field capacity, wilting point, retention curves, infiltration rate), (iv) site characteristics (mean temperature, thermal amplitude, albedo, latitude), (v) microbiological soil properties, (vi) meteorological variables (air temperature and humidity, precipitation, wind speed), and (vii) agronomic variables (land use, tillage, type of fertilizer). From these input data, several variables will be simulated such as fluxes and concentrations of nitrogen compound (NH_3 , NO_x , N_2O , NO_3^- , N_{tot}), the plant growth, the crop yield, the water and nitrogen content as well as the temperature in the different layers of the soil. There is a specific module for each parameter and so for N_2O emissions. This module is NOE for CERES-EGC for example. DNDC was used in many countries to simulate N_2O emissions by arable soils and grasslands at the plot and landscape scales (Brown et al. 2002; Desjardins et al. 2010; Saggar et al. 2010), as well as CERES (Dufosse et al. 2013; Langensiepen et al. 2008; Xiong et al. 2008) (Figure 13).

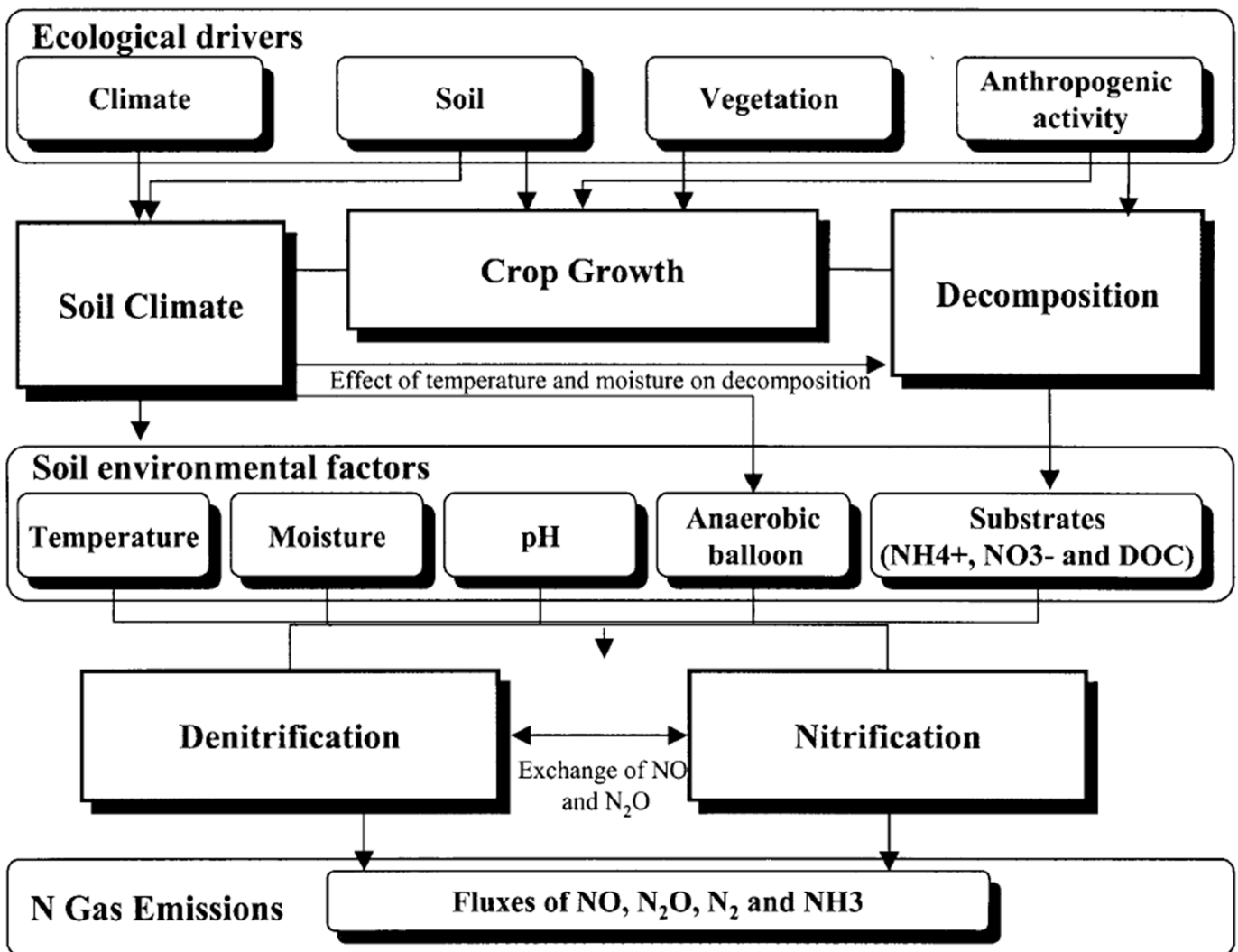


Figure 13: Basic principle of the DNDC model (Smith et al. 2002).

Chapter 2: The experimental site: description and previous studies

I. Experimental site description

The OS² site (“Observatoire Spatialisé Orléanais des Sols”) is the support of several projects of the Soil Science Research Unit since 2008, and is mainly focused on the N₂O emissions. This 20 km² experimental site is representative of crop sites dominated by cereals. Cereal farms are polycultural. Data on agricultural practices (fertilization, crop rotation, soil tillage, straw treatment) are obtained since 2008 from annual agricultural surveys realized with farmers.

1. Geographical situation

The OS² site is located on the edge of the small natural regions of Beauce Chartraine and Faux-Perche, near the Loir river source. OS² is located 120 km southwest of Paris, at the north of the city of Illiers-Combray, in the Eure-et-Loir department, Center region, France (Figure 14). 87% of the cultivated plots are tile-drained (Figure 15). Creeks that run through the site are mainly fed by agricultural drainage water. Creeks are discharged entirely in the Loir river. The creeks and the Loir river, are temporary streams, which no longer flow in dry periods.



Figure 14: Localization of the OS² site

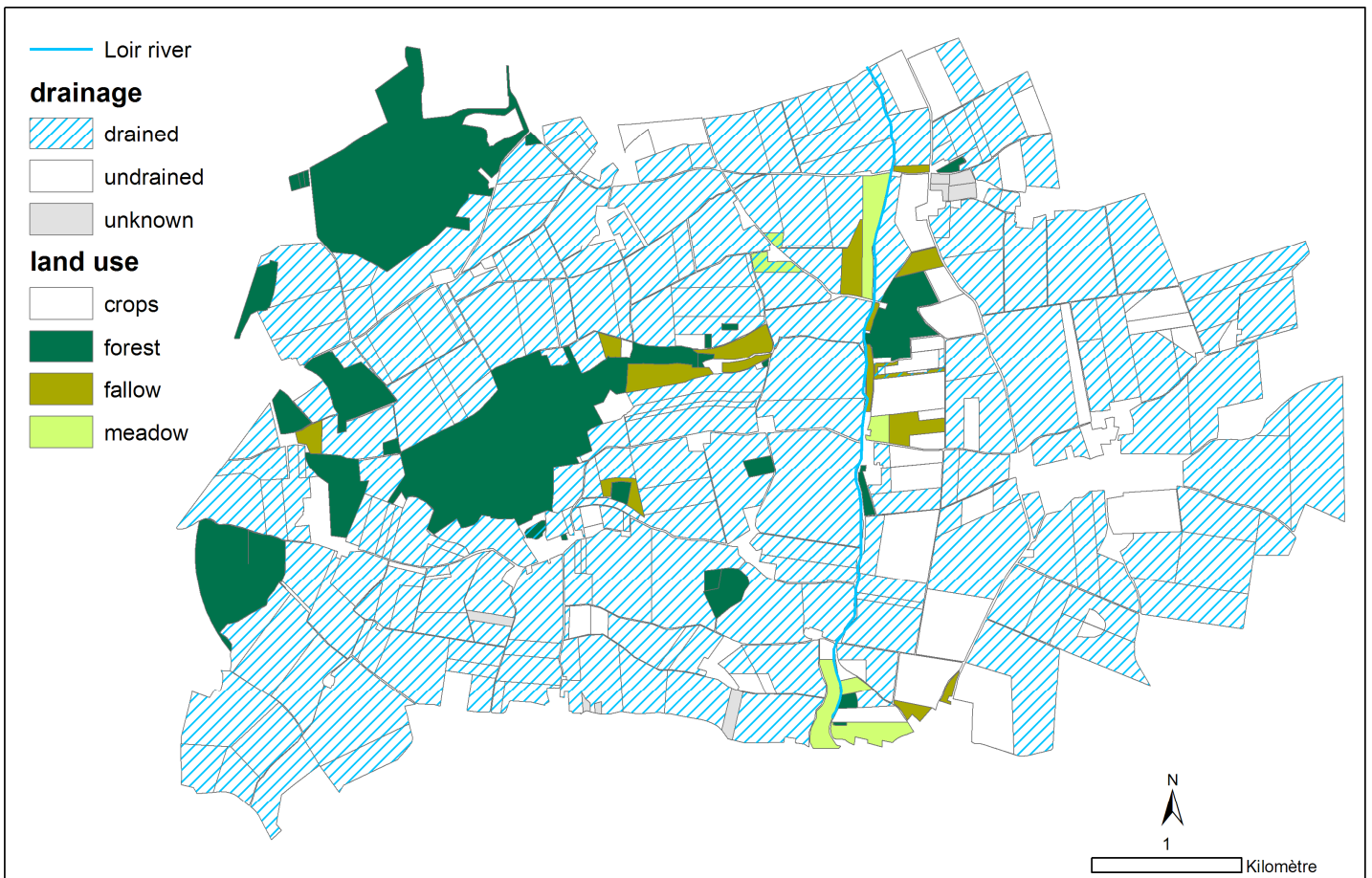
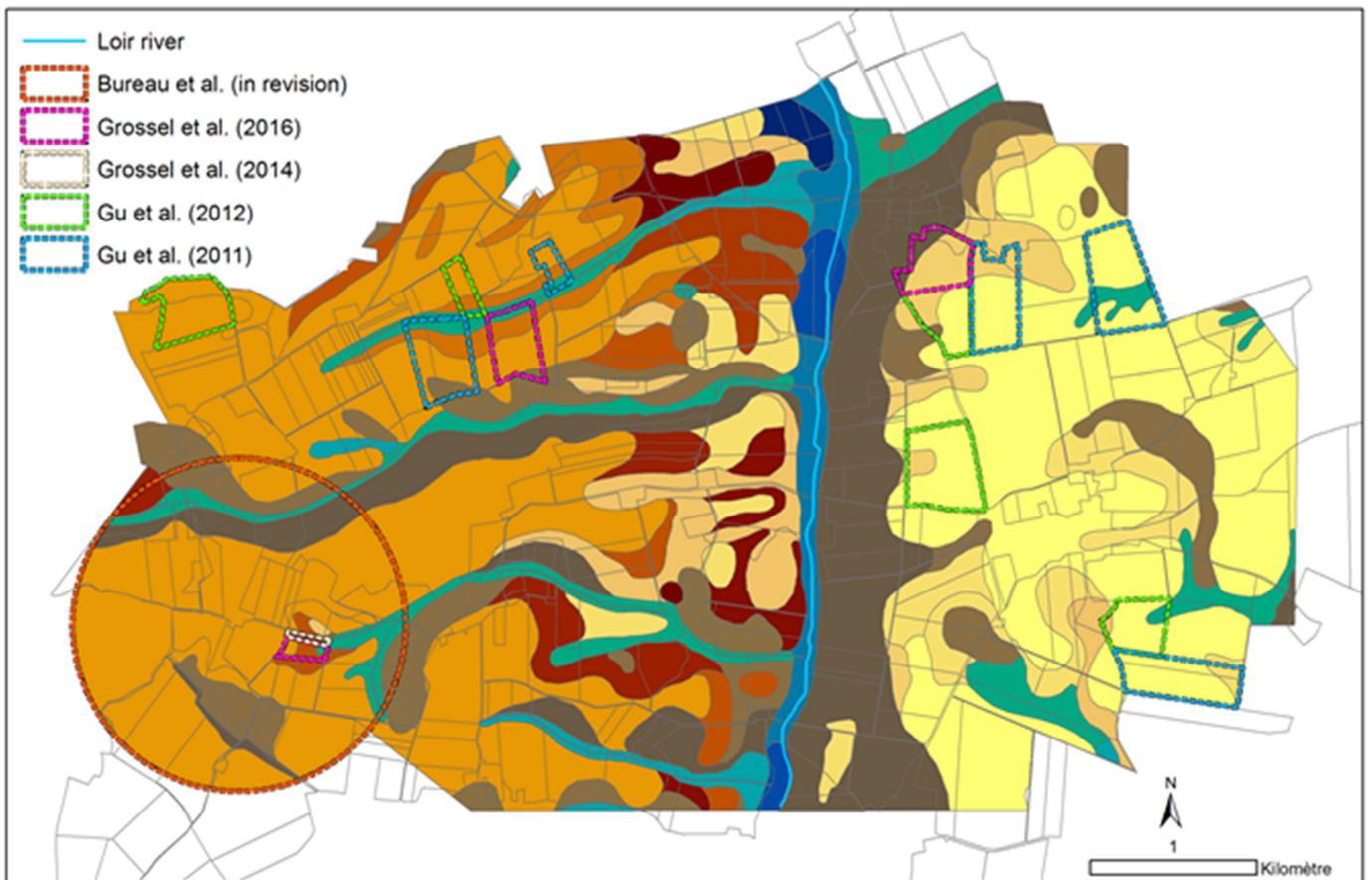


Figure 15: OS² map representing the land use and the presence or not of drainage

2. Pedology and geology

The OS² site mainly presents silty soils: degraded Luvisols (hydromorphic soils) that are more or less deep and stony, and Colluviosols and Fluviosols down the slope near the creek and the Loir (Figure 16). These soils are representative of the soils in France. The soils are silts, developed on a tertiary formation of impermeable flint clay which can reach thirty meters of thickness.



- Silty soil, deep of Beauce Chartraine
- Silty-clay soil, deep, with deep temporary hydromorphy of Beauce Chartraine
- Silty to silty-clay soil, deep, with shallow temporary hydromorphy of Beauce Chartraine
- Silty to silty-clay soil, with big quantity of flint on clay with flint or "grison" (30 to 50 cm)
- Silty to silty-clay soil, with little quantity of flint on clay with flint or "grison" (60 cm)
- Silty soil with shallow temporary hydromorphy on shallow clay with flint (60 to 80 cm) of Beauce Chartraine
- Silty soil, with shallow big quantity of flint on clay with flint or "grison" (40 to 80 cm)
- Silty colluvic soil, deep, with shallow temporary hydromorphy of secondary valley
- Silty colluvic soil, shallow, with shallow temporary hydromorphy on clay with flint (50 cm)
- Silty-clay soil, with deep groundwater semi-permanent, of Loir valley
- Clay soil, with deep groundwater semi-permanent, of Loir valley
- Silty soil, fragic, with shallow temporary hydromorphy
- Silty soil, fragic, eroded, with shallow temporary hydromorphy
- Silty-clay soil, eroded, with shallow temporary hydromorphy, on clay with flint or "grison" (60 to 90 cm)
- Silty soil, with shallow temporary hydromorphy, on clay with flint or "grison" (70 to 100 cm)
- Silty soil, with shallow temporary hydromorphy
- Silty soil, eroded, with shallow temporary hydromorphy
- Silty soil, deep and eroded, with shallow temporary hydromorphy, on clay with flint or "grison" (85 cm)
- Stony soil, on old alluvial deposit, of Loir valley

Figure 16: Types of soil in the OS² site and localization of the studies done in this site

3. Topography

The highest point of the site is 214 m above sea level and the lowest is 168 m (Figure 17).

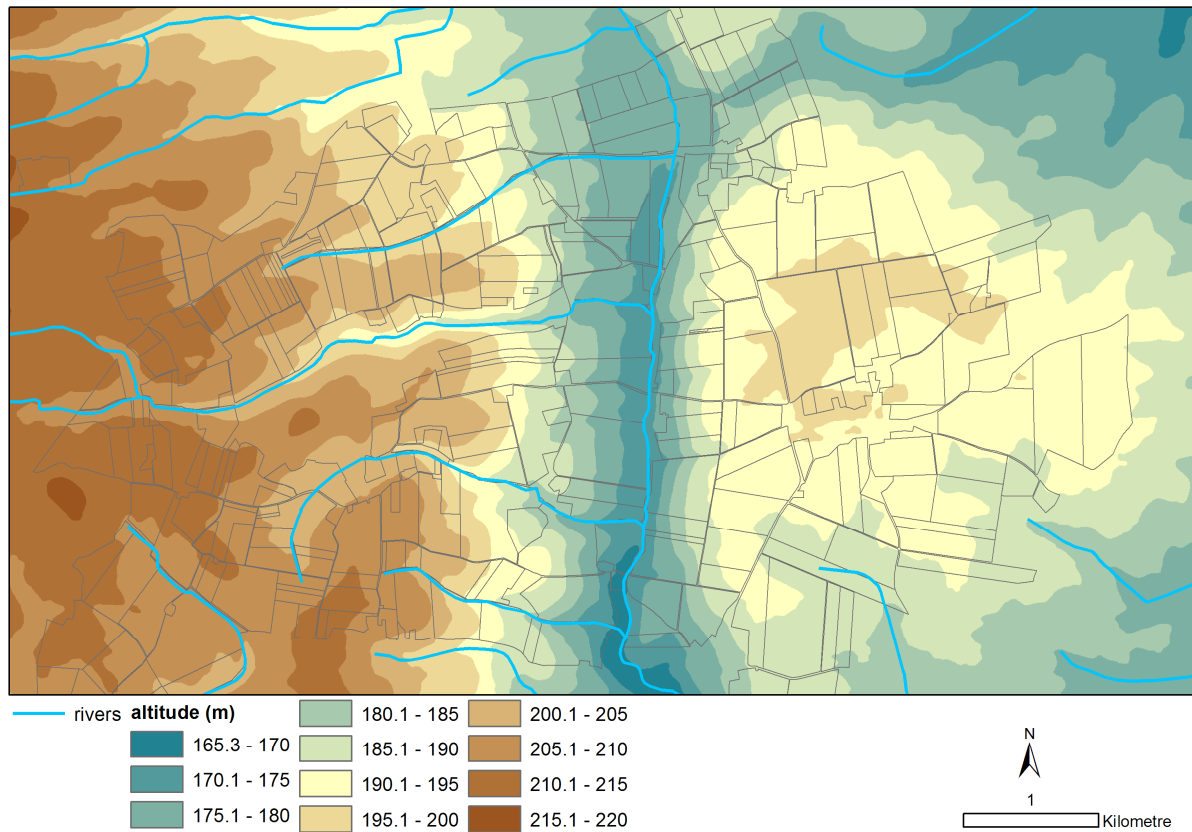


Figure 17: Topography of the OS² site

4. Climate

The site is under degraded oceanic climate with annual rainfall of 598 mm, an average annual temperature of 10.6 ° C and an evapotranspiration potential of 740 mm. The long-term monthly average rainfall shows a moderately uniform distribution throughout the year.

5. Hydrology

Natural soils are rapidly clogged due to the impermeable substratum. They require proper artificial drainage to be cultivated. The clay layer that is found in depth limits the vertical transfers, so the transfers to the chalk sheet (170 m of altitude) are negligible. The Loir river and creeks are mainly fed by agricultural drainage waters.

6. Crop management

The site is in a region of cereal crops and offers 1% meadow (Figure 18). The main rotations encountered are rapeseed-wheat-wheat or rapeseed-wheat-barley, with nearly 50% of the area seeded with wheat (Figure 18). The main rotation head is rapeseed with about 30% of the surface. Winter barley is the third cereal the most seeded with 15%. Most farmers practice plowing and the straw is mostly buried, except that in general there is no plowing before seeding wheat following rapeseed. The plots are limed regularly about every 5 years in summer. Inputs of exogenous organic matter are regularly applied.

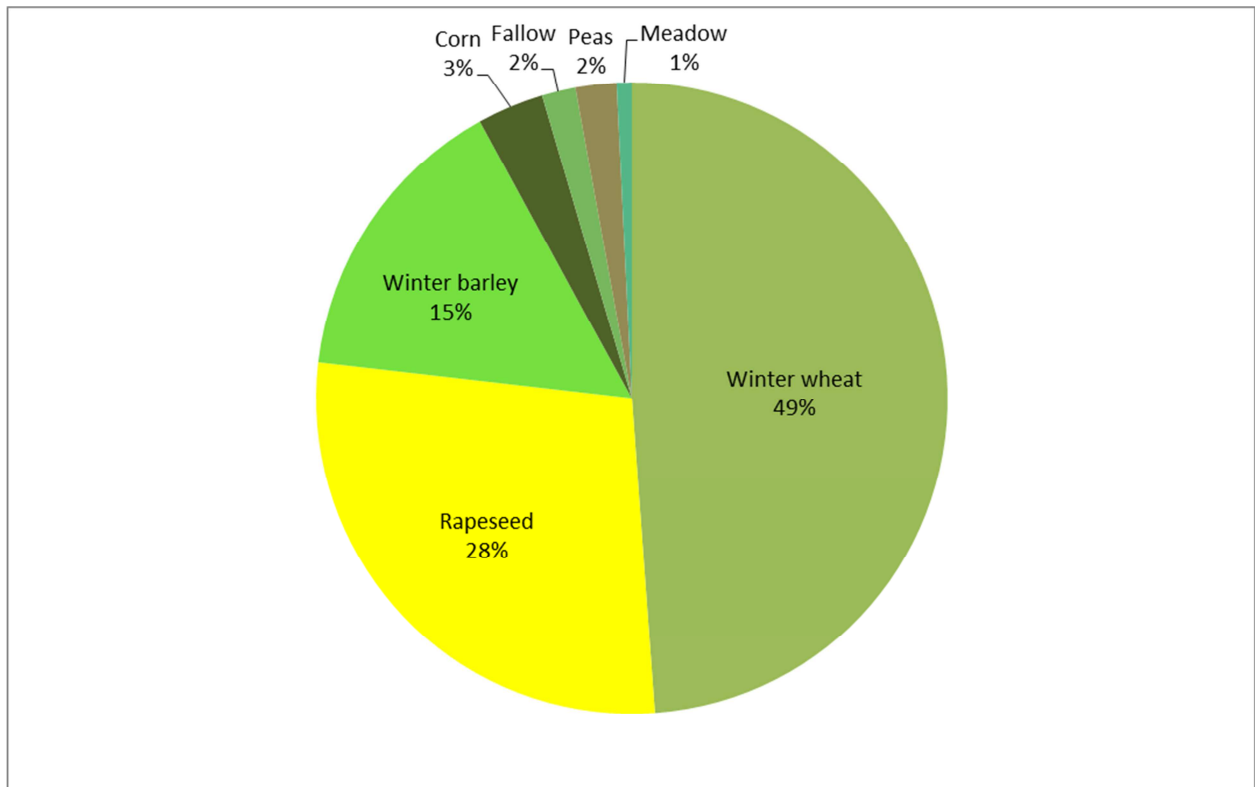


Figure 18: Crop management of the OS² site, averaged from 2009 to 2015

II. N₂O emission measurements

Both direct and indirect – water emitting N₂O due to the lixiviation of the soil NO₃⁻ - N₂O flux measurements were conducted since 2009 (Grossel et al. 2016; Grossel et al. 2014; Gu et al. 2013; Gu et al. 2011). N₂O emissions were measured with the chamber method, using non steady-state chambers designed and operated as described in Rochette and Bertrand (2008), or one fast-box at weekly to monthly time step. Measurements were done on different sites at different dates: (i) at shoulder and foot-slope positions along three sloping sites from late February to April 2009 and late February to May 2010 (Gu et al. 2013; Gu et al. 2011), (ii) in a barley/wheat field on hydromorphous soils, on March and April 2011 and March 2012 (Grossel et al. 2014), and (iii) on 4 different plots - 2 undrained plots and 2 drained

plots – during 2 growing seasons, from seeding to harvest (November to July), in 2010–2011 and in 2012–2013 (Grossel et al. 2016). In all cases, the highest N₂O emissions were measured during spring after fertilization.

The mean N₂O fluxes reported in Grossel *et al.* (2016) were 71 µg of N-N₂O m⁻² h⁻¹ and were larger in the undrained plots than in the drained plots, in both growing seasons, with pulse emissions comprised between 400 and 800 µg of N-N₂O m⁻² h⁻¹ on undrained soils. In Grossel *et al.* (2014), measured fluxes were comprised between 0 and 1500 µg of N-N₂O m⁻² h⁻¹. For drained soil cropped with wheat, lower pulses of N₂O in the range of 0-120 µg of N-N₂O m⁻² h⁻¹ have been observed previously by Gu *et al.* (2011)

Indirect N₂O fluxes were also measured on the Loir stream, with a floating chamber connected to an analyzer (Grossel et al. 2016). Indirect N₂O emissions were estimated to contribute to the total N₂O emissions to 1.6%, with a mean value of 190 µg of N-N₂O m⁻² h⁻¹. However this result needs more investigation in different sites due to the complexity of the measurement from non-permanent streams.

III. N₂O emissions determinism

Results of these measurement campaigns made on different sites on different conditions enable to study the determinism of N₂O emissions.

First, a link was systematically observed between N₂O emissions and well-known local factors such as soil water and nitrogen content. WFPS influenced the effect of soil inorganic N contents on N₂O fluxes. Differences in N₂O fluxes, between shoulder and foot-slope, correlated linearly with differences in WFPS. Spatial variations in N₂O emissions were regulated by the influence of hydrological processes on soil aeration intensity (Gu et al. 2011).

Secondly, in drained soils, soil texture (clay or silt content), pH and exchangeable magnesium (Mg) related significantly ($p < 0.05$) to N₂O emission factors, i.e. ratio between N₂O fluxes and N added. Suggestions were made that (1) soil clay content decreased gas diffusivity and promoted N₂O reduction thereby controlling N₂O emissions across the region, and (2) the effects of soil pH and Mg on N₂O emissions indirectly reflected the effect of soil texture due to the interactions of soil properties (Gu et al. 2013). Thus, soil texture may partly regulate the spatial variability of N₂O emissions in drained landscapes.

Last, the influence of distal factors such as topography has been studied. In Gu *et al.*, (2011), landscape positions had a significant effect on N₂O fluxes with larger emission in the foot-slope at only one of the 3 investigated drained sites. Topography did not affect N₂O emissions mostly because the topographic effects on soil hydrology were partly offset by tile-drainage. To further investigate the influence of artificial drainage on N₂O emission, measurements were made on drained and undrained plots (Grossel et al., 2016). The undrained soils showed significantly larger emissions than drained soils during both dry and wet years. The net effect of artificial drainage may be a large decrease in the direct N₂O emissions. Drainage was the main factor explaining the spatial variability of the N₂O emissions within the studied soils, and its effect was dominant over other permanent soil variables. This strongly suggests that drainage must be taken into account for N₂O emission inventory.

IV. Simulations

Simulations of N₂O emissions were also performed, using data collected on the OS² site. 2 approaches have been tested so far, using NOE and DNDC models. Grossel *et al.*, (2014) evaluated the possibility to simulate N₂O fluxes at scales finer than the plot, because of the very high variability at this scale, with hot spots of emissions. The frequency distributions

are asymmetrical and it is not taken into account in models. Grossel *et al.*, (2014) used NOE for their simulations. The model was tested deterministically in order to predict the flux dynamic and to reproduce the high emission points. Then the denitrification part of the model was tested stochastically to simulate the flux distributions. To do so, they used Monte Carlo simulation and randomly generated input variables from the measured frequency distributions. The deterministic prediction of flux dynamic provided a good agreement with measurements in 1 studied case out of 6. The denitrification process was considered to be the main source of N₂O in 5 cases out of 6. Moreover, the model acceptably simulated frequency distributions in 4 cases out of 5. As a result, this study proposed that simple process models like NOE, in association with Monte Carlo simulations, can be used to improve simulation of the biased frequency distributions of N₂O emissions. This study also provides valuable information about the range of spatial variations in N₂O fluxes.

Gu *et al.*, (2014) evaluated the possibility to simulate the inter-plot variability at the landscape scale using an ecosystem model. Gu *et al.*, (2014) used the DNDC model and modified non-linear empirical NOE model from data collected from a previous study (Gu *et al.* 2013). Necessary modifications of the model on the optimum crop production and both the field capacity and wilting point were done for DNDC to have a better agreement respectively with crop biomass yields and soil water content. In NOE, multiple effects of varying soil water and N contents on the fraction of N₂O emitted through the denitrification process were added. DNDC and NOE predicted with success, the background N₂O emissions and the pulses of emission due to the addition of fertilizer, in all the sites, during the experimental period but they respectively overestimated the daily fluxes on the sampling dates on average by 54 and 25 %.

Cumulative emissions were a bit overestimated by DNDC and underestimated by NOE, respectively by 4% and 15%. Differences between the 2 models assessments indicate

that low frequency measurements led to uncertainty in model validation, for daily and cumulative emissions. Nevertheless, DNDC represented correctly the effect of tile drainage on soil hydrology, as suggested by the validations for soil water content with daily resolution. Soil NH_4^+ and NO_3^- contents were overestimated by the model, mostly due to incorrect N partitioning when the solution of urea ammonium nitrate was applied.

**Chapter 3: Daily temperature variations effect
on the soil N₂O emissions**

La synthèse bibliographique (chapitre 1) a permis de resituer le contexte et l'étude et de montrer que de nombreux paramètres peuvent affecter les émissions de N₂O. L'étude du déterminisme des émissions de N₂O est une étape clé pour réaliser des changements d'échelle en permettant de développer des outils de quantification indirecte qui pourront être utilisés dans les modèles. Dans ce chapitre on s'intéresse aux effets de la variation journalière de température sur les émissions. Ces expérimentations ont été réalisées à partir de sols issus du site expérimental présenté chapitre 2.

Résumé

Une étude expérimentale a été conduite pour évaluer l'effet des variations journalières de température du sol sur les émissions de N₂O par les sols. Des échantillons de sols non-déstructurés ont été collectés sur un champ de blé et placés à différentes températures : 4°C, 16°C, et à une température variant de 4°C à 16°C en 12 h. Le but étant de recréer les conditions de terrain. Les échantillons ont été placés en conditions anaérobies et de l'acétylène a été ajouté dans la moitié des échantillons pour bloquer la réduction du N₂O en N₂ et ainsi étudier à la fois les émissions totales de N₂O et la dénitrification. Les concentrations en N₂O mesurées pour les échantillons avec acétylène étaient les plus fortes à 16°C, mais pour les échantillons sans acétylène, les concentrations en N₂O étaient plus élevées lorsque la température variait de 4 à 16°C. A 16°C, la réduction du N₂O est plus importante qu'à 4-16°C. Les résultats démontrent l'importance de prendre en compte les variations journalières de température du sol pour les modèles.

Mots-clés: Gaz à effet de serre, protoxyde d'azote, effet de la température, dénitrification, Q₁₀

Abstract

An experimental study was conducted to assess the effect of daily soil temperature variations on N₂O emissions by soils. Non-destructured soil samples were collected from a wheat field and placed at different temperature: 4°C, 16°C, and at a temperature varying from 4°C to 16°C within 12 h. The aim was to recreate field conditions. Samples were placed in anaerobic conditions and acetylene was added in half of them to stop the N₂O reduction into N₂ and then study both total N₂O emissions and denitrification. N₂O concentrations measured for samples with acetylene was higher at 16°C, but for samples without acetylene N₂O concentration was higher when temperature varied from 4 to 16°C. At 16°C, the N₂O reduction is more important than at 4-16°C. Results demonstrate the importance of taking daily temperature variations into account in models.

Keywords: greenhouse gas, nitrous oxide, temperature effect, denitrification, Q₁₀

I. Introduction

Nitrous oxide is naturally present in trace quantities in the terrestrial atmosphere, but its concentration increased since the industrialization period by approximately 15% (UNEP 2013). Human activities have amplified N₂O emissions, for example, by increasing the amount of reactive nitrogen in the biosphere through the use of synthetic fertilizers (Driscoll et al. 2003). There are several existing anthropogenic N₂O sources, with agricultural soils being the dominating N₂O emission source. 77% of the N₂O anthropogenic emissions are estimated to come from nitrogen present in mineral fertilizers and manure and applied to soils, and from other agricultural sources (UNEP 2013). The increase of the global population leads to an increase of food demands. To satisfy this demand, the agricultural production is expected to increase with a rise of the use of N fertilizers (Galloway et al. 2008), and thus, also with increasing N₂O emissions. This greenhouse gas has a warming potential of about 298 times the one of CO₂ (IPCC 2014), and it is also the most important trace gas driving the stratospheric ozone layer depletion (Ravishankara et al. 2009). N₂O is estimated to contribute to approximately 8% of the global anthropogenic warming, with mean global temperature being expected to rise between 1 and 4°C by 2100 (IPCC 2007; IPCC 2014; Rustad et al. 2001). Reducing agricultural N₂O emissions has thus become a key focus in national mitigation strategies targeting the agricultural sector.

N₂O is emitted by soils by different biotic processes. Nitrification and denitrification, which are respectively aerobic and anaerobic processes, are the main mechanism responsible for the N₂O production (Butterbach-Bahl et al. 2013; Syakila and Kroeze 2011). Moreover, N₂O can be consumed in soils, most likely by denitrification, so that the flux of N₂O observed at the soil-atmosphere interface is the net result of simultaneously occurring production and consumption processes (Conrad 1996). Furthermore, aerobic and anaerobic sites can exist in

close vicinity in soils, so that the attribution of N₂O emissions to specific microbial or physico-chemical source and sink processes remains difficult (Butterbach-Bahl et al. 2013). Moreover, the contribution of the main source process of denitrification to observed N₂O emissions depends on environmental conditions (Mathieu et al. 2006a) such as water content and oxygen availability, soil nitrate, organic matter availability, pH and temperature. Temperature stimulates the metabolism and the functioning of microbial communities (Avrahami and Bohannan 2007; Pietikainen et al. 2005), and, thus, stimulates organic matter mineralization, and soil C and N cycling as e.g., indicated by increased rates of N₂O emissions or soil respiration (Luo et al. 2012). As a consequence, a positive correlation between the increase of temperature and the increase of N₂O emissions is often observed in field studies (Smith et al 2003). There are optimal temperatures for both nitrification and denitrification processes and a threshold at 11°C was proposed by Stanford (1975) under which rates of denitrification sharply decrease. The optimum temperature for denitrification was found to be around 37°C (Braker et al. 2010). Also, nitrification has been found to be temperature sensitive (Breuer et al. 2002) and to decrease with the decrease of the temperature from 20°C to 5°C (Russell et al. 2002). However, microorganisms are able to adapt to their environment, and so it remains difficult to define a universal temperature function (Breuer and Butterbach-Bahl 2005; Farquharson and Baldock 2008). Furthermore, significant emissions of N₂O also occur during following soil freezing and thawing in response to increased substrate availability, tight coupling of oxidative and reductive processes and increased anaerobic soil conditions in such periods (de Bruijn et al. 2009; Morkved et al. 2006; Teepe et al. 2001).

The study of denitrification process alone can be done in anaerobic conditions to promote denitrification over nitrification. Nevertheless, as N₂ cannot be measured easily, measurements of denitrification activity in soils often relies on the use of high concentrations

of acetylene (approximately 10% in volume), in the headspace of incubation vessels. Acetylene blocks the N₂O reductase of the denitrification chain, so that, the end product of denitrification is the more easily measurable N₂O and not N₂ (Yoshinari et al. 1977). However, several problems can appear with the use of acetylene such as an underestimation of the denitrification rates due to scavenging of the denitrification intermediate NO as promoted by acetylene and O₂, slow diffusion of acetylene to sites of actual denitrification in soils, or decomposition of acetylene degrading microbes (Butterbach-Bahl et al. 2013; Groffman et al. 2006). However, at least the scavenging effect can be avoided if the acetylene blockage technique is used under anaerobic conditions.

There are few publications that quantify the temperature impact on N₂O emissions. They are either based on laboratory experiments (Dobbie and Smith 2001; Kurganova and de Gerenyu 2010; Luo et al. 2013; Stanford et al. 1975; Zhang et al. 2016) or on field measurements (Luo et al. 2013; Papen and Butterbach-Bahl 1999). They showed that soil N₂O emissions generally increase with increasing temperatures, though a second strong optimum can be found around 0°C due to the above mentioned freeze-thaw effects on soil N₂O production, and that this effect depends on soil texture, soil organic carbon concentrations and pH. However, previous studies were not all performed at the same temperature, at the same percentage of total water content and they also used different type of soils, but all were done under static conditions with no temperature variations. The change in emission rate is characterized by the Q₁₀, which is the emission rate at (T + 10°C) / emission rate at T°C. In this study, we propose to investigate the effect of a varying temperature on N₂O emissions by soils, and so, be closer to the real field conditions. Indeed, we measured N₂O emissions in a range of temperature that is common in April in France, when fertilization occurs and N₂O emissions are high (Grossel et al. 2016; Gu et al. 2013). No studies have been done in these

realistic conditions so far. Q_{10} are important because they can be used in N₂O emissions models such as NOE (Henault et al. 2005).

The objective of this paper is to study the effect of temperature on both denitrification and total N₂O emissions by soil, at a constant temperature and at an increasing temperature, and to compare their rates.

II. Materials and methods

1. Site description

Soil samples were collected from the experimental site OS² (“Observatoire Spatialisé Orléanais des Sols”) located in the valley of Loir in Faux Perche (48°23’N, 1°11’E, elevation 202 m above sea level), about 30 km southwest of Chartres, France. The climate records (1971-2000) in Chartres (28070001, 4°27’N, 1°30’E, elevation 155 m above sea level) show a mean annual temperature of 10.6 °C, precipitation of 598 mm and potential evaporation of 740 mm. Monthly precipitation is evenly distributed throughout the year. The sampling field was cultivated with wheat.

2. Soil sampling

36 non-destructured soil samples were collected on the 19th of February 2015 following the sampling plan presented in Figure 19, allowing the constitution of 6 groups of samples, each containing a sample from each subplot. Sampling was done using 6.5 cm high and 7 cm diameter stainless steel cylinders, representing a volume of 250 cm³. Soil samples were collected from the surface after removal of the litter and aboveground layers. Samples were then placed at 4°C.

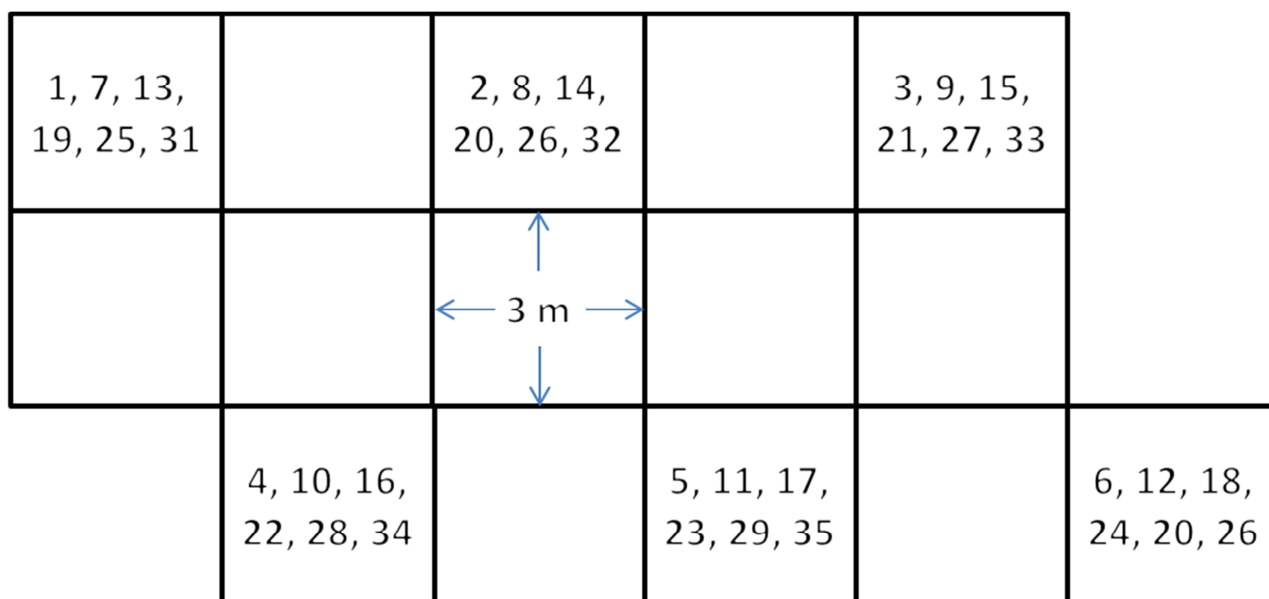


Figure 19: Sampling plan for the soil collection of the 36 cylinders on a wheat field. Samples 1-6 and 7-12 were placed at 16°C, samples 13-18 and 19-24 at an increasing temperature from 4°C to 16°C, and samples 25-30 and 31-36 at 4°C.

Cylinders of soils were placed in 750 cm³ glass jars (Figure 20). On the following day, 20 mL of a KNO₃ solution (0.02 M) was added to each sample to simulate field fertilization (20 mg N kg⁻¹ of soil).

In order to define experimental conditions for conducting our experiment, we used monitored temperature dynamics of spring 2013 at the experimental site where soil samples were collected. A temperature variation from 4 to 16°C over a 12h-period was selected, as it was observed on April 2013 at 5 cm deep (Figure 21). Glass jars were separated in three groups. Twelve (2 groups of 6) of them were placed at 16°C in an air-conditioned laboratory, twelve of them at 4°C in a cold chamber, and twelve of them also at 4°C in a cold chamber before the experiment and then in a climatic chamber where temperature increased from 4°C to 16°C within 12 hours (Figure 22).



Figure 20: Cylinder of soil placed into a glass jars with inlet and outlet tube on the top.

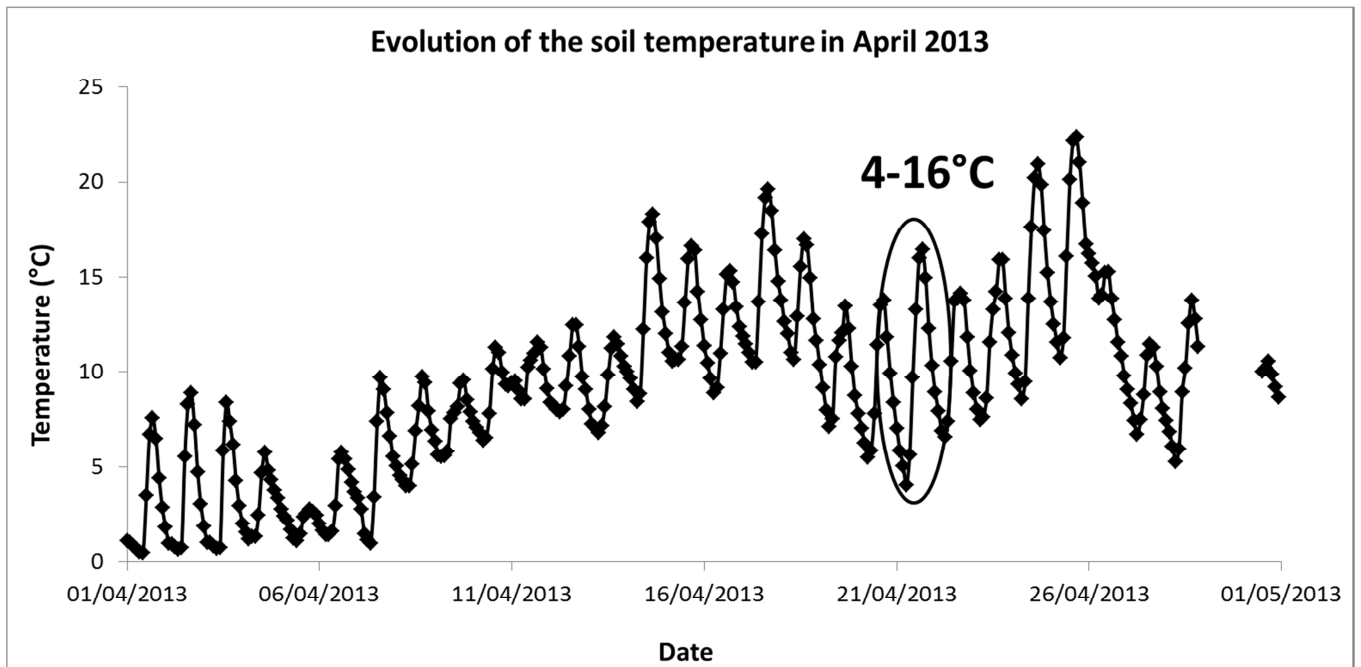


Figure 21: Evolution of the soil temperature, in 5 cm soil depth, in April 2015, on the experimental site where samples were collected in 2013.

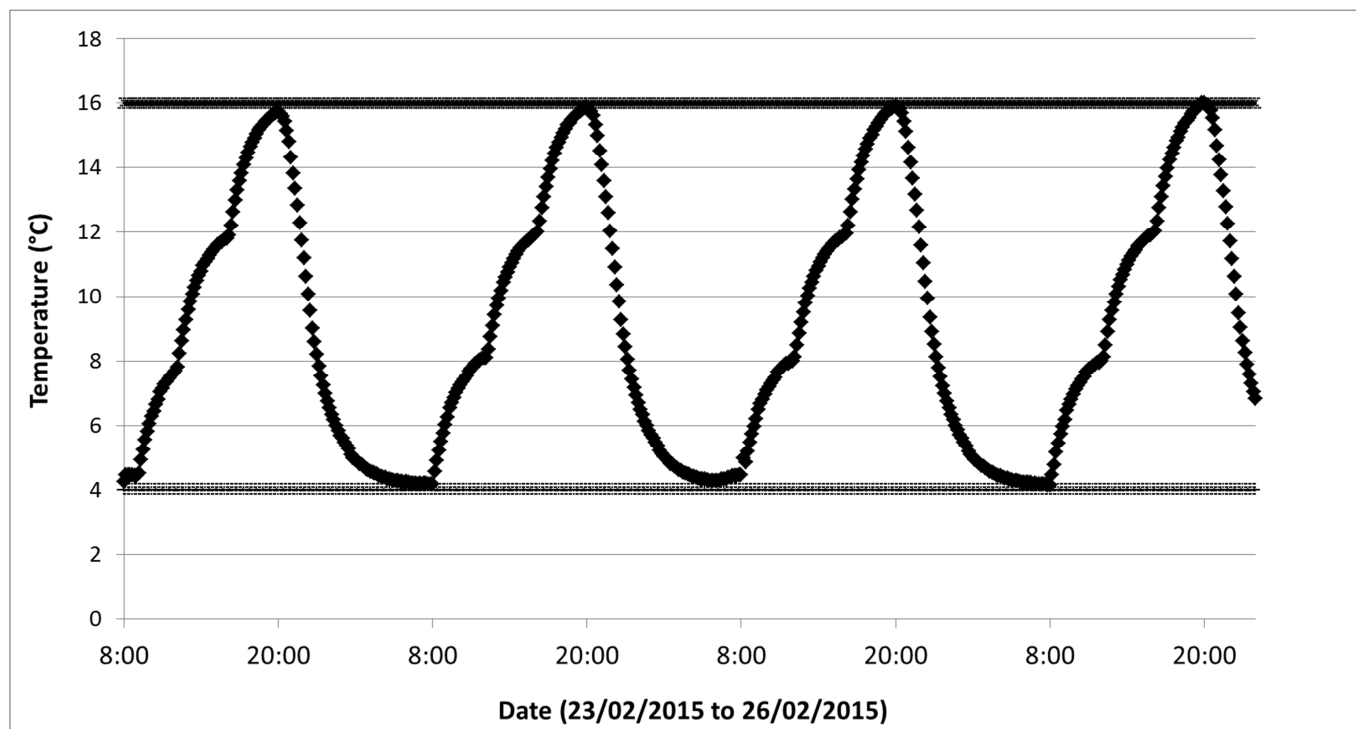


Figure 22: Temporal variation of the incubation temperature for the 4-16°C treatment. The top and bottom line indicate the other treatments, where temperatures were maintained constant at either 4°C or 16°C.

4. Experiment

The experiment started 4 days after sampling. Glass jars were hermetically closed and the headspace of the jars was flushed for 5 minute with pure N₂ to remove all of the N₂O and O₂. Following headspace N₂ flushing, 1 mL of Krypton (Kr) was added to each sample. Finally, in half of the jars of each group, 50 mL of acetylene was injected in the headspace to block the N₂O reductase, enzyme of denitrification under anaerobic conditions. At each temperature, N₂O production and total denitrification were measured in samples without and with acetylene. For this, 20 mL of headspace gas was sampled through a septum with a syringe. The gas sample was injected into vacuumed glass vials (t_0) (Figure 23). In the

following, gas samples were taken every 2 hours for twelve hours during the four days of the experiment.

5. N₂O reduction ratio

Without acetylene, N₂O emissions are the result of the combination of both N₂O production and N₂O reduction during denitrification. With acetylene, N₂O reduction to N₂ is blocked and the measured N₂O emissions reflect total rates of denitrification i.e., N₂O + N₂ forms. To calculate the ratio *r* of the reduction of N₂O into N₂, the following equation was used:

$$r = \frac{N_2O \text{ flux measured without acetylene}}{N_2O \text{ flux measured with acetylene}} = \frac{N_2O}{N_2O + N_2} \quad \text{Eq. (3.1)}$$

The lower the ratio, the higher is the reduction of N₂O to N₂ in relation to N₂O production.

6. Gases analyzes and flux calculation

Gas samples were analyzed with a gas chromatograph (GC Thermo GC (ECD detector, Ar/CH₄ as vector gas, filled porapak Q column)) for the determination of N₂O concentrations in the headspace gas samples (Figure 23). A micro gas chromatograph (μ GC SRA GC (TCD detector, He as vector gas, porapak Q capillary column for CO₂, O₂ molecular sieve)) was used for measuring concentrations of O₂, CO₂ and Kr. Determination of Kr allowed to check for leaks of the incubation vessels, while determination of O₂ concentration allowed us to ensure that incubation conditions were indeed anaerobic. From the measurements of CO₂ concentrations, carbon (C) mineralization was calculated.

With the N₂O and CO₂ concentration measured in ppm, the volume of the jar and cylinder, the pressure and the temperature, fluxes of N₂O in g N-N₂O ha⁻¹ d⁻¹ were calculated.

Flux values were averaged across the 6 treatment replicates. Variability of N₂O emission rates are reported as standard errors.



Figure 23: Photo of a vacuumed vial used for gas sampling and the gas chromatograph where gases were analyzed.

7. Q_{10}

Q_{10} were calculated for each day using samples at 4°C and samples at 16°C. Q_{10} were calculated following this equation:

$$Q_{10} = \frac{R_{16^{\circ}\text{C}}}{R_{4^{\circ}\text{C}}} \left(\frac{10}{16-4} \right) \quad \text{Eq. (3.2)}$$

With R being the rate of the reaction of N₂O emission production $R = \frac{[N_2O]_{emitted,t}}{t}$

8. Auxiliary measurements

Treatment specific analysis of the soil nitrogen contents was realized at the end of the experiment with 3 times 8 g of soil. The remaining soil samples were then weighted and dried into the oven at 105°C for 24h to calculate the density, porosity and water-filled pore space.

9. Statistical analysis

Statistical analyses were performed using XLSTAT® for testing linearity of kinetics (linear regression tests), correlations between activity rates and soil factors (ANOVA) and mean comparisons (t-tests). Statistical significance for all tests was set at $p < 0.05$.

III. Results

1. Incubation condition characterization

Both Kr (0.1 %) and O₂ concentration (5%) were constant over time, revealing the absence of leaks during incubations and partial anaerobic conditions all along the experiment.

At the end of the 4 days of incubation, soil WFPS was as high as expected (> 80 %). Nevertheless, WFPS of soils incubated at 16°C were in tendency lower than at the other temperatures probably due to condensation of water at the wall of the glass vessels (Table 1).

		16°C	4-16°C	4°C
Flux (g N ha ⁻¹ d ⁻¹)	With acetylene	957,8	600,3	286,0
	Without acetylene	63	93	46
WFPS (%)		83,4	84,9	87,5
Total mineral N (mg kg ⁻¹)		7,3	8,0	10,5
NO ₃ ⁻ (mg kg ⁻¹)		3,7	4,8	7,2

Table 1: N₂O mean fluxes over a 4-days incubation period. Water-Filled Pore Space (WFPS), soil total mineral nitrogen and nitrates content were measured at the end of the experiment.

Soil nitrate contents varied in the range of 3.7 and 7.2 mg N-NO₃⁻ kg⁻¹ of soil, and were slightly lower in soils of the 16°C treatment as compared to soils of the other treatments. Moreover the soil NO₃⁻ content was always lower in presence of acetylene while the NH₄⁺ content was higher, suggesting that (i) nitrification was inhibited by the high acetylene concentrations, and (ii) still some nitrification activity occurred under the micro-aerobic conditions present in our experiments. WFPS and soil total N were correlated (p value < 0.05) but they were not correlated to the fluxes with or without acetylene (Table 2). Final soil nitrates contents were correlated to fluxes for the plus acetylene treatments, but not for the minus acetylene treatment.

Variables	WFPS (%)	N min tot (mg kg ⁻¹)	NO ₃ ⁻ (mg kg ⁻¹)	Flux with acetylene (g N ha ⁻¹ d ⁻¹)	Flux without acetylene (g N ha ⁻¹ d ⁻¹)
WFPS (%)	0	0.041	0.096	0.126	0.672
N min tot (mg kg ⁻¹)	0.041	0	0.056	0.085	0.712
NO ₃ ⁻ (mg kg ⁻¹)	0.096	0.056	0	0.030	0.768
Flux with acetylene (g N ha ⁻¹ d ⁻¹)	0.126	0.085	0.030	0	0.798
Flux without acetylene (g N ha ⁻¹ d ⁻¹)	0.672	0.712	0.768	0.798	0

Table 2: Correlation (p value) calculated between N₂O fluxes, Water-Filled Pore Space (WFPS), total mineral nitrogen and nitrate content.

2. CO₂ production

For all treatments, the CO₂ concentration always increased linearly over the entire 12-hours incubation period, i.e., the hypothesis of a linear increase could not be rejected ($p < 0.05$). CO₂ production rates were higher at 16°C than at 4°C and 4 to 16°C incubations. In presence of acetylene, CO₂ production rates were going from $90 \pm 6 \mu\text{g C-CO}_2 \text{ kg}^{-1}$ of soil (day 4) to $165 \pm 18 \text{ C-CO}_2 \text{ kg}^{-1}$ of soil (day 1) at 16°C, from $50 \pm 3 \mu\text{g C-CO}_2 \text{ kg}^{-1}$ of soil (day 4) to $77 \pm 5 \text{ C-CO}_2 \text{ kg}^{-1}$ of soil (day 1) at 4-16°C and from $38 \pm 5 \mu\text{g C-CO}_2 \text{ kg}^{-1}$ of soil (day 4) to $54 \pm 7 \text{ C-CO}_2 \text{ kg}^{-1}$ of soil (day 1) at 4°C (Figure 24). Without acetylene addition, CO₂ production rates were going from $74 \pm 8 \mu\text{g C-CO}_2 \text{ kg}^{-1}$ of soil (day 4) to $143 \pm 29 \text{ C-CO}_2 \text{ kg}^{-1}$ of soil (day 1) at 16°C, from $53 \pm 5 \text{ C-CO}_2 \text{ kg}^{-1}$ of soil (day 4) to $88 \pm 13 \text{ C-CO}_2 \text{ kg}^{-1}$ of soil (day 1) at 4-16°C and from $49 \pm 4 \text{ C-CO}_2 \text{ kg}^{-1}$ of soil (day 4) to $89 \pm 11 \text{ C-CO}_2 \text{ kg}^{-1}$ of soil (day 1) at 4°C. CO₂ production decreased with the length of the experiment, for samples with and without acetylene, and for each temperature (Figure 25). Whatever the day and temperature incubation, acetylene did not affect the CO₂ production rate.

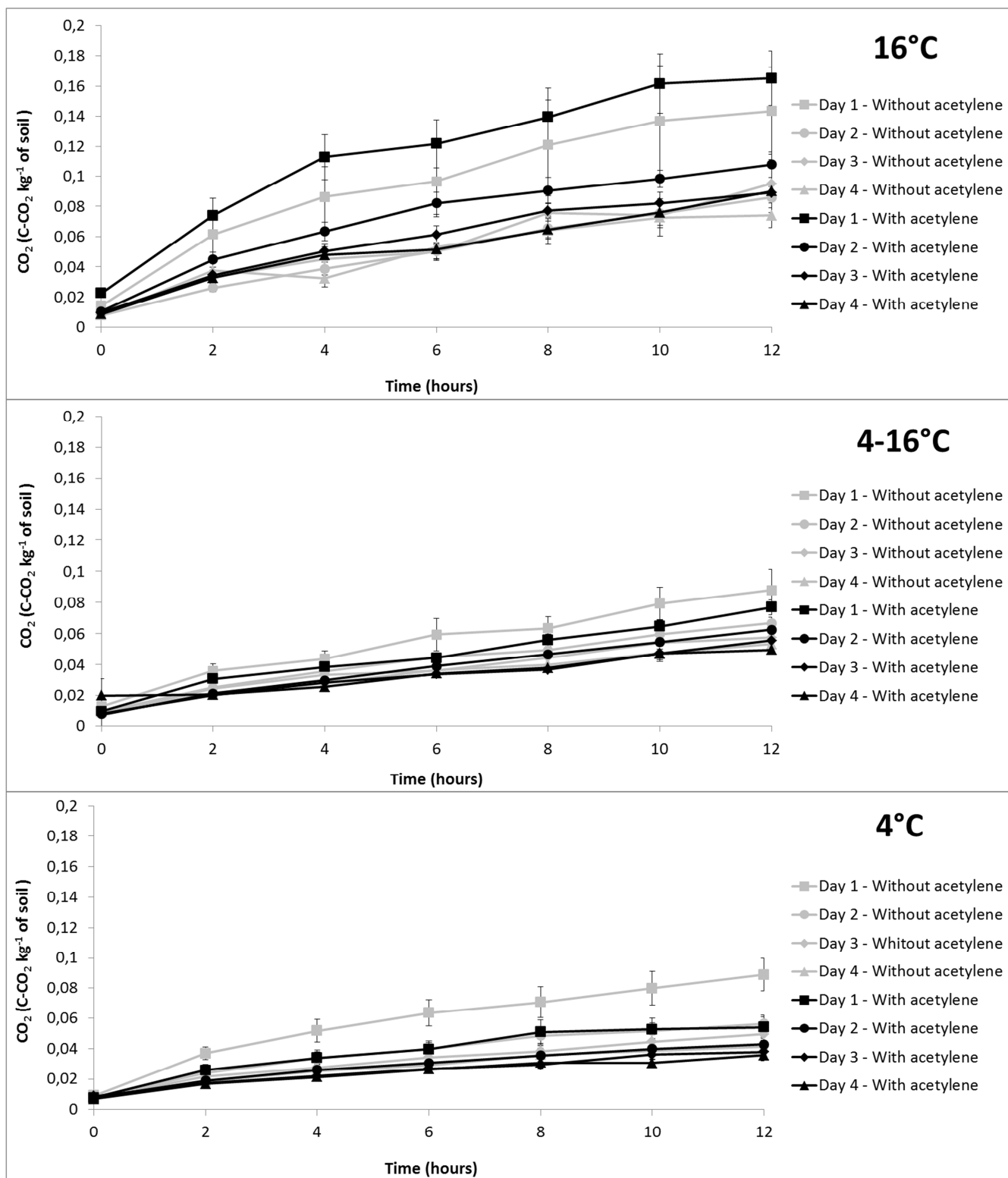


Figure 24: Evolution of the CO₂ production for samples placed at 16°C, 4-16°C and 4°C, during 12h, day 1 to 4.

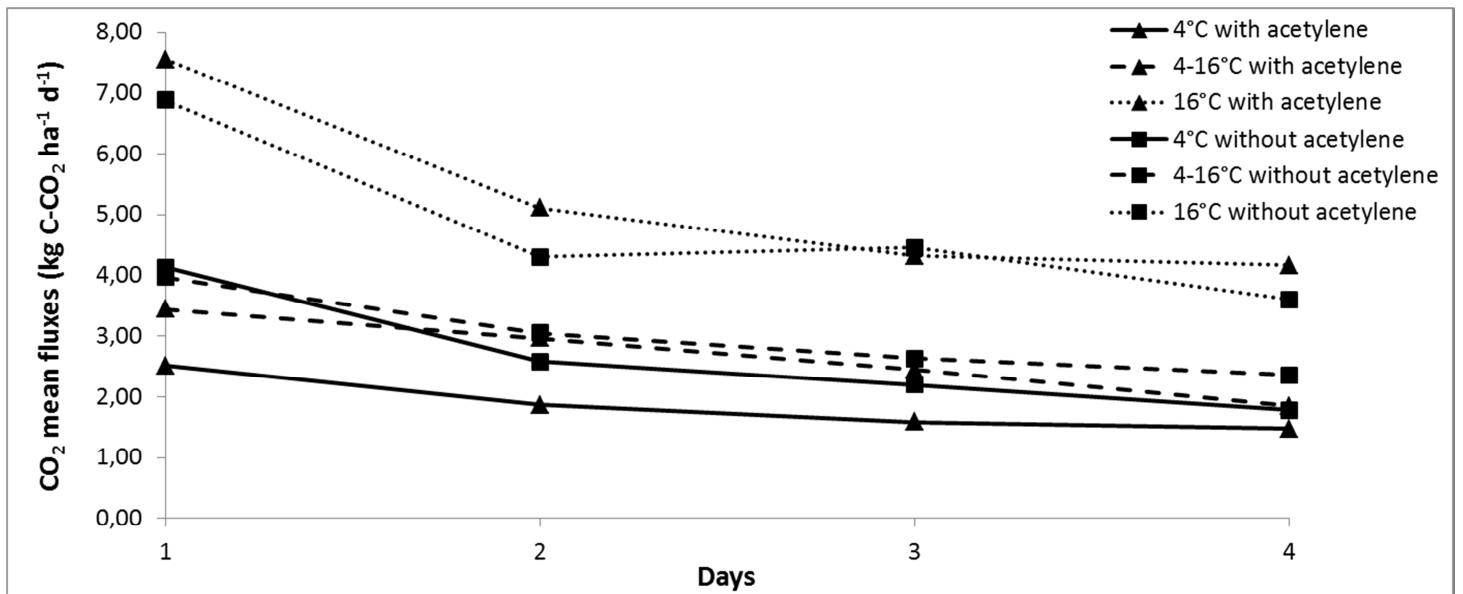


Figure 25: CO₂ mean fluxes measured after 12h along the days, averaged on 6 samples, for each temperature and for each treatment.

3. N₂O fluxes and part of N₂O emission during denitrification

N₂O concentrations increased in all flasks over the entire 12-hours incubation periods (Figure 26). Linear regressions of N₂O concentration in flask over time were all significant ($p < 0.05$). Nevertheless, a slight but significant acceleration in N₂O production was observed after 8 hours of incubation (corresponding to 12°C) during incubations with increasing temperatures both in presence and absence of acetylene.

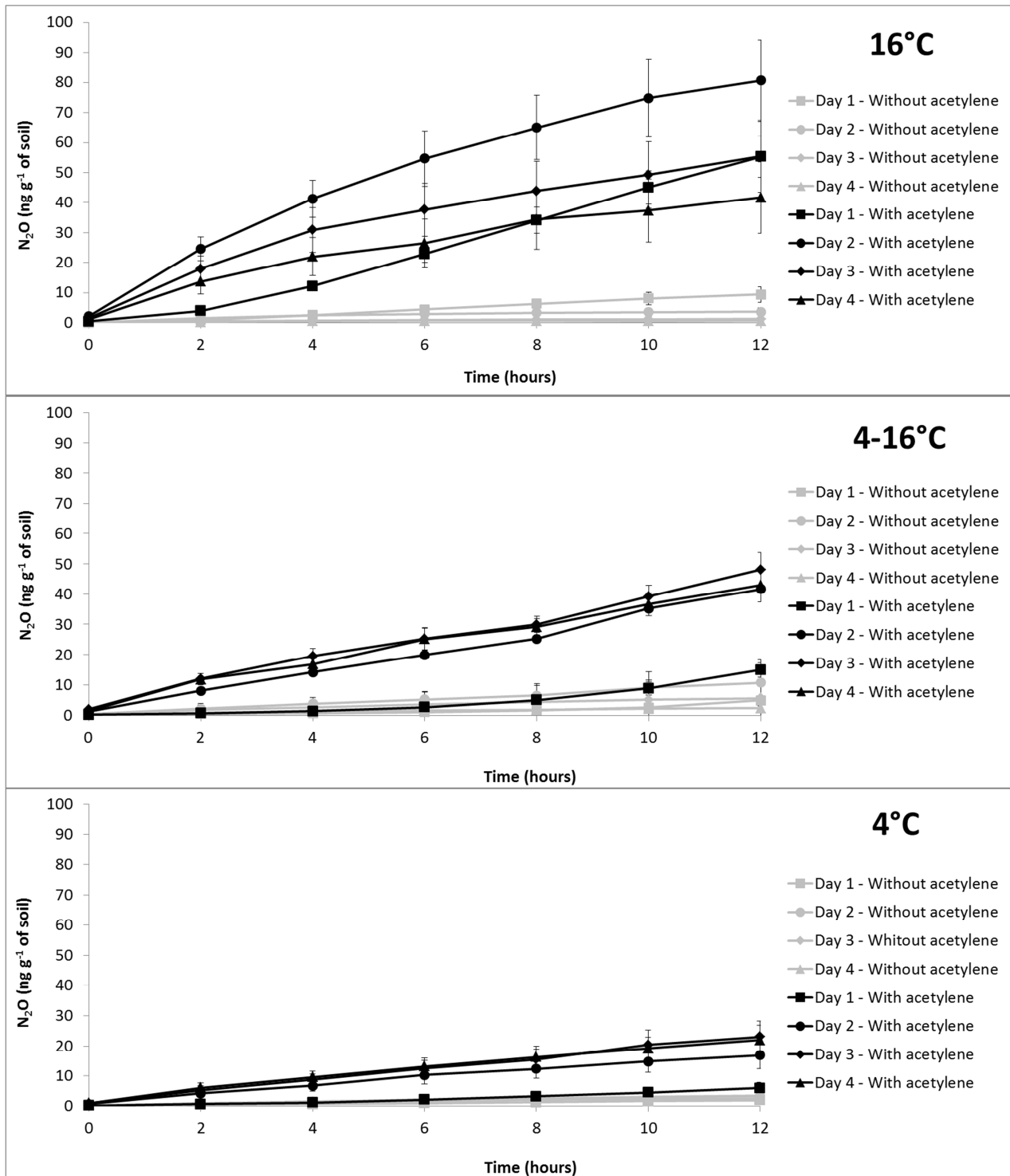


Figure 26: Evolution of the N₂O production for samples placed at 16°C, 4-16°C and 4°C, during 12h, day 1 to 4.

Rates of denitrification (incubations with acetylene) over the 12 hours incubation period varied from 42 ± 12 ng N-N₂O g⁻¹ of soil (observed on day 4) to 81 ± 14 ng N-N₂O g⁻¹ of soil (observed on day 2) at 16°C, from 15 ± 3 ng N-N₂O g⁻¹ of soil (observed on day 1) to 48 ± 7 ng N-N₂O g⁻¹ of soil (observed on day 3) during incubation with increasing temperature from 4 to 16°C and from 6 ± 2 ng N-N₂O g⁻¹ of soil (observed on day 1) to 23 ± 5 ng N-N₂O g⁻¹ of soil (observed on day 3) at 4°C (Table 3).

Mean N ₂ O flux (ng N-N ₂ O g ⁻¹ of soil)	D1	D2	D3	D4
16°C	9 ± 3	4 ± 1	1 ± 1	1 ± 0
Without C ₂ H ₂				
4-16°C	5 ± 1	11 ± 3	6 ± 2	2 ± 1
4°C	2 ± 1	3 ± 1	3 ± 1	2 ± 1
16°C	55 ± 7	81 ± 14	55 ± 12	42 ± 12
With C ₂ H ₂				
4-16°C	15 ± 3	42 ± 7	48 ± 7	43 ± 6
4°C	6 ± 2	17 ± 4	23 ± 5	22 ± 5

Table 3: Mean N₂O fluxes in ng N-N₂O g⁻¹ of soil and their standard error, obtained for the different temperature and acetylene treatments over a 4-days period.

N₂O emissions (incubations without addition of acetylene) were varying from 1 ± 0 ng N-N₂O g⁻¹ of soil (observed on day 4) to 9 ± 3 ng N-N₂O g⁻¹ of soil (observed on day 1) at 16°C, from 2 ± 1 ng N-N₂O g⁻¹ of soil (observed on day 4) to 11 ± 3 ng N-N₂O g⁻¹ of soil

(observed on day 2) during incubation with increasing temperature, and from 2 ± 1 ng N-N₂O g⁻¹ of soil (observed on day 1) to 3 ± 1 ng N-N₂O g⁻¹ of soil (observed on day 2) at 4°C.

Whatever the temperature of incubation, N₂O production of soils with acetylene was always higher as of soils without acetylene, demonstrating both the efficiency of the N₂O reduction during the experiment and of its inhibition by acetylene. Surprisingly, N₂O emissions at day 3 and 4 were not higher at 16°C than at 4°C or 4-16°C while denitrification rates were always higher at 16°C than at 4°C and higher than at 4-16°C unless on day 4.

The mean N₂O production at each sampling time (0, 2, 4, 6, 8, 10, 12 h) over the four incubation days, calculated for each temperature reveals that N₂O emissions from soils incubated under increasing temperature from 4 to 16 °C were higher as compared to soils constantly incubated at 16°C (Figure 27). In contrast, the total denitrification and C mineralization were the highest for soils incubated at 16°C. While denitrification rates and N₂O production were either constant or slowly decreasing over the 12 hours incubations at constant temperatures, denitrification rates and soil N₂O production were increasing with time in incubation with increasing temperature. It should be noted that an apparent acceleration occurred after 8 hours of increasing temperatures, which corresponds to an incubation temperature of 12°C.

The ratio of N₂O released to the headspace during denitrification was dependent on the incubation temperature (Figure 28). During the 1st day of experiment and for the treatments 4 and 4-16°C, it was around 0.3, i.e., 30% of the total denitrification rate (N₂O + N₂) was emitted as N₂O. This value decreased to 0.1 for the 4°C treatment and to 0.05 for the 4-16°C treatment after 4 days, i.e., the end of the experiment. The N₂O production rate during denitrification for the 16°C treatment was 0.17 during the first day of incubation and < 0.015 in the following days.

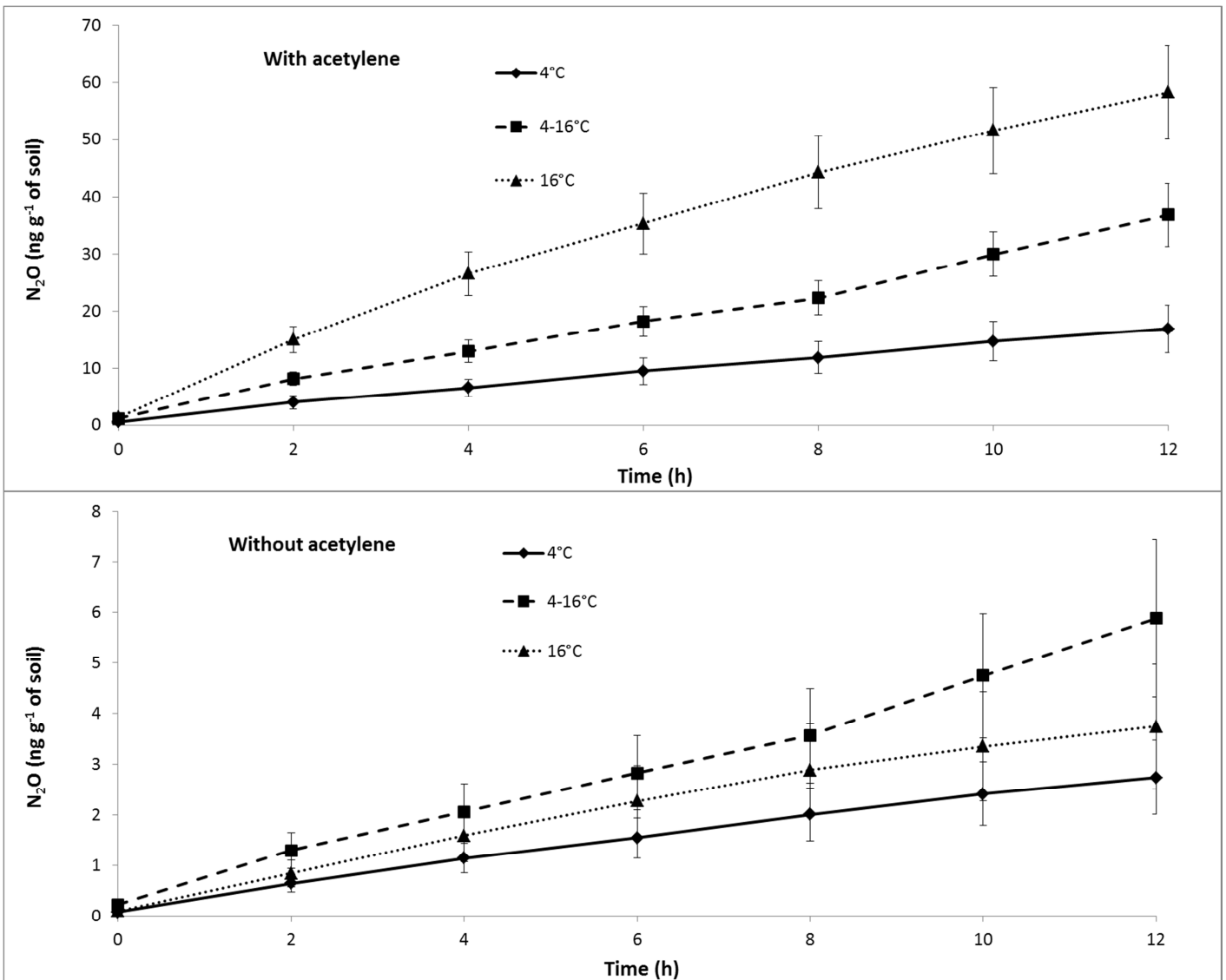


Figure 27: Evolution of the N₂O production for samples placed at different temperature, averaged on the four days, with and without the addition of acetylene.

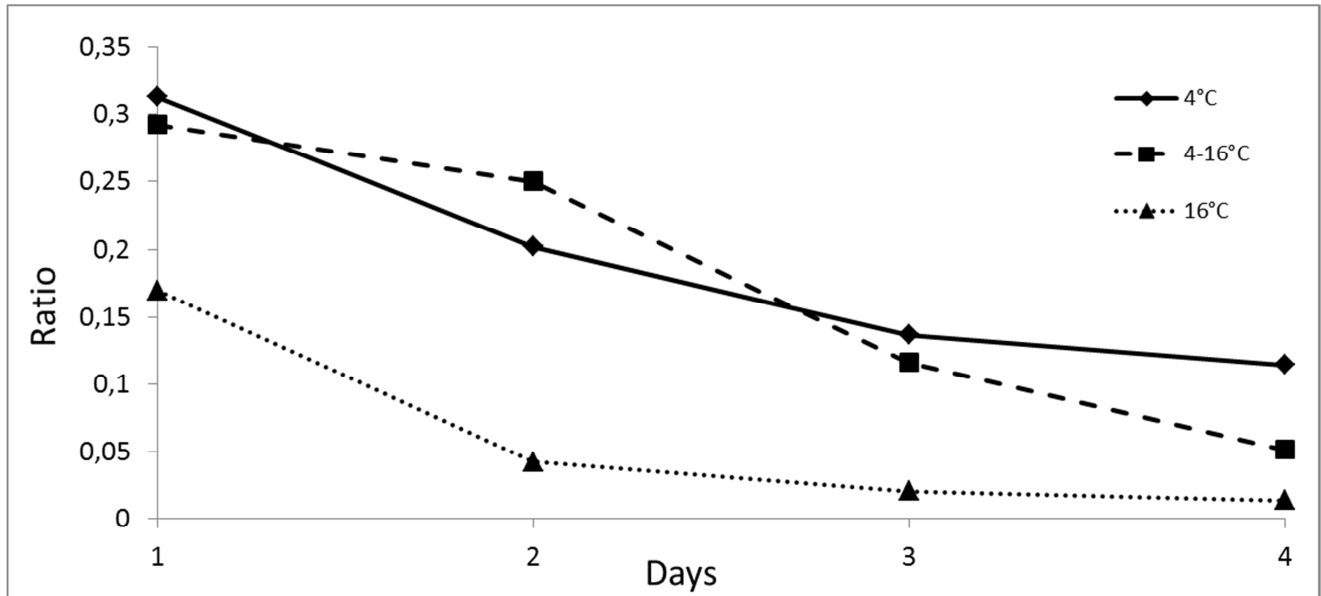


Figure 28: Evolution of the ratio of N₂O emission to total denitrification for the different temperature treatments.

4. Apparent Q₁₀ values (i.e. sensitivity of biological functions to temperature)

Concerning CO₂ production, Q₁₀ values were all around 2, (range: 1.49-2.38). Q₁₀ values for denitrification and N₂O emissions were variable. For each treatment, Q₁₀ values decreased over time (Figure 29). For denitrification, the Q₁₀ decreased steadily throughout the 4 incubation days, from 6.47 to 1.72. For N₂O emissions, the Q₁₀ decreased from 3.80 on day 1 to 0.34 on day 4.

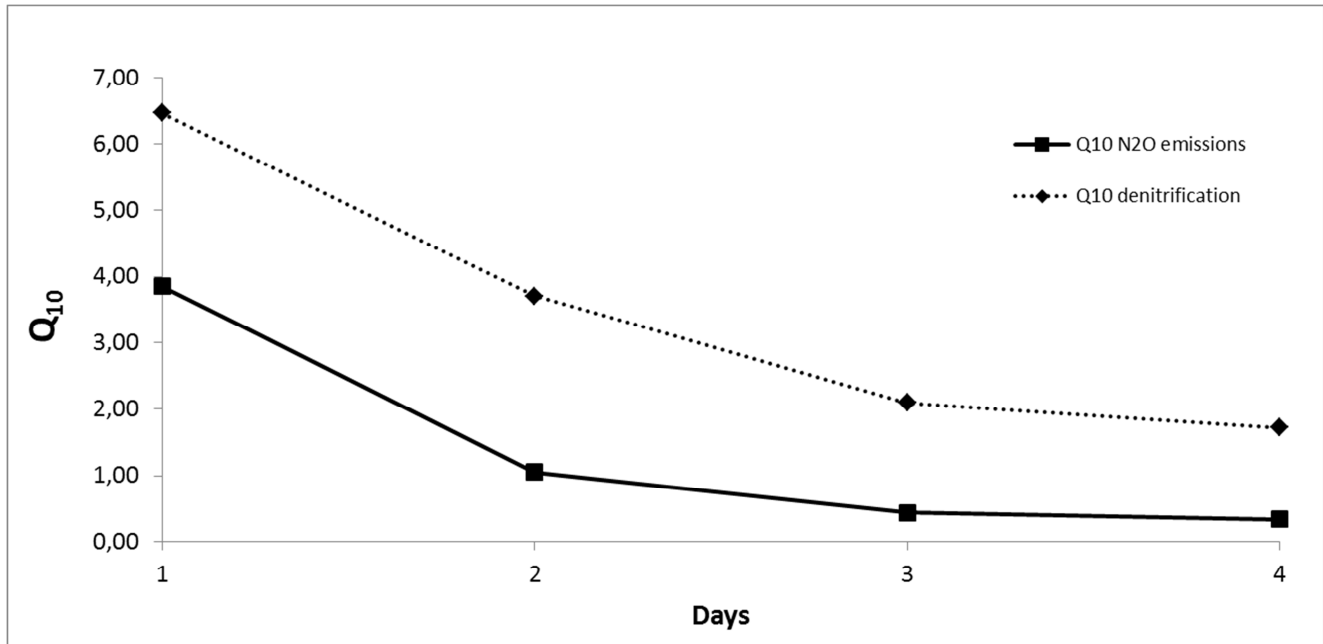


Figure 29: Q_{10} calculated from N₂O fluxes at 4 and 16°C for the plus acetylene (denitrification) and the minus acetylene (N₂O emissions) treatments, over the 4-days observation period.

IV. Discussion

The originality of our experiment was to perform soil incubations at varying temperatures. These conditions were defined to be relevant with field conditions and were associated with more classical conditions for laboratories experiment, i.e. incubations at constant temperature, framing the varying temperature.

Results obtained for CO₂ production are very classical: observed CO₂ production rates were quite low but comparable to observed rates of C mineralization in agricultural soils in other studies (Buscot and Varma 2005). The Q_{10} value of respiration in our study was around 2, i.e., a value previously observed in other studies (Song and Zhang 2009; Uvarov et al. 2006; Zhang et al. 2016). A Q_{10} of 2 is also used to describe the temperature response of C

mineralization in models such as CENTURY or DAYCENT (Del Grosso et al. 2001; Kelly et al. 2000; Parton et al. 1998).

If the 0°C anomaly is excluded, which is linked to soil freezing-thawing effects on microbial processes, soil N₂O emissions are generally observed to increase with temperature (Dobbie and Smith 2001; Kurganova and de Gerenyu 2010). Dobbie and Smith (2001), Kurganova and de Gerenyu (2008), had observed Q₁₀ values comprised between 1.2 and 50 for N₂O emissions (Table 4) and models used for simulating N₂O emissions assume as well a positive response of N₂O production to increasing temperature (Heinen 2006) (Table 5). In contrast, our experiments did not show that N₂O emissions for soils of the 16°C treatment were higher as those of the 4°C treatment or N₂O emissions observed for the treatment where temperature increases from 4 to 16°C over a 12h-period. In tendency and close to be significantly different, soil N₂O emissions at 16°C were even lower as observed for the other treatments. Recently Zhang et al. (2016) had also observed slightly higher soil N₂O emissions at 8°C both in pine and meadow ecosystems in China as compared to those measured at 18°C or even at 28°C (only for the meadow soil). Accordingly, they calculated Q₁₀ values less than 1, which is different from those reported by other researchers in a temperate forest ecosystem (Bagherzadeh et al. 2008) and in a maize field (Song and Zhang 2009). Based on their observations, Zhang et al. (2016) suggested that the effect of climate warming on N₂O would differ across regions.

	Stanford (1975)	Dobbie & Smith (2001)	Kurganova & de Gerenyu (2010)	Zhang (2016)	This study (2017)
Process studied	Denitrification	N ₂ O emissions	N ₂ O emissions	N ₂ O emissions	N ₂ O emissions and denitrification
Type of soil		Arable and grassland	Arable	Forest and grassland	Arable
Cylinder of soil	non-intact	intact	non-intact	non-intact	intact
WFPS	no data	63 and 88%	60, 75, 90%	no data	75-97%
Temperature	5, 10, 15, 25, 35, 45 °C	5, 12 and 18 °C	5, 10, 15, 20, 25 °C	8, 18 and 28°C	4-16°C
Days	2	11	14	50	4
Gas sampling	after 2, 4, 6, 8, 12, 24 and 48h	after 2.5h and every day at the same hour during 4 days, then at the 7th and the 11th day	at day 1, 2, 4, 7, 10 and 12	Every 24h	Every 2 h during 12 h on each day
Addition	3 mg of glucose in 20 mL of water + 60 ppm of NO ₃ ⁻	water + 10 g N.m ⁻²	80 mg N.kg ⁻¹ of NH ₄ NO ₃	no data	20 mL of a KNO ₃ solution (0.02 M)
Q ₁₀	89 pour T < 11°C	Arable 5-12°C : 50	WFPS 60% + 5-15°C : 1.2	8-18°C: 0,82-1.06	N ₂ O emissions: 3.85-0.33
	2 pour T > 11°C	Arable 12-18°C : 8,9	60% + 10-20°C : 2.2	18-28°C: 0.91-1.22	Denitrification: 6.47-1.72
		Grassland 5-12°C : 3,7	60% + 15-25°C : 1.4		
		Grassland 12-18°C : 2,3	75% + 5-15°C : 2.8		
			75% + 10-20°C : 4.2		
			75% + 15-25°C : 3.4		
			90% + 5-15°C : 5.4		
			90% + 10-20°C : 20		
			90% + 15-25°C : 33		

Table 4: Different laboratory conditions and results on studies about the effect of temperature on N₂O emissions and denitrification

Q ₁₀	Model
2.0	NUCM
2.0	LEACHMN
2.0	MATHILD
2.2	WANISIM
2.2	CREAMS-NT
2.3	LEACHM
3.0	SOILN
3.0	WAVE
2.1 / 89	NEMIS, STICS

Table 5: Q₁₀ used by different models simulating N₂O emissions (Heinen 2006).

Our study treatments with acetylene showed that the ratio of N₂O emission to total denitrification was lower for the 16°C treatment compared to the 4°C or 4-16°C treatment. This difference in the denitrification efficiency, or formation of the end product N₂ in favor of N₂O, might also explain that N₂O emissions did not increase with temperature in our experiment. Indeed N₂O reduction appears less efficient at low temperature and varying temperature than the first steps of denitrification (more sensitive at low temperature) which leads to at least a stabilization and probably a decrease of N₂O emissions with increasing temperatures.

Incubations at increasing temperature reveal an acceleration of the denitrification rates at 12°C, which is consistent with observations of Stanford et al. (1975) currently taken into account in the NOE model (Henault et al., 2005).

The biodiversity of soil microorganisms able to mineralize organic C has been found to be much larger than the ones able to denitrify and reduce N₂O (Philippot and Germon 2005). Large biodiversity is coupled to functional redundancy, which is expected to protect essential soil functions, such as denitrification, against environmental disturbances (Coleman

et al. 2004). While a temperature sensitivity of microbial processes with a Q_{10} of 2 could be admitted as the norm, we observed that the C mineralization was not affected by the different temperature treatments (constant 4°C or 16°C, or a 12 h-increase from 4 to 16°C), but that denitrification and moreover N₂O reduction decreased with time.

This study also questions current approaches for simulating effects of temperature on soil N₂O emissions due to denitrification as our study indicates controls at 2 levels. First, Q_{10} values observed for CO₂ production were about constant over the 4 days of our study, while the Q_{10} for denitrification rates declined from values as high as 6.47 at day 1 to finally reach 1.72 at day 4. Therefore, the current assumption in denitrification models that the temperature sensitivity of denitrification remains constant with time is too simplistic. Secondly, this study also suggests that the temperature dependencies of denitrification varies for the different enzymatic steps, i.e., as in our study, that the temperature dependency of N₂O production markedly differs from that of the N₂O reduction to N₂. Finally, our experiment also confirmed that N₂O reduction to N₂ is the final process determining soil N₂O emissions.

V. Conclusion

This study has clearly demonstrated that the temperature and the temperature variations significantly affect soil denitrification, N₂O production and reduction by denitrification. Surprisingly, at our highest incubation temperature of 16°C, soil N₂O emissions were, in tendency, lower than for the treatments at 4°C or 4-16°C, while total denitrification was however higher at higher temperature. This observation appears to be due to a relative lower ratio of N₂O reduction to N₂O production at lower soil temperatures. It remains unclear however, if this result can be generalized for other soils in the region or

elsewhere, as such experimental approach, as realized in this study, has not been realized before. Our results suggest that a dynamic parametrization of the temperature dependency of the different enzymatic steps might be required to realistically simulate N₂O production and emissions from soils.

Acknowledgement

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**Chapter 4: N₂O emission measurements at the
plot and landscape scale, using 3 different
methods**

Après avoir travaillé à l'échelle du cylindre de sol dans le chapitre 3 sur l'effet de la température du sol sur les émissions de N₂O, et ce sur un sol prélevé sur le site expérimental présenté au chapitre 2, nous allons maintenant présenter des résultats de mesures directes d'émissions de N₂O, réalisées sur le site dont était issu le sol du chapitre 3. Dans ce chapitre, le regard que nous allons porter sur les émissions de N₂O se situe à l'échelle de la parcelle mais également à celle du paysage. Ce regard sera orienté vers la mesure directe et le déterminisme multifactoriel.

Résumé

La variabilité spatiale des flux de protoxyde d'azote (N₂O) par les sols est large, quelle que soit l'échelle d'étude, rendant très importantes les incertitudes sur les émissions de N₂O par les sols. L'objectif de cette étude était d'estimer les flux de N₂O à l'échelle du paysage en combinant les résultats de mesures faites à différentes échelles. Pendant une campagne de 2 mois (mi-mars à mi-mai 2015), les flux de N₂O ont été mesurés sur une petite surface agricole (~km²) (i) continuellement à l'échelle de la parcelle avec des chambres automatiques sur un champ de blé, (ii) ponctuellement sur un groupe de 16 parcelles incluant différents types de sols et cultures en utilisant une chambre mobile (appelée fast-box), (3) continuellement à l'échelle du paysage avec eddy covariance en utilisant un mât de 15 m en association avec 2 modèles d'advection-dispersion (les modèles FIDES et Kormann et Meixner) pour déterminer les empreintes des mesures d'eddy covariance. De plus, les propriétés des sols ont été mesurées sur tous les sites pour fournir une meilleure compréhension des facteurs contrôlant la variabilité des flux de N₂O. Les flux de N₂O mesurés par les différentes méthodes ont

montré un bon accord en terme de magnitude et de dynamique temporelle, surtout lorsque les chambres automatiques étaient dans l’empreinte du mât d’eddy covariance. Les moyennes des émissions de N₂O ont été de $53 \pm 6 \mu\text{g N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ pour les chambres automatiques, $45 \pm 7 \text{ N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ pour le système d’eddy covariance et $37 \pm 9 \text{ N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ pour les mesures fast-box, lorsque l’on regarde uniquement les périodes où les systèmes de mesures automatiques fonctionnaient. Les flux de N₂O mesurés par les chambres automatiques and par la fast-box étaient positivement corrélés à l’humidité du sol ($p < 0.01$), la teneur en eau ($p < 0.01$) et la teneur en nitrate du sol ($p < 0.01$). Les combinaisons champs de culture intermédiaire – pois/maïs émettaient plus de N₂O que les champs de blé et de colza, et bien plus que les forêts.

Mots-clés : gaz à effet de serre, mesure par chambres, eddy covariance

Abstract

The spatial variability of soil nitrous oxide (N₂O) fluxes is large - regardless of the study scale - resulting in very large uncertainties in soil N₂O emission assessments. The objectives of this study were to assess the N₂O flux at the landscape scale by coupling the results of measurements performed at different scales and to propose a method for obtaining emission maps based on these results. During a 2-month campaign (mid-March to mid-May 2015), N₂O fluxes were measured in a small cropland area (~km²) (i) continuously at the plot scale using automatic chambers in a wheat field, (ii) punctually on a group of 16 plots including different types of soils and crops using a mobile chamber (fast-box), and (iii) continuously at the landscape scale by eddy covariance using a 15-m height mast and 2 advection-dispersion models (the FIDES and Kormann and Meixner models) to determine the eddy covariance

measurement footprints. The soil properties were measured at all sites to provide a better understanding of the factors controlling the variability of the N₂O flux. The N₂O fluxes, measured by the different methods, showed good agreement in magnitude and temporal dynamics, especially when the automatic chambers were in the eddy covariance mast footprint. Overall, the mean measured N₂O emission was $53 \pm 6 \mu\text{g N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ for the automatic chambers, $45 \pm 7 \text{ N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ for the eddy covariance system and $37 \pm 9 \text{ N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ for the fast-box, for periods when both automatic measurement systems were functioning. The N₂O fluxes measured by the automatic chambers and the fast-box were positively correlated with soil humidity ($p < 0.01$), water-filled pore space ($p < 0.01$) and nitrate soil content ($p < 0.05$). Catch crop-pea and catch crop-corn fields emitted more N₂O than wheat and rapeseed fields, and much more than forests.

Keywords: greenhouse gas, chamber measurements, eddy covariance

I. Introduction

N₂O has been the subject of concern due to its impact on global warming and ozone layer depletion (UNEP 2013). There are several N₂O sources, but agriculture is by far the main anthropogenic N₂O emission source. Indeed, 77% of N₂O emissions due to anthropogenic activity are estimated to come from mineral and organic fertilizer application to agricultural land and other agricultural sources (UNEP 2013). Monitoring N₂O emissions from agricultural fields is a key step to better constraining N₂O sources and determining the underlying processes driving emissions in order to develop mitigation recommendations. N₂O is produced at the microscale mainly by microbial processes, but the effects of its increased atmospheric concentration are visible at the global scale. N₂O emissions can be studied at the aggregate, field, landscape, regional, national and global scales. Regardless of the scale, the very high spatial and temporal variability of N₂O emissions from soil make its quantification difficult (Henault et al. 2012). Furthermore, N₂O emissions depend on numerous factors such as crop type, fertilizer type, and N application rate, as well as soil properties, such as soil organic carbon content, humidity, pH, and texture (Stehfest and Bouwman 2006).

Several measurement methods have been developed to monitor N₂O emissions, with increasing accuracy, providing flux estimates at different scales. Chambers, which provide a gas-tight enclosure of a certain soil surface area while measuring the changes in gas concentrations in the chamber headspace, provide flux estimates at the plot scale. They can be used to assess (i) the spatial variability of N₂O fluxes if they are mobile (Flechard et al. 2007; Grossel et al. 2014) and (ii) the temporal variability if they are static, i.e., remain at a fixed position (Henault et al. 1998; Laville et al. 1997). High-frequency measurements can be obtained using automatic chambers (ButterbachBahl et al. 1997; Christensen et al. 1996; Neftel et al. 2010). The use of a micrometeorological mast/tower - to estimate the fluxes from meteorological conditions and gas concentrations - based either on eddy covariance (EC)

(Christensen et al. 1996; Flechard et al. 2007; Laville et al. 1999; Molodovskaya et al. 2011), relaxed eddy accumulation (Baker 2000; McInnes and Heilman 2005), or the flux gradient method (Desjardins et al. 2010; WagnerRiddle et al. 1997; Zhang et al. 2015) provides information on the temporal variability over a wide spatial area, the so-called footprint, which is defined mainly by the height of the mast (plot, landscape and regional scale). Using aircraft (Desjardins et al. 2010; Pattey et al. 2006) to measure N₂O in the atmosphere provides information at an even larger scale (regional). These methods have been used to measure the biosphere-atmosphere exchange of trace gases for different ecosystems, including grassland (Clayton et al. 1994; Neftel et al. 2010; Smith et al. 1994), forests (Breuer et al. 2000; ButterbachBahl et al. 1997), wheat stubble (Christensen et al. 1996), corn (Laville et al. 1999), cotton (Wang et al. 2013), and mixed fields (Desjardins et al. 2010; Flechard et al. 2007; Zhang et al. 2015), during different seasons: spring (Clayton et al. 1994; Henault et al. 1998; Smith et al. 1994), summer (Christensen et al. 1996; Molodovskaya et al. 2011; Neftel et al. 2010) and autumn (Laville et al. 1997), and for different durations, ranging from 4 days (Molodovskaya et al. 2011) to 4 years (Desjardins et al. 2010).

Each of the many methods used to measure N₂O emissions from soils has specific advantages and limitations (Denmead 2008). The fluxes obtained by the chamber method are generally associated with very large uncertainties because (i) the very small surface area covered by the chamber is not representative of the ecosystem and (ii) the gas-tight closure of the chamber affects natural gas diffusion gradients across the soil-atmosphere-interface (Davidson et al. 2002), which is a non-linear phenomenon and should be considered when calculating the flux (Pihlatie et al. 2013). The fluxes obtained by micrometeorological methods are dependent on the wind conditions during the measurement period, therefore, they do not represent a static area over time. Moreover, micrometeorological flux measurements are most suitable for flat terrain and provide only an integrated flux over a varying footprint

Chapter 4: N₂O emission measurements at the plot and landscape scale, using 3 different methods area. Their installation, maintenance and data evaluation require a very high technical level and are expensive in terms of instrumentation and scientific man-power (Henault et al. 2012). Schematically, micrometeorological methods are the most appropriate for estimating gas fluxes in situations representative of ecosystems while chamber methods are the most appropriate for comparing emissions related to different agricultural practices.

For micrometeorological methods, the footprint area depends on the measurement height, so higher masts can be used to survey entire landscapes. Nevertheless, these methods rely on assumptions of horizontal homogeneity and non-advective conditions; data collected in complex terrain are difficult to analyze and the choices of sites are biased towards flat and homogeneous areas (Novick et al. 2014). While studies have addressed these problems for ecosystem CO₂ fluxes (Gockede et al. 2004), this has so far not been done for N₂O fluxes. N₂O fluxes are more difficult to measure due to atmospheric concentrations in the ppb range and because the pulses of N₂O fluxes are often sporadic. Additionally, high spatial variability needs to be considered. Fertilized croplands have been shown to be important sources of N₂O emissions, but crop type, fertilization and field management across a landscape is mosaic, challenging the assumption of the homogeneity of EC measurements.

In addition to the EC measurements, footprint models can be used. Footprint models, such as the Kormann and Meixner model (K&M) (Kormann and Meixner 2001) and the FIDES model (Loubet et al. 2010; Loubet et al. 2009; Loubet et al. 2001), calculate from the wind speed and direction, the origin of the air flux coming. Thereby, the N₂O flux source areas can be known. Furthermore, footprint models will allow a better comparison between the different N₂O measurement methods.

During a N₂O emission measurements campaign, the objectives were (i) to know if N₂O fluxes measured with several methods covering several scales of the landscape are

comparable, (ii) to see if the spatial and temporal variability can be covered, and (iii) to determine which type of crop emit the most.

II. Materials and Methods

1. Experimental site

A campaign of N₂O emission measurements was performed from 16 March 2015 to 19 May 2015 at the OS² (“Observatoire Spatialisé Orléanais des Sols”) experimental site, located 120 km southwest of Paris. Previous experiments conducted on this site with manual chambers since 2009 have shown N₂O emission pulses following spring fertilization in March-April (Grossel et al. 2016; Gu et al. 2013; Gu et al. 2011). The 30-years mean temperature at this site is 10.6°C, while the mean annual rain fall is 600 mm. A 15-m tall mast was erected and emission measurements were focused on an area within a radius of 1 km around this mast (Fig. 30). Within this area, different types of crops and land uses are found: wheat (21 fields, surface 112 ha, representing 29% of the area), rapeseed (14 fields, 93 ha, 24%), winter barley (4 fields, 63 ha, 16%), catch crop – pea combination (1 field, 8 ha, 2%), catch crop – corn combination (1 field, 18 ha, 5%), fallow (4 fields, 8 ha, 2%) and forest (5 forests, 87 ha, 22%). The wheat, rapeseed and winter barley plots were fertilized during the experiment. Generally on wheat fields, a fertilization was brought shortly before the campaign begins (12 to 27 March, median amount 78 kg N ha⁻¹, liquid form) and a third one during the campaign (25 April to 12 May, median amount 62 kg N ha⁻¹, liquid or solid form). On rapeseed fields, a fertilizer input was brought earlier than for wheat (7 to 25 March, median amount 80 kg N ha⁻¹, liquid or solid form). Barley fields also received a fertilizer input shortly before the campaign (20 to 25 March, median amount 69 kg N ha⁻¹). Corn was seeded on the 13 April (in green manure freshly ground in the plot) during the campaign and received

20 kg N ha⁻¹ at seeding and 100 kg N ha⁻¹ on the 10 May. Last, the pea field was seeded on the 10 March, also in a green manure freshly ground.

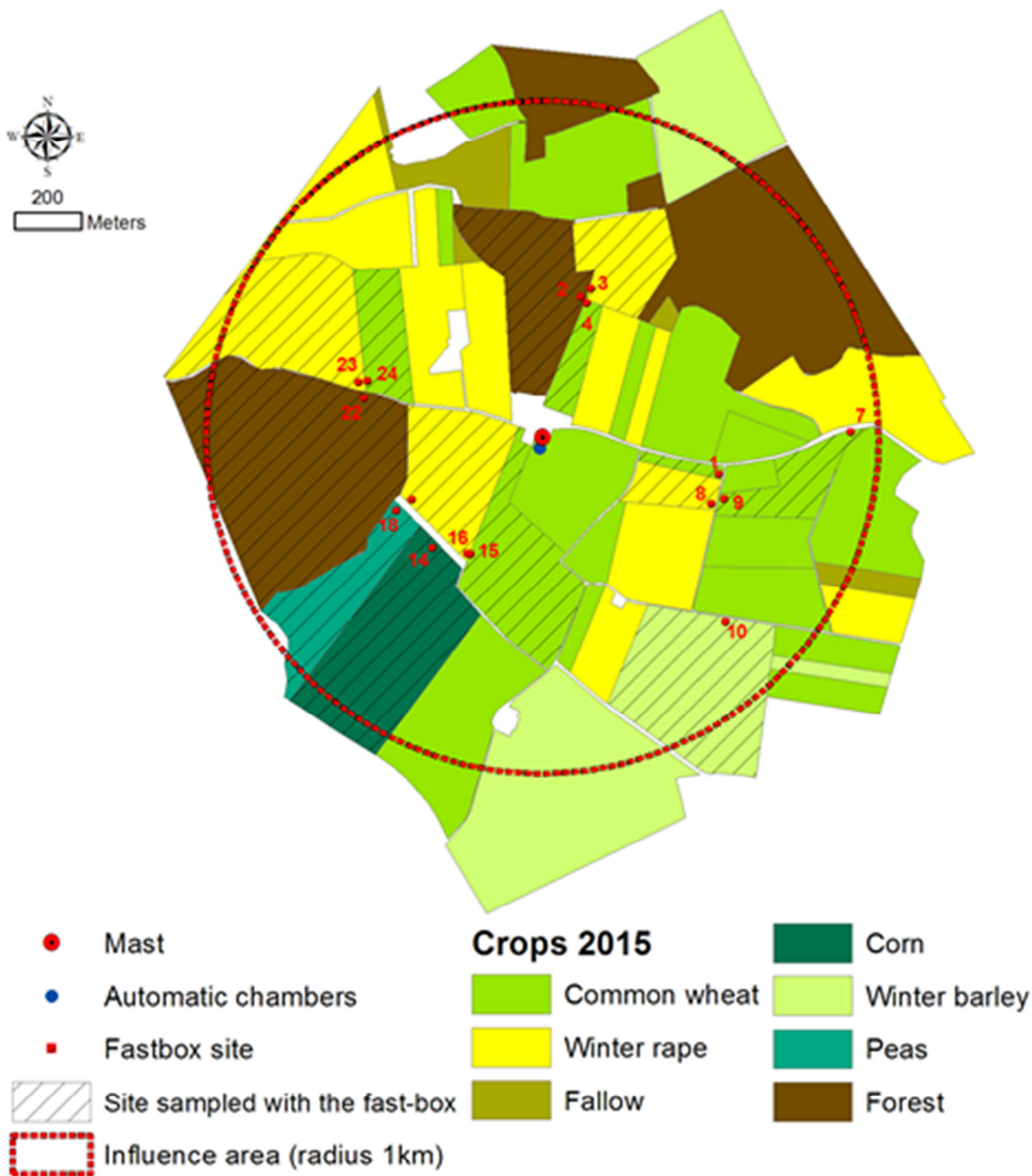


Figure 30: Experimental site with the location of the EC mast, the automatic chambers and the 16 fast-box sites.

2. Experimental design

To assess both the spatial and temporal variability of N₂O flux from the plot to landscape scale, 3 measurement methods were applied simultaneously: (1) automatic chambers placed on a wheat field next to the mast for continuous plot-scale measurements to study the local temporal variability; (2) fast-box measurements inside a 1-km radius from the mast at various plots to study the spatial variability, and (3) a 15-m tall EC system to provide continuous spatially integrated N₂O fluxes at the landscape scale.

2.1. Automatic chamber measurements

8 automatic chambers were deployed in the plot next to the EC mast from 21 March to 12 May 2015. The chambers (50 cm x 50 cm x 15 cm; total volume of 37.5 L) consisted of an aluminum frame in which Plexiglas panels were fixed. Frames were inserted 2 cm deep into the soil. Chambers were connected to a gas chromatograph equipped with an electron capture detector (GC-ECD) placed in a truck (Figure 31). The N₂O concentrations were measured in 2 groups of 4 closed chambers. These 2 groups were randomly selected, and placed as far as possible from the wheel traces. A measurement cycle for the 2 groups took 2 hours (30 min for each chamber, 12 cycles per day). In case of rain, the chambers were opened and the measurements were stopped to limit experimental biases; otherwise, measurements were performed continuously up to 12 times per day over the entire observation period. The whole system was described in a previous paper (ButterbachBahl et al. 1997).

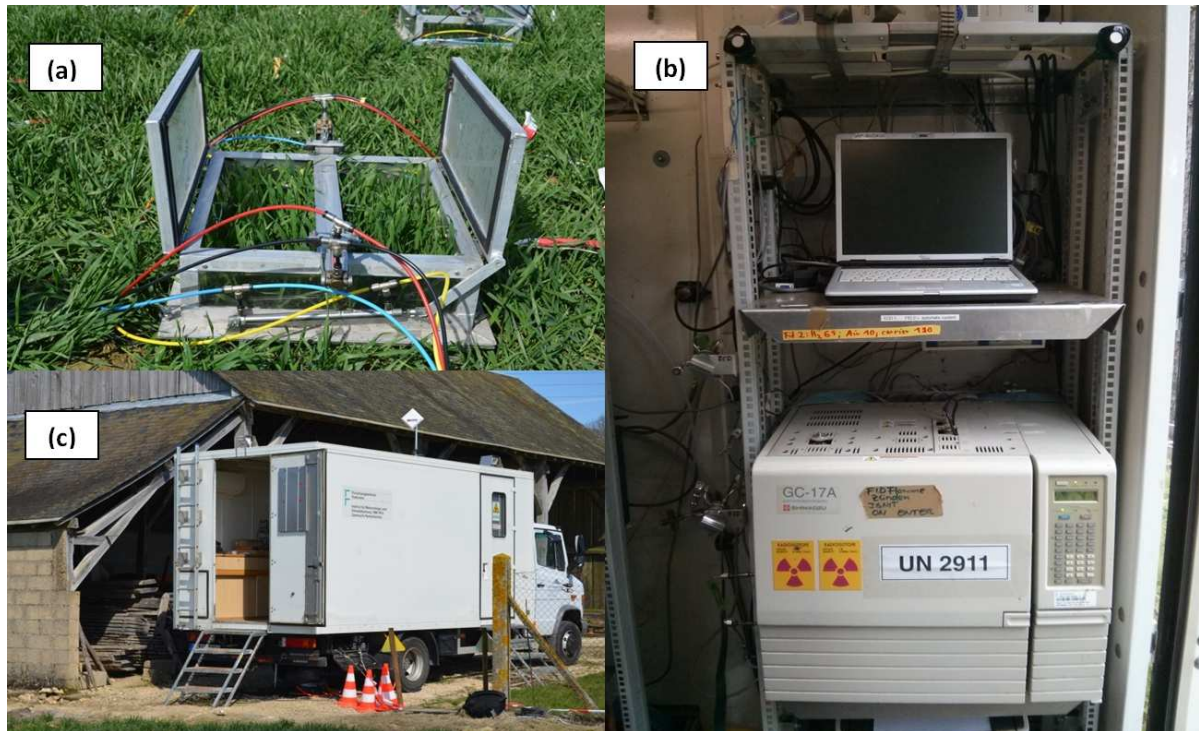


Figure 31: (a) One automatic chamber to measure N₂O emissions, (b) the gas chromatograph measuring N₂O concentration in each chamber, (c) the truck connected to the automatic chambers where measurements are done with the gas chromatograph

2.2. Fast-box measurements

Eight snap-shot campaigns were performed during the experimental period using a fast-box system coupled to a lab-built QCL (Quantum Cascade Laser) spectrometer called SPIRIT (Guimbaud et al. 2011; Guimbaud et al. 2016). The fast-box was a 50 cm x 50 cm x 15 cm chamber pressed directly onto the soil surface without the pre-installation of frames (Figure 32). Soft rubber foam (5 cm wide) on the chamber edges ensured tight sealing of the chamber headspace, and any leakage was assessed by on-line CO₂ analysis. The SPIRIT analyzer was equipped with a QCL emitting at 4.5 μm , to measure the N₂O dry mixing ratio (vmr) at 0.7 Hz. The spectrometer was placed in a van to move among sites within the mast footprint. Sixteen sampling locations were selected based on their accessibility and their

representativeness of soil occupation and soil type in the investigated area. We were able to investigate 7 to 9 of the 16 sites per measurement day, with 4 measurements per site. During each of the 8 snap-shot campaigns, downwind sites were systematically sampled and incremented by other sites chosen to optimize the number of measurements (distance, accessibility). The fast-box sites and the types of crop in the mast footprint are presented in Figure 30.

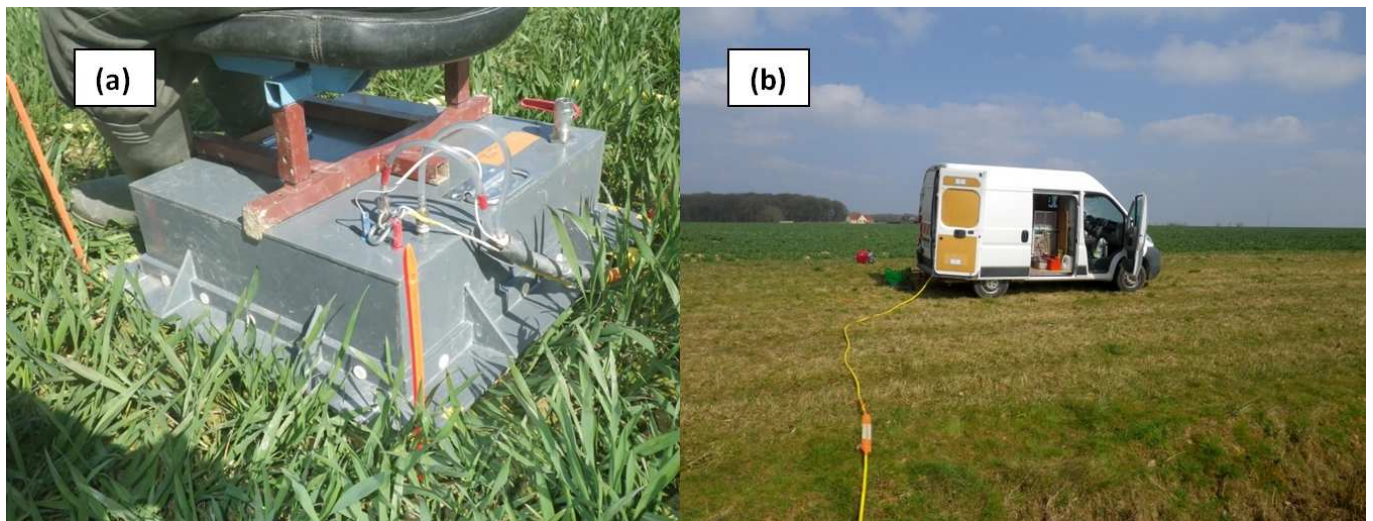


Figure 32: (a) the fast-box to measure N₂O emission, (b) the van with the SPIRIT inside connected to the fast-box

2.3. Eddy covariance measurements

The EC system was placed on the top of the 15-m tall mast (Figure 33). Wind was measured using a 3D ultrasonic anemometer (R3-50, Gill, UK). Air was sampled through a 40-m long (3/8 inch internal diameter) heated and insulated PFA tube at a flow rate of 55 L min⁻¹ using a pump (SV-1010-B, Busch, Switzerland) while ensuring the turbulent flow necessary to lower the tube low-path filtering on the N₂O signal. Air was analyzed using a closed-path QCL spectrometer (Aerodyne Inc., USA) operating at 7.8 μm, to provide

Chapter 4: N₂O emission measurements at the plot and landscape scale, using 3 different methods simultaneous measurements of the N₂O, CH₄ and H₂O dry vmr. Water vapor was not filtered, but a correction for water vapor was applied to the N₂O measurements. Data were recorded at 10 Hz. Measurements were performed from 16 to 19 March and from 1 April to 19 May. There was no measurement from 19 March to 1 April due to a QCL failure.



Figure 33: (a) The 15 meters mast, (b) The anemometer at the top of the mast and the inlet of gas, (c) the quantum cascade laser spectrometer to measure N₂O concentration

2.4. Additional measurements

The automatic chamber system was complemented by temperature (TC Direct, UK) and humidity probes (TDR CS616, Campbell Scientific) placed in the soil at depths of 5, 10 and 20 cm (3 replicates per depth) which measured at a 1-h time step, and by a pluviometer (ARG100, Campbell Scientific). Furthermore, during each fast-box snap-shot campaign, soil temperature and soil humidity were measured with a probe placed 10 cm deep in the soil, for the sites investigated daily. Moreover, soil samples were collected from these sites at a depth of 0-20 cm and brought to the laboratory to measure mineral nitrogen (N), including both

Chapter 4: N₂O emission measurements at the plot and landscape scale, using 3 different methods ammonium (NH₄⁺) and nitrate (NO₃⁻) by colorimetry after extraction in K₂SO₄ 0.5M according to Cataldo (1975) and pH using a glass electrode in a soil suspension diluted in a potassium chloride solution (1:5 ratio, NF ISO 10390). In each site, 3 undisturbed soil cores using 9 cm diameter cylinders (0.5 L) were taken in April to measure bulk density in the 5-15 cm layer, as a trade-off between available experimental devices and representativeness of the tilled layer. Soil samples were also taken in the 0-20 cm layer, dried at room temperature and sieved at 2 mm mesh to analyze soil texture, total nitrogen and carbon content at LAS (Soil Laboratory Analysis, France).

2.5. Flux calculation methods

For the automatic chambers, fluxes were calculated from the linear change in 4 measurements of the chamber headspace gas concentrations. The overall N₂O flux was calculated every 2 hours as the mean value of the 8 flux estimates based on the measurements performed during each 2-hour cycle. The standard error was calculated for each point value from the 8 chambers. For the fast-box system, N₂O emissions were calculated based on the increase in headspace during 4 min, assuming a linear or non-linear increase with the Hutchinson and Mosier model as described by Pedersen (Pedersen et al. 2010). The emissions from each location were estimated based on the mean value of the 4 flux measurements performed on each sampling date. The standard error was also calculated. Moreover, the N₂O emissions from each crop type were estimated as the average of the fast-box measurements for the specific crop during the whole period. The momentum, heat and N₂O fluxes were calculated by the EC method based on the maximum covariance during 30-min intervals. The state of the art EC methodology was used in Eddypro software (EddyPro® Version 5, 2015, Lincoln, NE. LI-COR). Briefly, first 2D-rotation was applied on the wind components; then de-spiking was applied. Spectral corrections for low-pass and high-pass filtering effects were applied according to Moncrieff's studies (Moncrieff et al. 2005; Moncrieff et al. 1997).

Moreover, a recursive running mean filter was applied on the raw N₂O signal to remove artificial fluctuations due to temperature variation. These fluctuations were due to offset drift on the raw N₂O signal, probably caused by temperature variations in the analyzer box. The time constant required for the filter (50 s) was determined using Allan variance analysis (Mammarella et al. 2010). The lag time between the N₂O mixing ratio and w was automatically adjusted in a 1.5-s window around a median value of 2.3 s. The total random uncertainty was calculated according to Finkelstein and Sims (Finkelstein and Sims 2001). The EC calculations also provided the wind direction (WD) and wind speed at mast height z , $\bar{u}(z)$, as well as the friction velocity (u^*), sensible heat flux (H), Obukhov length (L), and the standard deviation of the horizontal cross-wind component of the wind velocity σ_v , which were used by the footprint models.

2.6. Footprint defined by micrometeorological approaches

The contribution of each surface area (landscape element) to the N₂O flux measured by the EC system is by definition the footprint of this surface (Wilson, 1991). The footprint was determined inside a 1 km radius around the mast at all times by both the Kormann and Meixner model (K&M) (Kormann and Meixner 2001) and the FIDES (Loubet et al., 2010; Loubet et al., 2009; Loubet et al., 2001) footprint models, the latter being similar to the K&M model, but with a parameterized lateral dispersion and a different way to include the reference height. The input data of these models are mast height, field coordinates, WD , u^* , L , σ_v , as well as the dynamic roughness length z_0 estimated in neutral conditions using the definition of the logarithmic wind profile in the boundary layer (Kaimal and Finnigan, 1994):

$$\bar{u}(z) = \frac{u^*}{k} \ln\left(\frac{z-d}{z_0}\right) \quad \text{Eq. (4.1)}$$

where k is the Von Karman constant ($k = 0.414$) and d is the displacement height which, in a simplified approach was assumed to be constant for all wind directions and equal to $d = 0.0469$ m. z_0 theoretically depends on the land use (crop type, canopy height, forest and presence of buildings). In our approach, z_0 was calculated from all the $\bar{u}(z)$ measurements and averaged over four directions in order to separate the main forests area (at north and southwest) from the main crop areas.

By definition of the footprint, the N₂O flux at the mast at time t $F_{N_2O,mast,t}$ is:

$$F_{N_2O,mast,t} = \sum_{i=1} (F_{N_2O,i,t} \times A_{i,t}) \quad \text{Eq. (4.2)}$$

Where i is a landscape element, $A_{i,t}$ is the footprint of this area at time t , and $F_{N_2O,i,t}$ is the N₂O flux emitted from the given area.

2.7. Statistics

Statistical analyses based on regression techniques, correlations and tests of hypotheses were performed using XLSTAT® and MATLAB®. ANOVA and the Newman-Keuls post-hoc test (were used for the fast-box and soil data to test the null hypothesis that the type of crop or land use did not affect soil N₂O emissions. The Newman-Keuls was chosen as post-hoc test because even if it is less conservative, it appears more powerful than pairwise comparisons and Tukey's range test. It is largely used in soil science (Martin-Laurent et al. 2001; Ouédraogo et al. 2001; Ruser et al. 2006). Linear regressions were performed for the soil N₂O emissions against each of the ancillary variables. Statistical significance for all tests was set at $p < 0.05$.

III. Results

1. N₂O flux measurements during the campaign

1.1. N₂O fluxes detected by the automatic chambers

Several pulses of N₂O emissions were measured by the automatic chambers (Figure 34). During the first days of the experiment (March 20th-24th), the N₂O emissions were equal to 21 $\mu\text{g N-N}_2\text{O m}^{-2} \text{ h}^{-1}$. N₂O emissions pulses were observed on 25, 27 and 29 March, reaching followed by the highest pulse, reaching 708 $\mu\text{g N-N}_2\text{O m}^{-2} \text{ h}^{-1}$ on 30 March and an additional pulse on 4 April. After this period of high emission, the N₂O emissions decreased asymptotically to reach the initial level. At the beginning of May, the N₂O emissions increased for 4 days. Some diurnal fluctuations were observed throughout the experimental period. The total emissions measured on this plot during the experiment (53 days) were $909 \pm 103 \text{ g N-N}_2\text{O ha}^{-1}$, which was extrapolated to $8.0 \pm 0.9 \text{ kg N-N}_2\text{O}$ for the 8.8 ha field.

Regarding the measured ancillary variables, the N₂O fluxes measured by the automatic chambers were correlated with soil moisture ($p < 0.01$) and soil temperature ($p < 0.01$).

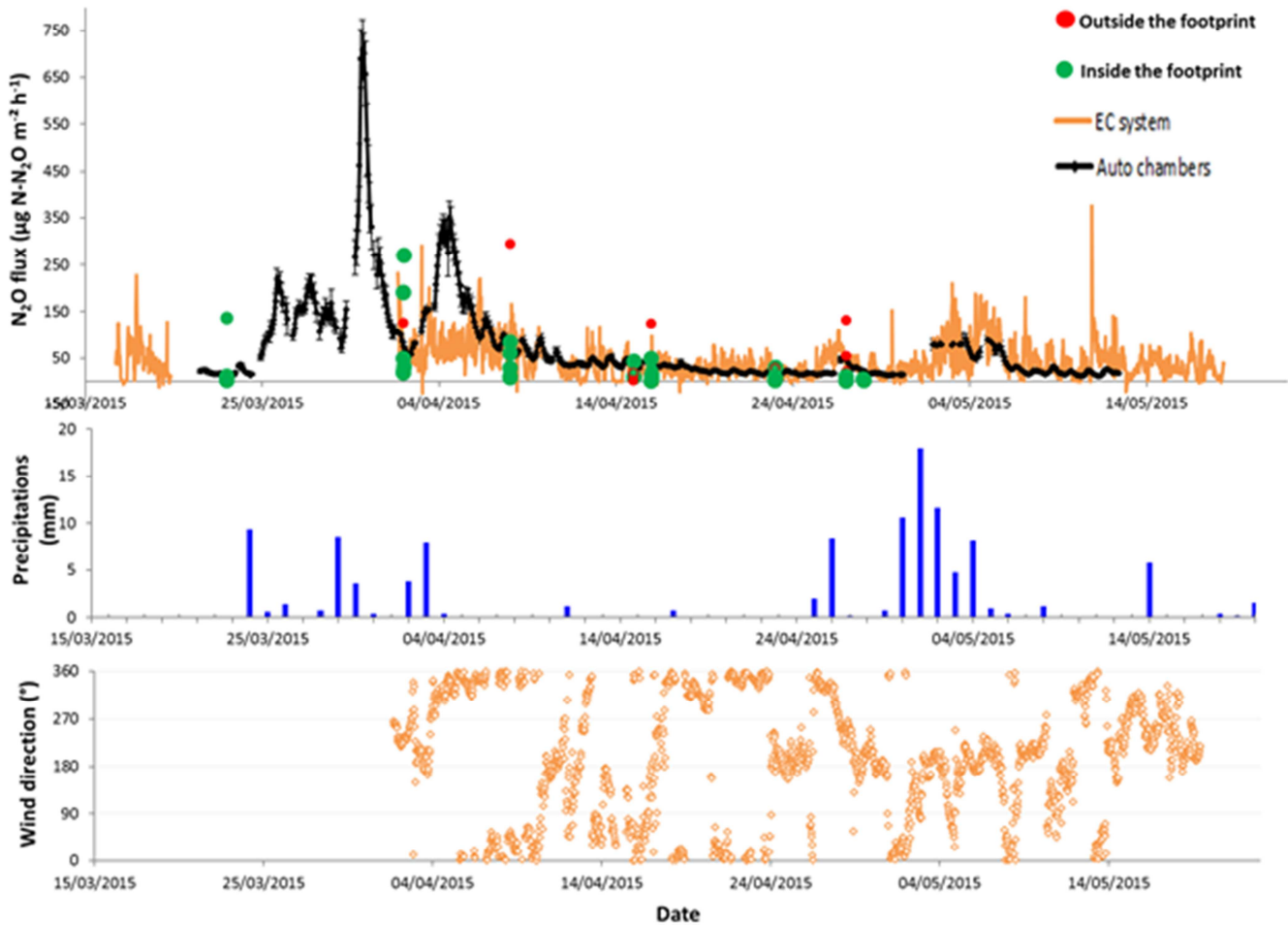


Figure 34: Top: N₂O fluxes ($\mu\text{g N-N}_2\text{O m}^{-2} \text{h}^{-1}$) measured by the EC system, the automatic chambers and the fast-box. Middle: daily precipitations during the campaign. Bottom: wind direction measured by the EC system..

1.2. N₂O fluxes and fast-box measurements

The fluxes measured by the fast-box method are shown in Fig. 35. N₂O accumulation into chambers were non-linear in about 30% of cases justifying the use of the HM model (Pedersen *et al.*, 2010; Brümmer *et al.*, 2017). The mean fluxes measured during each snapshot campaign ranged from 2 ± 2 to $101 \pm 19 \mu\text{g of N-N}_2\text{O m}^{-2} \text{h}^{-1}$. A maximum was observed on 8 April with $295 \pm 69 \mu\text{g of N-N}_2\text{O m}^{-2} \text{h}^{-1}$, which is consistent with the automatic chamber observations. The maxima for the different crops varied by date (Table 6). Following

the emissions peaks at the beginning of April, the fluxes decreased towards the end of the measuring period.

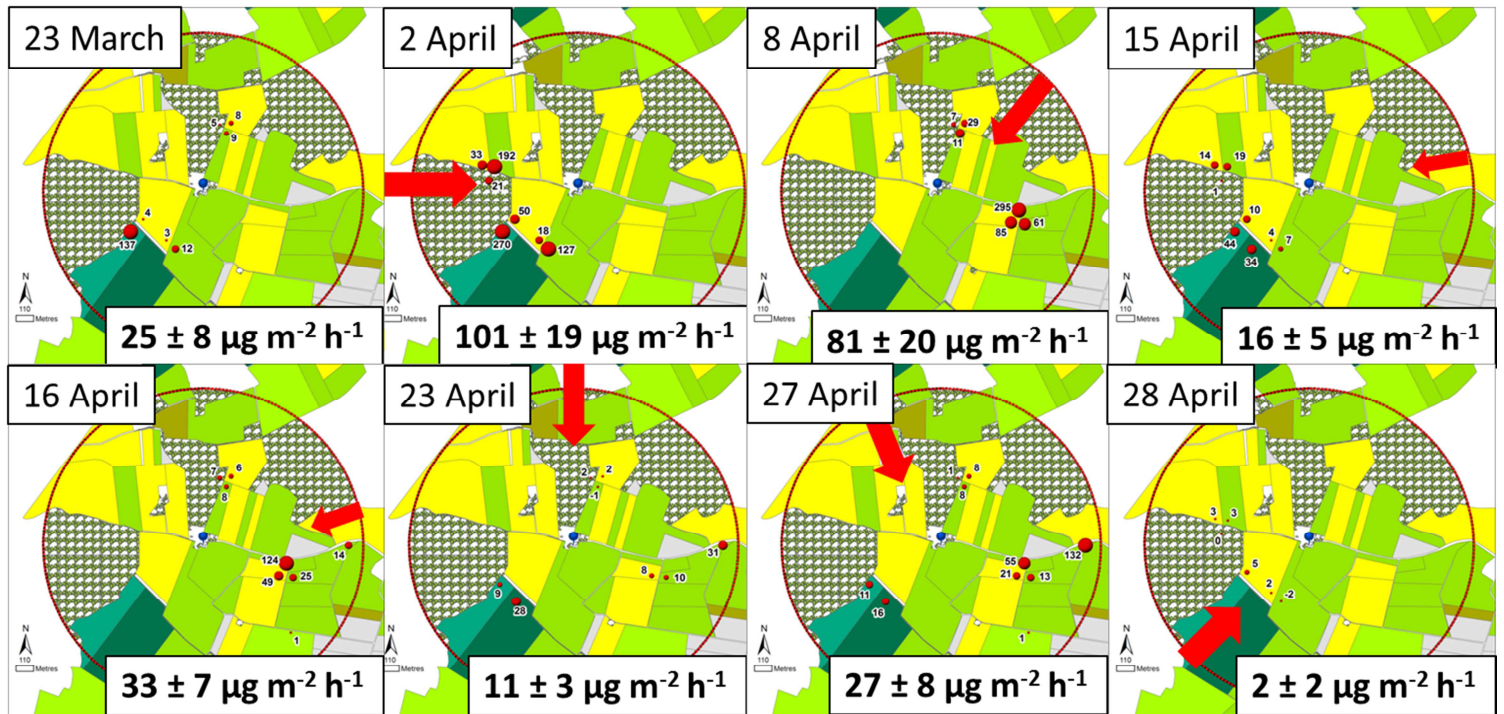


Figure 35: N₂O fluxes (numbers in $\mu\text{g N-N}_2\text{O m}^{-2} \text{h}^{-1}$) measured by the fast-box on the different sites during the 8 days of measurements. The mean value for each day is recorded. Red arrows show the prevailing wind direction, with the size of the arrow proportional to wind speed.

Date	Mean flux \pm standard error ($\mu\text{g of N-N}_2\text{O m}^{-2} \text{h}^{-1}$)	Max flux \pm standard error ($\mu\text{g of N-N}_2\text{O m}^{-2} \text{h}^{-1}$)	Type of crop with the highest flux
23 March	25 \pm 8	137 \pm 43	Catch crop - pea
2 April	101 \pm 19	270 \pm 40	Catch crop - pea
8 April	81 \pm 20	295 \pm 69	Wheat
15 April	16 \pm 5	44 \pm 13	Catch crop - pea
16 April	33 \pm 7	124 \pm 22	Wheat
23 April	11 \pm 3	31 \pm 9	Wheat
27 April	27 \pm 8	132 \pm 41	Wheat
28 April	2 \pm 2	5 \pm 4	Rapeseed

Table 6: Fluxes measured with the fast-box on every measurement day, with the mean flux, the maximum flux and the type of crop where the maximum flux was measured.

Regarding the measured ancillary variables, the N₂O fluxes measured with the fast-box were correlated with soil moisture ($p < 0.01$), water-filled pore space (WFPS) ($p < 0.01$) and NO₃⁻ soil content ($p < 0.05$).

1.3. N₂O fluxes detected by the eddy covariance method and the associated footprint defined by micrometeorological approaches

EC measurements showed N₂O emissions throughout the experimental period (Figure 34). A high N₂O emission pulse of 291 $\mu\text{g N-N}_2\text{O m}^{-2} \text{h}^{-1}$ was reached on 3 April. After this pulse, the mean fluxes decreased from 10 to 25 April. On 26 April, a smaller pulse of N₂O emissions was observed, with emissions increasing in the following days until 3 May, followed by a couple of days with emission pulses. The apparent total N₂O emissions

measured from the arable soils inside the 1-km radius footprint (389.29 ha) during the experimental period (48.6 days) were estimated at 194 ± 33 kg of N-N₂O.

1.4. Comparison of N₂O fluxes obtained by the different techniques

Table 7 presents the mean and standard error of the global fluxes measured with the different techniques considering either all the data or only periods when all the data were measured simultaneously. The means vary from 37 ± 9 to 71 ± 8 $\mu\text{g N-N}_2\text{O m}^{-2} \text{ h}^{-1}$. While all the values are of the same order of magnitude, the variability is consistent with the well-known spatial and temporal variability. The combination of the different measurement techniques reveals that the wheat field investigated using the automatic chambers emitted higher fluxes than most of the fields within the investigated area.

		Mean ($\mu\text{g N-N}_2\text{O m}^{-2} \text{ h}^{-1}$)	Standard error ($\mu\text{g N-N}_2\text{O m}^{-2} \text{ h}^{-1}$)
Eddy covariance mast	All data	45.7	7.5
	Only when both automatic systems were measuring simultaneously	45.2	7.5
Automatic chambers	All data	71.5	8.1
	Only when both automatic systems were measuring simultaneously	53.0	6.0
Fast-box	All data	37.0	6.2

Table 7: Mean and standard error of global fluxes measured with different techniques considering either all data or only periods when all data were measured simultaneously.

2. Footprints

As the main wind directions during the experimental period were north (April) and south (May), the forest on the north and the fields directly south of the EC mast, where the automatic chambers were placed, were the main contributors to the footprint of the EC flux measurements during the campaign (Figure 36). Both footprint models predicted a larger contribution of the fields near the EC mast than fields further away. FIDES assessed a larger contribution of the fields in the south – north corridor, leading to a larger contribution of fields cultivated with wheat, rapeseed, and winter barley. In contrast, K&M included contributions of fluxes from the western part of the experimental site in its footprint prediction, leading to a larger contribution of fields cultivated with catch crop-pea, catch crop-corn, fallow and forest. Moreover, FIDES assumed a larger contribution of the wheat plot to the total N₂O flux, i.e., where the automatic chambers were placed, than the K&M model.

Nevertheless, the plot contributions to the footprint obtained with both micrometeorological models were significantly correlated ($p < 0.001$), (Figure 37). Neither model attributed any contribution (even a very weak contribution) of fluxes from the wheat field during the first days of the experiment to the total observed EC-measured N₂O flux as the wind was blowing from other directions. This factor led to the very low contribution of this plot to the signal observed at the top of the EC mast, although high N₂O fluxes were measured during this period by the automatic chamber system. In contrast, during the second part of the experiment, the magnitude of fluxes attributed to the wheat plot were consistent with those observed by the chambers.

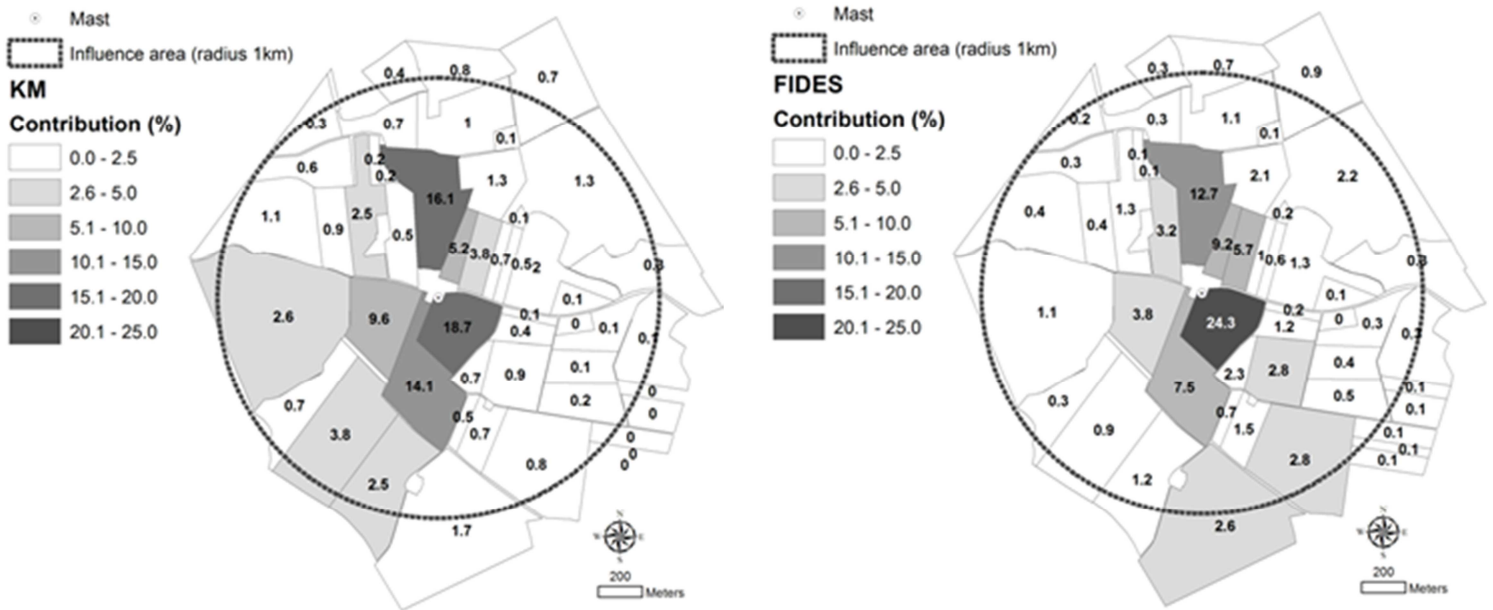


Figure 36: On the left: contribution of each crop to the total footprint of the eddy covariance flux during the campaign, obtained by using the Kormann and Meixner footprint model. On the right: the same information obtained using the FIDES footprint model. The 2 circles show the 1-km radius around the eddy covariance mast.

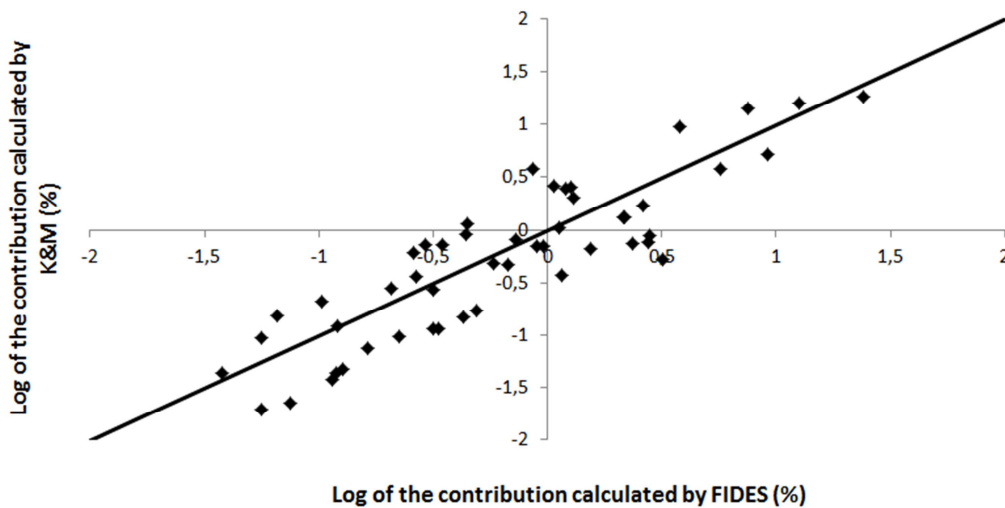


Figure 37: Contributions of the fields in the 1-km radius of the total footprint calculated using K&M as a function of those calculated by using FIDES, together with the 1:1 line, during the whole campaign. The level of correlation between the 2 models gives p values less than 0.0001.

IV. Discussion

1. Comparisons between methods

In this study, we compiled a database of continuous N₂O fluxes using different measurement techniques at different scales. The results obtained directly by the EC system and the fast-box located inside the footprint were generally consistent with low values on 15, 16, 24 and 28 April. On 2 April, both high and low values from the fast-box revealed strong spatial variability, and the emission values from the mast were included in this variability. Nevertheless, the fast-box results were all low, whereas high values were observed by the mast on 8 and 27 April. This means that the overall spatial variability was not completely covered by the fast-box system and that there were other N₂O sources inside the footprint at these times. Fast-box measurements are snapshots of fluxes for a given time and location, so “hot moments” might have been missed and “cold spots” could have been surveyed.

The EC fluxes had the same dynamics as those observed by the automatic chambers when both systems were working and when the automatic chambers were upwind from the mast. There was an increase in the flux at the beginning of April, followed by an asymptotic decrease and steady values, with a significant pulse at the end of the month and at the beginning of May. These pulses can be explained by the anaerobic soil conditions following precipitation events that occurred immediately before the emission pulses were observed. The highest emission pulse observed by the automatic chambers on 4 April was not detected by the EC system because the wind blew from the north (Figure 34) and the chambers, located south of the mast, were not in the mast footprint at this time. Nevertheless, during periods when the wind came from the south, the results of the mast and the chambers were in agreement, with background emissions and small pulses with similar values for both systems.

Similar results were observed over a carrot and a wheat stubble field, with similar values measured by both systems with dependence on wind (Christensen et al. 1996).

For the automatic chambers, the gaps in the N₂O emissions measurements were caused by the interruption of N₂O measurements due to the detection of precipitation. The field was fertilized on the 24 March, followed by a rain event on 29 March, triggering a high emission pulse on 30 March. N₂O pulse emissions showed a delay of several hours or days following rain events. The mean value of the total campaign for the automatic chamber (71 μg of N-N₂O $\text{m}^{-2} \text{h}^{-1}$) was almost twice as high as the mean value obtained from the fast-box (37 μg of N-N₂O $\text{m}^{-2} \text{h}^{-1}$) and the EC system (42.5 μg of N-N₂O $\text{m}^{-2} \text{h}^{-1}$). This can be explained by the fact that for the automatic chambers, only one location was measured, whereas for the fast-box, the mean value was measured across different crops (e.g., wheat, rapeseed, forest) and locations, and for the EC system an integrated mean value was obtained from different fields and crops in the footprint.

2. Spatial variability inside the 1-km radius area

N₂O emissions were very dependent on the location and type of crop. Such variability was observed by Hargreaves (1996) when comparing N₂O fluxes measured over an arable cropland with an EC system at a height of 5 m for carrot, wheat stubble, potatoes, spinach, onions and wheat and by Molodovskaya (2011), who compared measurements with an EC system at 3.5 m for corn and alfalfa fields. On average, rapeseed and wheat showed the same order of magnitude of N₂O emissions, forest and winter barley appeared to emit very small amounts of N₂O and the catch crop-pea and corn combination emitted more than wheat and rapeseed. Differences between these emissions might be due to the different types of soil, agricultural practices, soil properties, or a combination of these factors. The results obtained for winter barley were probably biased by the dates of the measurements, which were all

performed during periods of low emissions. Regarding the high N₂O emissions by the catch crop – pea plot, the pea had just been seeded, and the high emissions were probably due to catch crop decomposition, although the mineral N content measured in soil was not especially high. An increase in N₂O emissions of approximately 0.1 kg N ha⁻¹ y⁻¹ globally has been attributed to catch crop (Pellerin et al. 2015), and our results were probably influenced by a corresponding event. Correlation tests indicated an influence of soil humidity, WFPS and NO₃⁻ soil content on the N₂O flux. High soil humidity and WFPS are favorable to denitrification (Butterbach-Bahl et al. 2013). The presence of oxygen decreases with water content (Rabot et al. 2014); therefore, denitrification is favored. The NO₃⁻ soil content also favors denitrification, potentially favoring both N₂ and N₂O production (Firestone and Davidson 1989).

V. Conclusion

N₂O fluxes measured using several methods covering different scales of the landscape gave consistent results. The mean measured N₂O fluxes were 42.5 ± 7 µg N-N₂O m⁻² h⁻¹ for the EC mast and 37 ± 9 µg N-N₂O m⁻² h⁻¹ for the fast-box over a similar area, while the mean N₂O flux measured by the automatic chambers over a fertilized wheat field was 71 ± 8 N µg N-N₂O m⁻² h⁻¹. The N₂O fluxes measured by the automatic chambers and the fast-box were positively correlated with soil humidity (p < 0.01), water-filled pore space (p < 0.01) and nitrate soil content (p < 0.05). Catch crop-pea and catch crop-corn fields emitted more N₂O than wheat and rapeseed fields, and much more than forests.

Acknowledgement

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**Chapter 5: Development of flux attribution
methods for mapping N₂O emissions by
agricultural soils**

Dans ce chapitre, nous allons spécifiquement travailler sur le changement d'échelles entre celle de la parcelle et celle du paysage agricole. Les résultats des mesures présentées dans le chapitre 4 vont être utilisés pour tenter de préciser les sources des émissions de N₂O. En effet, les mesures d'eddy covariance vont être combinées avec les mesures de fast-box pour attribuer des flux de N₂O à une parcelle spécifique en suivant le principe d'une approche top-down. Les mesures réalisées avec les chambres automatiques vont quant à elles nous servir à valider la méthode d'attribution de flux.

Résumé

La variabilité spatiale des flux de protoxyde d'azote (N₂O) est large, quelque soit l'échelle d'étude, rendant très importantes les incertitudes sur les estimations des émissions de N₂O par les sols. Les objectifs de cette étude étaient d'estimer les flux de N₂O à l'échelle du paysage en couplant les résultats de mesures effectuées à différentes échelles et de proposer une méthode pour cartographier les émissions de N₂O basées sur ces résultats. Pour faire la carte des émissions de N₂O sur la surface totale, nous avons évalué 2 méthodes d'attribution des flux permettant d'estimer les flux de N₂O de chaque champ sur la période totale. Ces méthodes ont utilisé un modèle de footprint combiné avec les mesures fast-box sur chaque type de culture, pour déterminer la contribution de chaque champ au flux mesuré par le mât d'eddy covariance. Deux modèles de footprint ont été comparés (les modèles FIDES et Kormann et Meixner) et 2 hypothèses sur la dépendance des émissions de N₂O par rapport à la distribution des cultures et sur la teneur en nitrate du sol ont été testées. Les chambres automatiques ont été utilisées pour évaluer les méthodes d'attribution. Sur toute la surface et pendant la période expérimentale de 2 mois, les flux de N₂O ont variés de 0.18 à 0.44 kg N-

N₂O ha⁻¹ mois⁻¹ selon la surface. La plus simple méthode d'attribution des flux, prenant en compte seulement l'utilisation des terres, a montré de bonnes similarités avec les mesures aux champs fournies par les chambres automatiques (10%-13% de différence). Cette étude démontre le potentiel de cette méthodologie à représenter la variabilité spatiale des émissions de N₂O à l'échelle du paysage et de réduire les incertitudes dans son évaluation.

Mots-clés : gaz à effet de serre, mesures par chambres, eddy Covariance, méthode d'attribution des flux, effet de l'utilisation des terres

Abstract

The spatial variability of soil nitrous oxide (N₂O) fluxes is large - regardless of the study scale - resulting in very large uncertainties in soil N₂O emission assessments. The objectives of this study were to assess N₂O fluxes at the landscape scale by coupling results of measurements performed at different scales and to propose a method to retrieve emission maps based on these results. To map the N₂O emissions of the entire area, 2 flux attribution methods were evaluated which allowed estimating the N₂O flux of each field during the whole period. These methods used a footprint model in combination with fast-box measurements over each crop type to determine the contribution of each field to the flux measured at the eddy covariance mast. Two footprint models were compared (the FIDES, and the Kormann and Meixner models) and 2 hypotheses on the dependency of N₂O emissions on crop distribution and soil nitrate contents were tested. Automatic chambers were used to evaluate the attribution methods. Over the whole area during the 2-month experimental period, the N₂O flux varied from 0.18 to 0.44 kg N-N₂O ha⁻¹ month⁻¹ depending on the attribution method and footprint

model. The simplest flux attribution method, taking only land use into account, showed very good agreement with the field measurements provided by the automated chambers (10%-13% difference on the mean flux). Our study demonstrates the potential of flux attribution methods for catching spatial variability of soil N₂O emission at the landscape scale and reducing uncertainties in its evaluation.

Keywords: greenhouse gas, chamber measurements, eddy covariance, flux attribution method, land use effect

I. Introduction

In order to quantify N₂O emissions at the landscape scale, combining EC measurements with chamber measurements has been proven useful as it provides additional information on spatial variability as well as the temporal variability of fluxes for defined plots (Eugster and Merbold 2015). 2 types of approach are currently available to link micrometeorological measurements with chamber measurements. The first is the bottom-up approach, which involves: (i) direct measurements at the soil surface and (ii) a method for extrapolating local results to larger scales of time and space, using basic extrapolation or ecosystem models such as Landscape-DNDC (Haas et al. 2013) or CERES-NOE (Gabrielle et al. 2006)). The second is the top-down approach, which involves (i) integrative micrometeorological measurements and (ii) atmospheric transport modeling. At the landscape scale, the Kormann and Meixner model (K&M) (Kormann and Meixner 2001) and the FIDES model (Loubet et al. 2010; Loubet et al. 2009; Loubet et al. 2001) calculate the contribution of fields to the total footprint involved in N₂O flux detection dependent on meteorological conditions. Although relevant, this information is insufficient for describing the spatial

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variability of N₂O emissions. Understanding this spatial variability (especially at the landscape scale) remains a key concern for mitigating soil N₂O emissions.

In this study, several scientific issues were raised: (1) Can the origin of the N₂O fluxes be retrieved from the integrated and local measurements? (2) What is the integrated N₂O flux and the spatial variability of this flux over a 1-km radius landscape occupied by a mix of croplands and forests? Finally, (3) which method would be the best, and how can its validity and uncertainty be estimated?

II. Materials and Methods

Methods were developed to estimate the contribution of each field to the EC flux and to map the spatial variability of the soil N₂O flux for the entire study area. These methods are referred to as the flux attribution methods, which are based on the combined results of the EC flux measurements and footprint analysis in consideration of the spatial information provided by the fast-box flux measurements.

Two attribution methods were tested. The first one used the land use (*lu*) - defined here as either forest or crop type (wheat, rapeseed, barley, catch crop – corn, catch crop – pea) - as the main factor controlling N₂O emissions (*LU* method), and the second used both the land use and soil nitrate (NO₃⁻) concentrations (*NCLU* method).

1. Flux attribution method for characterizing the spatial variability of N₂O emissions: assuming only land use is affecting the N₂O emissions (*LU* method)

This first method is based on the basic assumption that only the type of land use affects the soil N₂O emissions (Freibauer and Kaltschmitt 2003). This hypothesis means that

the N₂O flux of a given land use lu at a given time t ($F_{N_2O,lu,t}$) is homogeneous in the landscape. It is useful to determine the ratio $\alpha_{lu,t}$.

$$\alpha_{lu,t} = \frac{F_{N_2O,lu,t}}{F_{N_2O,wheat,t}} \quad \text{Eq. (5.1)}$$

Wheat was chosen as the reference crop because it covered the largest area of the landscape. Here, $F_{N_2O,lu,t}$ is the mean N₂O flux measured for land use lu at time t . Combining Eq. (4.2) and Eq. (5.1) and considering the sum over each land use instead of the sum over each crop leads to:

$$F_{N_2O,mast,t} = F_{N_2O,wheat,t} \sum_{lu} (\alpha_{lu,t} \times A_{i,t}) \quad \text{Eq. (5.2)}$$

Further assuming that the variation of $\alpha_{lu,t}$ with time is small ($\alpha_{lu,t} \sim \langle \alpha_{lu} \rangle$), leads to:

$$F_{N_2O,mast,t} = F_{N_2O,wheat,t} \sum_{lu} (\langle \alpha_{lu} \rangle \times A_{i,t}) \quad \text{Eq. (5.3)}$$

This enables the determination of the dynamics of the N₂O flux in the reference crop (wheat):

$$F_{N_2O,wheat,t} = \frac{F_{N_2O,mast,t}}{\sum_{lu} (\langle \alpha_{lu} \rangle \times A_{i,t})} \quad \text{E(5.4)}$$

Finally, the N₂O flux in each land use lu can be estimated at each time t as:

$$F_{N_2O,lu,t} = \langle \alpha_{lu} \rangle \times F_{N_2O,wheat,t} = \langle \alpha_{lu} \rangle \times \frac{F_{N_2O,mast,t}}{\sum_{lu} (\langle \alpha_{lu} \rangle \times A_{i,t})} \quad \text{Eq. (5.5)}$$

$\alpha_{lu,t}$ was calculated on each date t and averaged over the 8 fast-box sampling dates to calculate the average $\langle \alpha_{lu} \rangle$. Moreover, data were taken only when at least 50% of the footprint calculated by both the FIDES and K&M models was within the 1-km radius. We supposed that N₂O was emitted homogeneously between the 1-km radius and beyond. The standard error $se_{\alpha_{lu}}$ was also calculated. The overall uncertainty of $F_{N_2O,lu,t}$ was calculated by error propagation, accounting for the uncertainty of the EC measurements ($F_{N_2O,mast,t}$) estimated

as the total random uncertainty and the uncertainty on $\langle \alpha_x \rangle$ estimated with the standard error (se_{α_x}).

$$\frac{se_{F_{N_2O,lu,t}}}{F_{N_2O,lu,t}} \leq \frac{se_{\alpha_{lu}}}{\langle \alpha_{lu} \rangle} + \frac{se_{F_{N_2O,mast,t}}}{F_{N_2O,mast,t}} + \sum_{lu} \frac{se_{\alpha_{lu}}}{\langle \alpha_{lu} \rangle} A_{lu,t} \quad \text{Eq. (5.6)}$$

2. Assuming land use and soil nitrate content are solely affecting the N₂O emissions (NCLU method)

The N₂O fluxes from denitrification are commonly described by empirical multiplicative models based on soil variables (Henault et al. 2005; Schmidt et al. 2000). Applying such a model over the landscape with crop type i and further considering that denitrification is dominant, in line with previous studies in the same region (Grossel et al., 2016), leads to the daily N₂O flux defined as:

$$F_{N_2O,mast,t} = \sum_{lu} \left[\sum_{i \text{ in } lu} ([NO_3^-]_{i,t} \times NF_{i,t} \times A_{i,t}) \right] \quad \text{Eq. (5.7)}$$

where i is the index for each field and $[NO_3^-]_{i,t}$ is the soil NO₃⁻ content of field i at time t .

Introducing the assumption that $NF_{i,t}$ is only a function of land use lu leads to

$$F_{N_2O,mast,t} = \sum_{lu} \left[NF_{t,lu} \sum_{i \text{ in } lu} ([NO_3^-]_{i,t} \times A_{i,t}) \right] \quad \text{Eq. (5.8)}$$

Again, taking wheat as the reference land use, we define the ratio based on normalized fluxes:

$$\beta_{lu,t} = \frac{NF_{N_2O,lu,t}}{NF_{N_2O,wheat,t}} \quad \text{Eq. (5.9)}$$

We can demonstrate that $\beta_{lu,t}$ is constant (see supplementary material) and noticing that $NF_{t,lu} = \langle \beta_{lu} \rangle \cdot NF_{t,wheat}$ and that $NF_{t,wheat}$ can be taken out of the summing operator (constant) leads to:

$$NF_{t,wheat} = \frac{F_{N_2O,mast,t}}{\sum_{lu} \left[\langle \beta_{lu} \rangle \sum_{i \text{ in } lu} ([NO_3^-]_{i,t} \times A_{i,t}) \right]} \quad \text{Eq. (5.10)}$$

Noticing that $F_{N_2O,i,t} = \beta_{lu(i),ref} \cdot NF_{t,ref} \cdot [NO_3^-]_{i,t}$, the flux in each crop can be calculated as:

$$F_{N_2O,i,t} = \langle \beta_{lu} \rangle \times \frac{F_{N_2O,mast,t}}{\sum_{lu} [\langle \beta_{lu} \rangle \sum_{i \text{ in } lu} ([NO_3^-]_{i,t} \times A_{i,t})]} \times [NO_3^-]_{i,t} \quad \text{Eq. (5.11)}$$

$[NO_3^-]_{i,t}$ is mainly driven by the fertilization date and amount and is different for each field i . It was calculated from the $[NO_3^-]$ background in each plot and from the $[NO_3^-]$ resulting from fertilization, taking into account the decrease in $[NO_3^-]$ over time as:

$$[NO_3^-]_{i,t} = [NO_3^-]_{background,i} + NO_3^-_{fert,i} * [1 - f_i(t - t_{fert,i})] \quad \text{Eq. (5.12)}$$

where f_i is an empirical function fitted to field measurements, increasing from 0 at $t = t_{fert}$ to 1 at t_{end} , $f_i(t - t_{fert}) = 1$ for $t < t_{fert}$ or $t > t_{end}$. For each plot, the exact date and amount of fertilizer were recorded. An input of 0.5 kg ha⁻¹ of NO₃⁻ was estimated for each kg ha⁻¹ of N input as the main fertilizer applied was ammonium nitrate (50% N-NH₄⁺ and 50% N-NO₃⁻).

$\langle \beta_{lu} \rangle$ was calculated from the fast-box measurements, on 8 sampling dates with $\frac{NF_{t,lu}}{NF_{t,wheat}}$. The same hypothesis of homogeneity beyond the 1-km radius applied for the LU attribution method was applied here. The standard error $se_{\beta_{lu}}$ was also calculated. The overall uncertainty on $F_{N_2O,i,t}$ was calculated by error propagation, accounting for the uncertainty on the EC measurements (F_{mast} , total random uncertainty) and the uncertainty on $\langle \beta_{lu} \rangle$ ($se_{\beta_{lu}}$ = standard error).

$$\frac{se_{F_{i,t}}}{F_{i,t}} \leq \frac{se_{\beta_i}}{\langle \beta_i \rangle} + \frac{se_{F_{mast,t}}}{F_{mast,t}} + \sum_i \frac{se_{\beta_i}}{\langle \beta_i \rangle} A_{i,t} [NO_3^-]_{i,t} + se_{\beta_i} \frac{s[NO_3^-]_{i,t}}{[NO_3^-]_{i,t}} A_{i,t} \quad \text{Eq. (5.13)}$$

Spatial and temporal dependencies on errors were not considered as their characterization is beyond the scope of this study.

3. Evaluation of the validity of the 2 flux attribution methods

As the fluxes measured with the automatic chambers were not used to estimate the spatial distribution of the N₂O fluxes, these data could be used to validate our calculation for a specific plot using a top-down approach. The *LU* and *NCLU* flux attribution methods were used to calculate plot-specific N₂O fluxes. Furthermore, the uncertainties were calculated for each value of N₂O flux obtained using the flux attribution methods. Only values whose uncertainties were lower than the calculated flux ($|\Delta F/F| < 1$) were considered, as done in a previous study (Mammarella et al. 2010) to remove unreliable fluxes with very large uncertainty, that were mostly large ones. The total N₂O emitted from each plot in the 1-km radius area during the entire campaign was calculated. The retrieved flux was compared to measurements on the field in which the automatic chambers were placed. This wheat field was considered representative of every wheat field in the area because despite the well-known spatial variability of N₂O fluxes, similar flux dynamics have been observed on 6 to 8 replicate sites over 2 years in this site in previous studies (Gu et al. 2014; Gu et al. 2011). The precision of the model was tested by calculating the coefficient of determination R^2 and its accuracy by considering the root mean square error and the relative root mean square error.

Last, we investigated the effect of the hypothesis about emissions outside the 1-km radius area. We used a bottom-up approach using Eq. (2) and replaced the N₂O flux $F_{N_2O_i}$ with the previously calculated flux. If 100% of the footprint was within the radius, we will find again the results obtained with the *LU* and the *NCLU* approaches.

4. Statistics

ANOVA and the Newman-Keuls test were used for the fast-box and soil data to test the null hypothesis that the type of crop or land use did not affect soil N₂O emissions.

III. Results

1. N₂O fluxes and fast-box measurements

ANOVA statistical analyses followed by the Neuwman-Keuls test revealed a significant effect of crop/land use on soil N₂O emissions, leading to the following groups: (1) catch crop - pea combination (A), (2) wheat, catch crop - corn combination and rapeseed (AB), (3) forest and winter barley (B) (Table 8).

Crop		Wheat (reference)	Rapeseed	Forest	Barley	Catch crop - corn	Catch crop - pea
Number of measurements	n	15	15	8	2	3	5
N ₂ O fluxes ($\mu\text{g N-N}_2\text{O m}^{-2} \text{h}^{-1}$)	Mean	53.19 ^{AB}	17.07 ^{AB}	5.70 ^B	0.93 ^B	26.05 ^{AB}	94.21 ^A
	Standard error	75.86	21.39	6.88	0.00	9.22	111.42
	min	-2,08	1.78	0.42	0.93	15.95	8,64
	median	16.29	7.99	3.22	0.94	28.19	44.30
	max	295.15	84.60	21.24	0.94	34.01	270.19
α_{lu}	Ratios	1.00	1.00	0.04	0.04	1.00	3.8

Crop		Wheat (reference)	Rapeseed	Forest	Barley	Catch crop - corn	Catch crop - pea
Number of measurements	n	19	20	8	2	3	5
[N-NO ₃ ⁻] (mg kg ⁻¹)	Mean	7.31 ^{AB}	3.88 ^{AB}	2.58 ^B	1.65 ^B	7.59 ^{AB}	4.48 ^A
	Standard error	8.17	3.51	1.10	0.48	1.50	1.78
	min	1.00	0.28	1.31	1.31	5.97	2.02
	median	4.78	2.38	2.67	1.65	7.89	5.45
	max	35.49	11.78	4.64	1.99	8.93	6.00
β_{lu}	Ratios	1.00	1.00	0.18	0.18	1.00	2.11

Table 8: (a) N₂O fluxes measured by manual chambers. The $\langle\alpha_{lu}\rangle$ ratios are the ratios of the flux of the given land use to the flux of the reference crop (wheat). A, AB and B are the different groups determined statistically. (b) Nitrate concentration in each land use type. The $\langle\beta_{lu}\rangle$ ratios are the ratios of the N₂O emission factors of the given land use to the emission factor of the reference crop (wheat). A, AB and B are the different groups determined statistically.

2. Spatial variability of N₂O emissions defined by the attribution methods

2.1. Definition of the NO₃⁻ function

The observations of a significant effect of the type of crop/land use and soil NO₃⁻ content on soil N₂O emissions support our assumptions underlying the *LU* and *NCLU* approaches. The α_{lu} and β_{lu} ratios were calculated for the three groups defined from the Newman-Keuls test (Table 8). The NO₃⁻ content was estimated for each plot from the equation obtained from the slope of NO₃⁻ consumption derived from the soil NO₃⁻ measurements (Fig. 38).

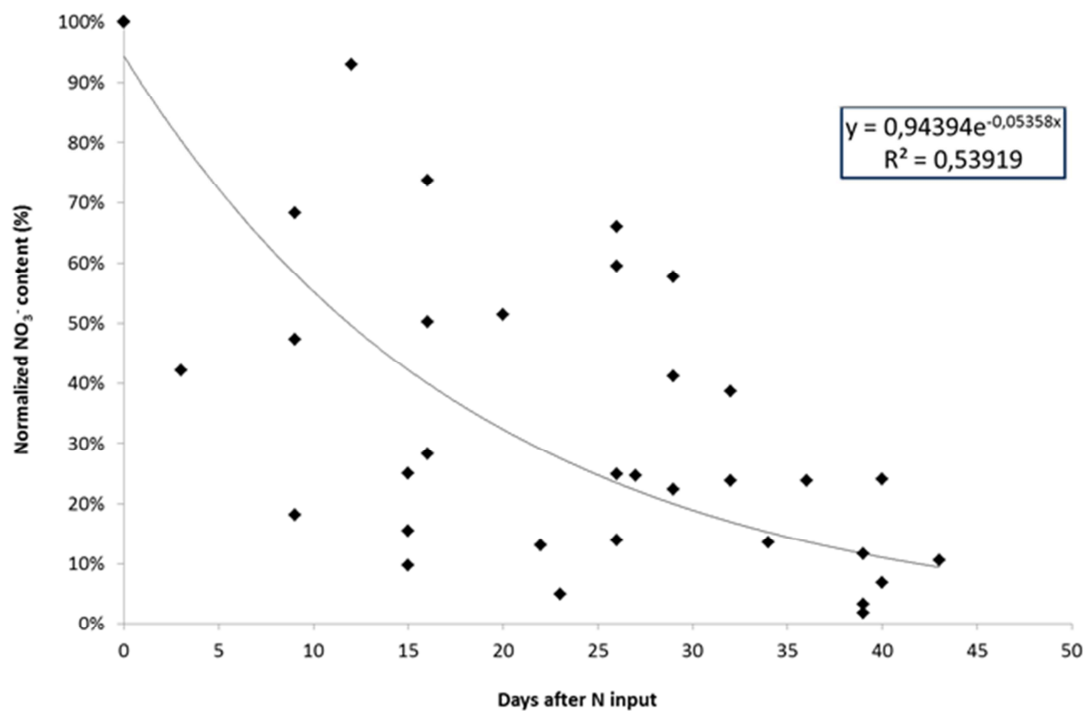


Figure 38: Soil nitrate content (0-20 cm depth) for all sampling date as a function of time following fertilization. The content is normalized by the nitrate content on the day of fertilization. The equation and the line show the function used to account for nitrate consumption over time.

2.2. Evaluation of the attribution methods

The performance of the attribution methods was tested at the plot scale using the data collected by the automatic chambers. The simulations obtained via the *LU* attribution methods were fairly consistent with the automatic chamber dynamics (Fig. 39), except for the first high pulse. However the values are always the same order of magnitude, and the mean values over the whole period were almost identical. However, for the *NCLU* attribution methods, the model over-estimated the fluxes on this plot, with high emission pulses throughout the campaign (Fig. 39). The mean values on this plot and the total N₂O emitted during the campaign were calculated for each method (Table 9). The *LU* values were almost the same as those measured by the automatic chambers, while the values were higher for the *NCLU* approach. Nevertheless, the best model precision was obtained with the *NCLU* method combined to the K&M footprint model ($R^2=0.50$). The RMSE is of the same order of magnitude than the mean flux for both approaches. The rRMSE ranged from 0.63 to 0.77.

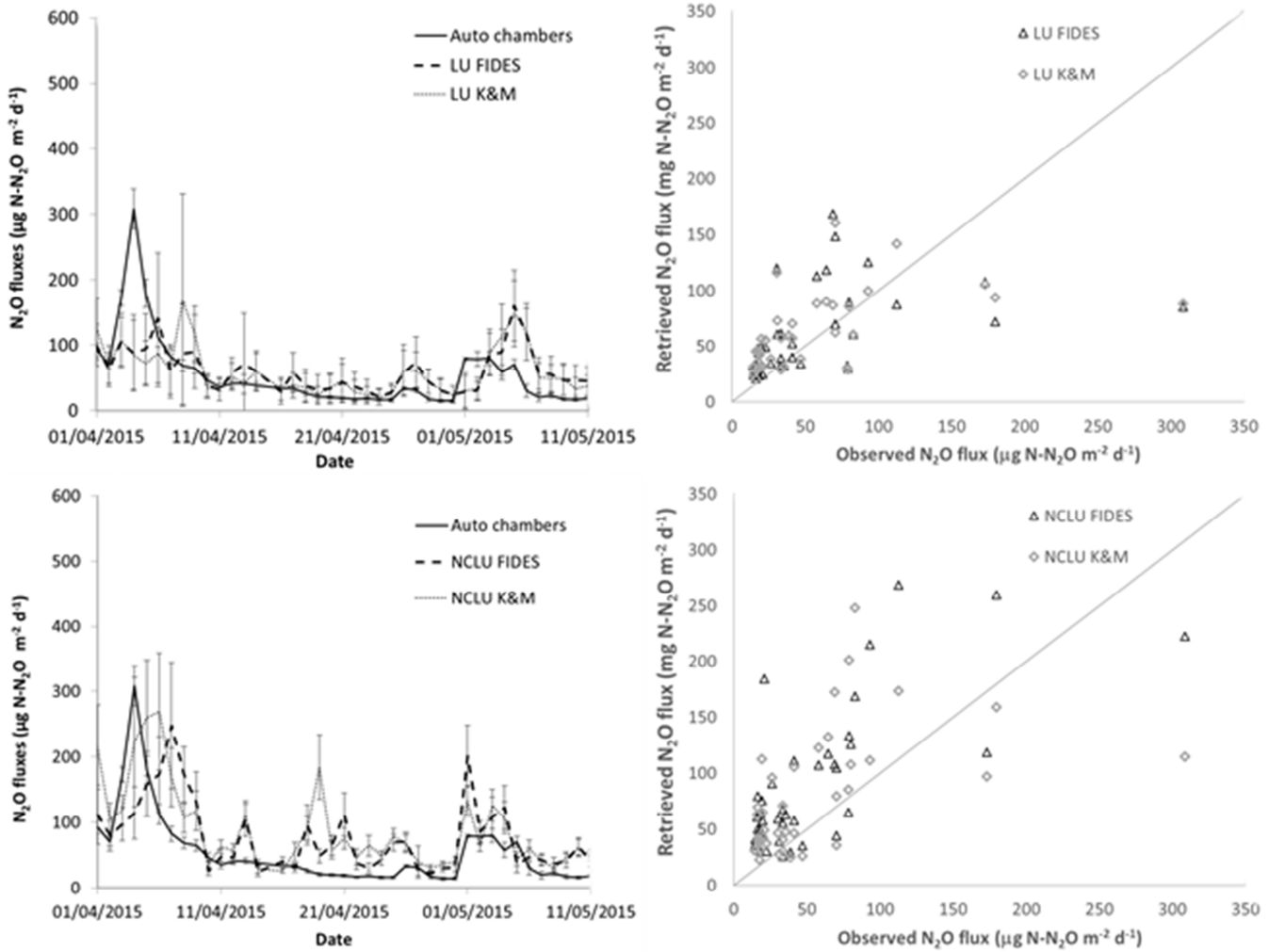


Figure 39: Comparison of the daily averaged N₂O flux ($\mu\text{g N-N}_2\text{O m}^{-2} \text{d}^{-1}$) estimated on the wheat field where the automatic chambers were placed, and the FIDES and K&M footprint models coupled with the *LU* and *NCLU* attribution approaches.

	Auto chambers	<i>LU</i> attribution method		<i>NCLU</i> attribution method	
		K&M	FIDES	K&M	FIDES
R ²	-	0.19	0.26	0.50	0.25
RMSE ($\mu\text{g m}^{-2} \text{h}^{-1}$)	-	52.6	49.1	58.3	59.5
rRMSE	-	0.67	0.63	0.74	0.77
Mean flux ($\mu\text{g m}^{-2} \text{h}^{-1}$)	54.4 \pm 6.2	59.9 \pm 30.3	61.7 \pm 33.8	89.8 \pm 22.5	77.4 \pm 21.6
Total N ₂ O emitted (kg)	4.7 \pm 0.5	5.2 \pm 2.6	5.3 \pm 2.9	7.8 \pm 1.9	6.7 \pm 1.9

Table 9: Comparison of the N₂O flux measured by the automatic chambers and the *LU* and *NCLU* attribution methods on the wheat field where the automatic chambers were installed throughout the campaign.

2.3. Spatial variability of N₂O emissions

The apparent N₂O emissions recorded by the EC system amounted to 0.31 kg N-N₂O ha⁻¹ month⁻¹ throughout the experimental period, and total emissions were estimated at 0.30 and 0.29 kg N-N₂O ha⁻¹ month⁻¹ using the *LU* flux attribution approach combined with FIDES and K&M, respectively, and 0.39 and 0.44 N-N₂O kg ha⁻¹ month⁻¹ using the *NCLU* flux attribution approach combined with FIDES and K&M, respectively. The N₂O emissions estimated using the attribution methods at the landscape scale were consistently higher for the

NCLU approach than those calculated from the results obtained by the EC system alone, which partially cover the total area of 1-km radius. On the other hand, the *LU* approach produces very similar results (Table 10).

The bottom-up approach results gave total emissions of 0.18, 0.19, 0.23 and 0.29 kg ha⁻¹ month⁻¹ N for *LU* + FIDES, *LU* + KM, *NCLU* + FIDES and *NCLU* + KM respectively, corresponding to 58% to 65% of the fluxes calculated using the *LU* and *NCLU* flux attribution approaches. Therefore, 58% to 65% of the N₂O fluxes were from the 1-km radius area.

The emission maps of the entire landscape, estimated from the *LU* and *NCLU* flux attribution techniques combined with the footprint models, show a clear pattern with crop cultivations as the main driver of N₂O emissions (Fig. 40). The catch crop - pea and corn combinations, wheat, and rapeseed fields dominated the emissions, while very low emissions were attributed to forests, winter barley and fallow fields. Correlation tests showed that the 2 flux attribution approaches were correlated (Table 11).

	Top-down				
	EC system	<i>LU</i> + FIDES	<i>LU</i> + K&M	<i>NCLU</i> + FIDES	<i>NCLU</i> + K&M
Mean flux ($\mu\text{g N-N}_2\text{O m}^{-2} \text{h}^{-1}$)	42.7	41.3	40.1	53.9	59.8
Mean N ₂ O flux ($\text{kg ha}^{-1} \text{month}^{-1}$)	0.31	0.30	0.29	0.39	0.44
Total N ₂ O emitted during the campaign (kg)	193.6	187.3	182.0	244.4	271.1
	Bottom-up				
	EC system	<i>LU</i> + FIDES	<i>LU</i> + K&M	<i>NCLU</i> + FIDES	<i>NCLU</i> + K&M
Mean N ₂ O flux ($\mu\text{g N-N}_2\text{O m}^{-2} \text{h}^{-1}$)	42.7	25.2	26.5	31.7	39.2
Mean N ₂ O flux ($\text{kg ha}^{-1} \text{month}^{-1}$)	0.31	0.18	0.19	0.23	0.29
Total N ₂ O emitted during the campaign (kg)	193.6	114.3	120.1	143.9	177.7

Table 10: Comparison of the N₂O flux measured by the EC system throughout the campaign with the N₂O flux calculated at the mast location using both top-down and bottom-up methods, with the *LU* and *NCLU* attribution methods using either the FIDES or Kormann and Meixner (K&M) footprint models over a 1-km radius area.

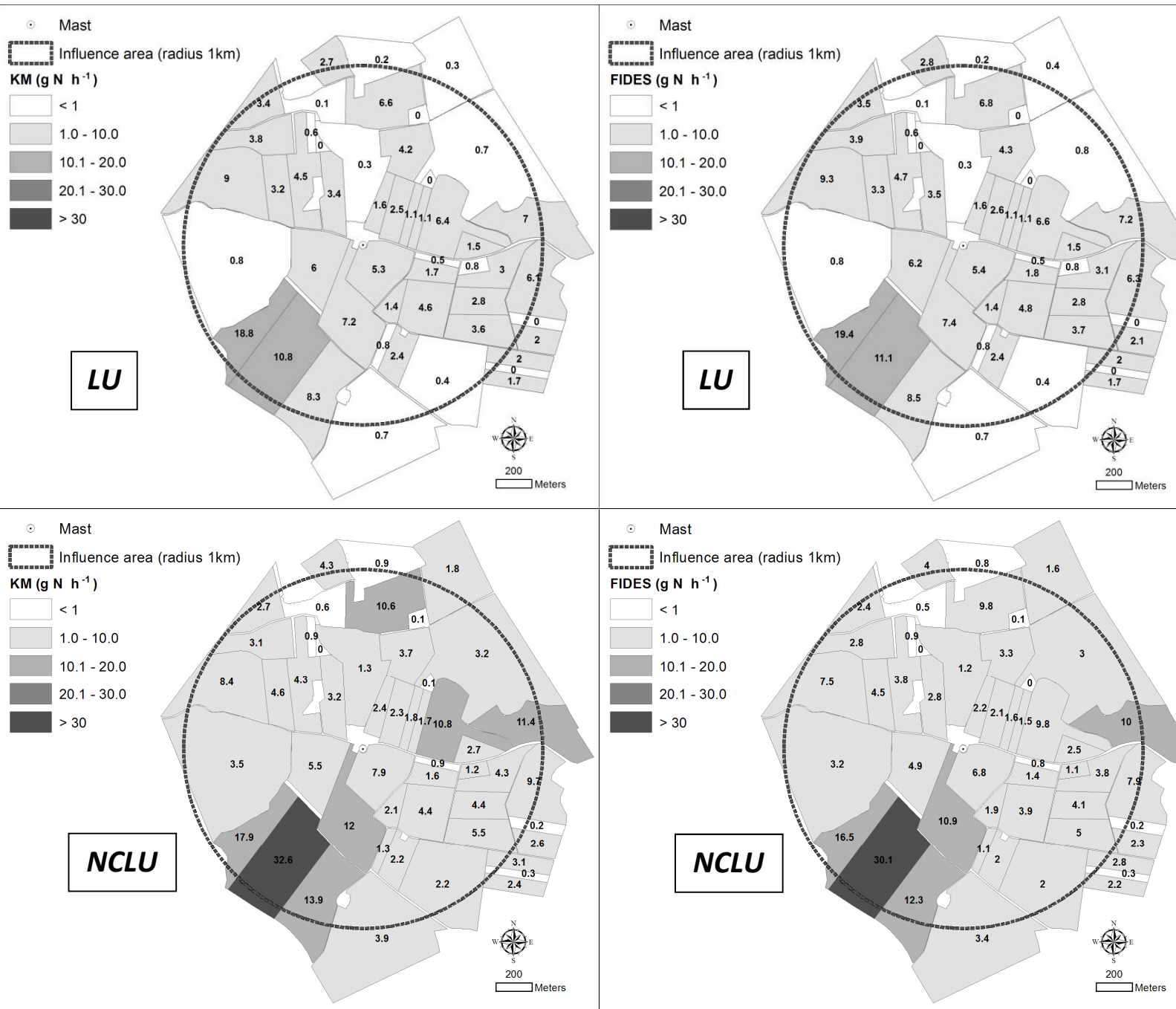


Figure 40: Averaged N₂O emission maps (g N-N₂O h⁻¹) over the whole campaign using the LU and NCLU flux attribution approach. The LU method assumes equal N₂O for each land use, whereas the NCLU method assumes an equal emission factor for each land use. The 2 methods are constrained by the eddy covariance method.

Variables	<i>LU</i> + FIDES	<i>LU</i> + K&M	<i>NCLU</i> + FIDES	<i>NCLU</i> + K&M
<i>LU</i> + FIDES	1	1,000	0,831	0,835
<i>LU</i> + K&M	1,000	1	0,831	0,835
<i>NCLU</i> + FIDES	0,831	0,831	1	0,999
<i>NCLU</i> + K&M	0,835	0,835	0,999	1

Table 11: Correlation matrix of N₂O emissions calculated over the whole area using the flux attribution methods.

IV. Discussion

1. Methods to assess the spatial variability

The main novelty of this study is the definition of different methods for estimating and mapping soil N₂O emissions at the landscape scale from a single temporal N₂O emission dynamics measured by an EC system. Combinations of different measurement methods to estimate N₂O emissions have been deployed previously, including chambers and EC measurements in combination with both top-down and bottom-up approaches using the use of footprint models (Griffis et al. 2013; Molodovskaya et al. 2011). None of these studies used measurements at this spatial scale with a 15-m mast or considered continuous observations over a 2-month period. The results obtained with the top-down approach resulted in N₂O emissions in the same range of magnitude as the N₂O emissions measured by the EC system. Both methods and both footprints models resulted in similar model precision and accuracy

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when comparing to the flux dynamics observed with automatic chambers in one field (Table 9). The best precision was obtained with the K&M model and the *NCLU* approach ($R^2=0.50$) probably because the first pulse is better reproduced with this approach; however, considering the mean flux over the campaign in this field, the *LU* flux attribution approach produced results closer to the measured results than those of the *NCLU* approach. This can probably be explained by the pulse at mid-April simulated by the *NCLU* approach when no pulse was actually measured. Simulation of N₂O fluxes by more complex models such as semi-empirical ones or crop models often result in moderate R^2 and RMSE on the same order than mean flux or larger (e.g. Gu et al., 2014; Gabrielle et al., 2006). This outlines the present difficulty to obtain good prediction of N₂O fluxes; in this view, the present results are satisfactory and both attribution approaches can be considered as consistent.

Automatic chambers measurements were added to the protocol to propose a validation method for the flux attribution approaches. The results obtained by the *LU* approach were, in term of mean value, closer to the measured values than those obtained with the *NCLU* approach (Fig. 39 and Table 9). Consequently, the addition of the NO₃⁻ function in the *LU* flux attribution approach does not significantly improve the model, probably because the empirical NO₃⁻ function is not sufficiently accurate. Indeed, we supposed that all the added NO₃⁻ was fully available one day after input, although NO₃⁻ is actually consumed by other processes such as plant uptake or leaching, and no consideration was taken about the time of diffusion and the type of input (liquid or solid form). On the other hand, the *NCLU* method was able to predict the absence of emission pulse at the third fertilization (11 May) when denitrification was limited despite large NO₃⁻ content because of soil dryness. This is also the reason why there was no correlation between N₂O emissions and NO₃⁻ on the field with automatic chambers.

2. Integrated fluxes and spatial variability over the 1-km radius area

2.1. Levels of N₂O emissions

The share of N₂O emissions from the N added to the fertilized zones during the fertilization period resulted in direct emission factors between 0.24 and 0.37%. These values are high in relation to the duration of the experiment, and if projected to an entire year, could be higher than the general IPCC N₂O estimation of 1% [0.3-3%] (IPCC 2006). N₂O emission observations in this area, typical of intensive agriculture in France, should therefore be monitored across entire years. The difference may also be due to the period of the experiment because the weeks following spring fertilization generally present the highest emissions, and previous studies have shown that high N₂O pulse emissions occur in April (Grossel *et al.* 2016; Gu *et al.* 2011; Henault *et al.* 1998). The magnitude of the N₂O fluxes reported for the wheat plots in this study are in general agreement with previous work, e.g., Grossel *et al.* (2016) (mean: 71 µg of N-N₂O m⁻² h⁻¹, pulse emissions: 400-800 µg of N-N₂O m⁻² h⁻¹, undrained soils). For drained soil cropped with wheat, lower pulses of N₂O in the range of 0-120 µg of N-N₂O m⁻² h⁻¹ have been observed previously (Gu *et al.* 2011). Another study in France measuring N₂O emissions from wheat and rapeseed plots reported fertilization-induced pulse emissions in the range of 2 to 292 µg N-N₂O m⁻² h⁻¹ in April (Henault *et al.*, 1998).

2.2 Spatial variability of N₂O emissions

The spatial variability predicted by the developed approach is expected to mirror the basic hypotheses about the chosen footprint model and chosen control factors for the attribution method (*LU* or *NCLU*). The 2 emission maps generated by the *LU* model are similar in terms of quantity and spatial distribution. The same observation is valid for the *NCLU* model. Hence, it does not matter whether the K&M or FIDES footprint model is used.

On the other hand, the use of *LU* and *NCLU* led to different results on total emission, with the *LU* model producing results similar to the direct measurements by EC and slightly larger results by the *NCLU* model (Table 10). In the *LU* method, the area covered by wheat/rapeseed (53% of the total area) emitted 72% of the total emissions; the forest/winter barley (40% of the total area) emitted 2% and the catch crop – pea/corn (7% of the total area) emitted 26%.

2.3. Uncertainties of the methods and perspectives

The quality and uncertainty of the emission map obtained depend on the design and schedule of the measurements with the fast-box system, although they are fairly small overall. For example, N₂O emissions by winter barley crops (representing 16% of the surface) were probably underestimated in the proposed emission map because N₂O emissions were measured only twice for this type of crop and only during the second part of the experiment when N₂O emissions were generally low. As fast-box measurements are labor consuming and depend on physical accessibility, a trade-off has to be defined between commitment and emission map quality before each measurement campaign. Nevertheless, the range of uncertainties obtained by our simulations remains low compared to the range of uncertainties obtained by applying the IPCC method: the confidence interval on the emission factor covers one order of magnitude (see previous paragraph), whereas the uncertainty calculated here on the predictions represents approximately 50% of the total emissions and the difference between the proposed attribution methods for the total emissions of the area is approximately a factor 2. Thus, the *LU* and *NCLU* attribution methods may be interesting tools to improve the quantification of N₂O emissions by a mixed crop/forest area while attributing the contribution of each land area.

The proposed flux attribution methods are based on the known effect of soil crop/land use and NO₃⁻ content on soil N₂O emission. The methods proposed here are intended to be

generic and should be tested in different areas over longer periods of time. Our hypothesis of controlling N₂O emission by soil crop/land use and soil NO₃⁻ content was statistically validated. Our results with the *NCLU* method indicate that the relationship between soil NO₃⁻ contents and N₂O fluxes should be revisited, with an experimental campaign developed until the harvest. Including longer periods may enable to determine a temporal variability of the parameters α and β (i.e. different crop dynamics in response to climatic conditions). The *NCLU* model may be improved by keeping an empirical response of soil NO₃⁻ (without representing the underlying processes of consumption) considering different functions for different crops, different fertilizer types and different plant stages. More data would be needed for testing this. A better predictor of soil N₂O flux may also be the soil excess total inorganic N rather than NO₃⁻ (Van Groenigen et al. 2010). Last, a more generic approach could be developed by improving the *LU* and *NCLU* flux attribution approaches using mechanistic models (e.g. Landscape-DNDC (Haas et al. 2013) or CERES-NOE (Gabrielle et al. 2006)) or based on the soil water and soil temperature dynamics and a mechanistic modeling of the NO₃⁻ dynamics, i.e. with consideration of the underlying processes of consumption, rather than the simple empirical function used in this study. Nevertheless the present objective was to provide a first approach based on simple empirical functions. Moreover, even with full crop or ecosystems models, it is still challenging to predict the dynamics of NO₃⁻ consumption in the upper soil layer (e.g. a case study with DNDC in Gu et al., 2014 and with CERES-EGC in Gabrielle et al., 2006, in the same region of France).

This campaign lasted only 2 months. Without measurements covering an entire year, our results cannot be scaled to annual flux, even though the likely key period of high N₂O emissions associated with fertilization was assessed. In view of present results, future campaigns may benefit of a more frequent fast-box sampling to help refining the α or β parameters. Such an approach could be applied in different situations, with an adaptation of

Chapter 5: Development of flux attribution methods for mapping N₂O emissions by agricultural soils factors to local conditions and scales. Application on other sites would probably need an assessment of local factors controlling the spatial variability of N₂O emissions. For example, in the case of hydromorphous areas in footslopes, we suggest to introduce simulation units based on both elevation and fields, using a digital elevation model.

The application of flux attribution method is becoming more feasible as the employed instrumentation is becoming more common, with prices expected to drop in the future (Eugster and Merbold 2015). As EC systems for monitoring N₂O emissions are becoming an integral part of the ICOS network (Integrated Carbon Observation System), which aims at quantify greenhouse gas fluxes over longer time periods for various ecosystem types, the developed approach for flux attribution is likely to become interesting for other groups.

V. Conclusion

During this study, 2 flux attribution methods were proposed to determine the spatial and temporal variability of N₂O emissions, one based on land use (*LU*) and the other based on both land use and NO₃⁻ content (*NCLU*). This study has demonstrated the capability of the proposed flux attribution method to determine both the spatial and temporal variability of the N₂O flux over a 1-km radius landscape. Some encouraging results were obtained: taking into account the fertilization with *NCLU* approach resulted in a better simulation of flux dynamics with the K&M model, but also over-estimated mean flux compared to the automatic chambers. On the other hand, the *LU* method showed close agreement with the results obtained by the automatic chamber method (10% difference on the mean flux). Therefore these method were applied on the whole site resulting in original maps of N₂O emissions at the landscape scale. Our results suggest that prior to the use of the fast-box method for flux

Chapter 5: Development of flux attribution methods for mapping N₂O emissions by agricultural soils monitoring, the spatial variability of the N₂O flux should be evaluated carefully. This would enable targeting measuring points that are representative of a wider area.

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Conclusions et Perspectives

I. Conclusions

1. Objectifs

Le changement climatique et la destruction de la couche d'ozone stratosphérique sont actuellement 2 des problèmes écologiques majeurs le plus fréquemment discutés. L'augmentation de la concentration des gaz à effet de serre dans la stratosphère en est la principale cause (IPCC 2014). Parmi ces gaz, le N_2O est particulièrement important car il est le 3^{ème} gaz responsable du réchauffement climatique et le 1^{er} gaz responsable de la destruction de la couche d'ozone. L'agriculture est la principale source anthropique des émissions de N_2O , dû à l'utilisation de fertilisants azotés. Au cours des dernières décennies, de nombreuses études ont tenté de déterminer quantitativement et avec une précision croissante, les différentes sources de N_2O . Les fortes incertitudes liées aux sources d'émissions, font que le N_2O reste un problème actuel.

Les objectifs de notre travail étaient (i) de progresser sur le déterminisme des émissions de N_2O et d'améliorer les outils de quantification indirecte par les modèles, avec un travail spécifique sur l'effet de la variation de température sur les émissions de N_2O , pour être intégré dans les modèles, (ii) de progresser sur la réalisation de mesures directes à l'échelle de la parcelle et du paysage, avec l'application de techniques de mesures intégratives dans le temps et le développement d'un dispositif de mesures intégratives dans le temps et l'espace, et, (iii) de progresser dans l'attribution des sources des émissions de N_2O , par le développement d'approches d'attribution de flux à partir des données collectées pendant la campagne de mesures.

Pour atteindre nos objectifs, une expérimentation en laboratoire a été réalisée sur l'effet de la variation journalière de température sur les émissions de N₂O. De plus, une campagne de mesure sur le terrain a eu lieu au printemps 2015, avec différentes techniques de mesures, à l'échelle de la parcelle et du paysage, pour mesurer les émissions de N₂O, et pour développer 2 méthodes d'attribution de flux à l'échelle du paysage. Nous avons également essayé de répondre aux questions scientifiques soulevées par cette thèse.

2. Effet de la variation de température sur les émissions de N₂O

Plusieurs questions scientifiques ont été soulevées sur l'effet de la variation de température sur les émissions de N₂O:

- Est-ce que les émissions de N₂O sont plus fortes lorsque la température augmente au cours du temps ?
- Qu'en est-il de la régulation par la température du processus de dénitrification et plus particulièrement du processus de réduction du N₂O ?
- Est-ce que les modèles prennent correctement en compte l'effet de la température ?

L'étude expérimentale a été conduite pour évaluer l'effet des variations journalières de température sur les émissions de N₂O par les sols. Les émissions totales de N₂O et la dénitrification ont été étudiées. Les résultats montraient que la température affectait les processus impliqués dans les émissions de N₂O par les sols cultivés en condition anaérobie. La dénitrification et la réduction du N₂O étaient plus élevées à 16°C qu'à 4°C et à 4-16°C mais, plus étonnamment, pas les émissions de N₂O. En comparaison avec la minéralisation du CO₂, cette étude révèle le contrôle très complexe des émissions de N₂O par la température avec des réponses différentes pour les processus de production et de réduction, qui varient également avec la température. Les incubations faites à une température changeante, plus en

adéquation avec les conditions de terrain, suggèrent qu'une paramétrisation dynamique des modèles doit être étudiée pour mieux prendre en compte l'effet de la température.

3. Mesures des émissions de N₂O à l'échelle de la parcelle et du paysage avec 3 méthodes différentes

Plusieurs questions scientifiques ont été soulevées sur la campagne de mesures des émissions de N₂O:

- Est-ce que les mesures faites à partir de 3 méthodes différentes et à différentes échelles peuvent fournir des valeurs comparables ?
- Est-ce que la variabilité spatio-temporelle peut être totalement couverte ?
- Quel type de culture émet le plus de N₂O ?

Les objectifs de cette campagne étaient d'évaluer les flux de N₂O à l'échelle du paysage en combinant les résultats des mesures réalisées à différentes échelles. De par leurs fréquences et leurs propres caractéristiques, ces méthodes ont fourni différentes informations sur les flux de N₂O and sur leurs variabilités spatio-temporelles. Par conséquent, ce fut intéressant de pouvoir utiliser ces méthodes ensemble et de comparer les résultats. Les résultats ont montré que les différentes techniques mesurant à différentes échelles pouvaient être utilisées simultanément pour mesurer les flux de N₂O et que ces valeurs obtenues étaient comparables lorsque les mesures étaient faites en même temps. Les résultats ont montré un bon accord en termes d'amplitude et de dynamiques temporelles. Le système EC et les chambres automatiques fonctionnaient en permanence, couvrant la variabilité temporelle du site. Cependant, les chambres automatiques couvraient seulement la variabilité temporelle d'un champ de blé, et le système EC d'une surface qui dépendait de la force et de la direction du vent. La variabilité spatiale a été couverte par les mesures fast-box réalisées sur 16 sites

différents. Cependant, en comparant ces résultats avec ceux du système EC, on a remarqué que la variabilité spatiale n'a pas été parfaitement couverte. Pendant cette campagne de 2 mois, la parcelle piège à nitrates – pois et piège à nitrates – maïs ont été les cultures les plus émettrices de N₂O. Ensuite vint les parcelles de blé et de colza, et enfin les forêts avec les plus faibles flux de N₂O émis.

Les flux de N₂O, mesurés par les chambres automatiques et la fast-box, étaient positivement corrélés à l'humidité du sol ($p < 0.01$), la teneur en eau ($p < 0.01$), et la teneur du sol en nitrate ($p < 0.05$). Cependant, la température n'est pas apparue comme un facteur de contrôle des émissions de N₂O. A la vue des résultats obtenus lors de l'expérimentation en laboratoire sur l'effet de la température sur les émissions de N₂O, ce n'est pas surprenant car la relation entre émissions de N₂O et température n'était pas linéaire. D'autres études sont nécessaires pour tester la cohérence entre le terrain et cette expérimentation en laboratoire.

4. Développement de méthodes d'attribution de flux pour cartographier les émissions de N₂O par les sols agricoles

Plusieurs questions scientifiques ont été soulevées sur le développement de méthode d'attribution des flux

- Est-ce que les origines des flux de N₂O peuvent être retrouvées à partir de mesures locales et intégratives ?
- Quelle méthode serait la meilleure pour cela et comment estimer sa validité et ses incertitudes ?
- Quelle est la variabilité spatiale des flux de N₂O sur un paysage d'un rayon de 1 km, occupé par un mélange de cultures et de forêts ?

Au cours de cette étude, les données provenant de la campagne de mesures (mesures de fast-box et d'EC) ont été utilisées pour développer 2 méthodes d'attribution de flux pour trouver l'origine des flux de N₂O. Les 2 méthodes d'attribution de flux proposaient de retrouver la variabilité spatiale et temporelle des émissions de N₂O sur un paysage d'un rayon de 1 km, l'une basée sur l'utilisation du sol (*LU*), l'autre basée sur à la fois l'utilisation du sol et de la teneur en NO₃⁻ du sol (*NCLU*). Pour tester la validité de ces méthodes d'attribution de flux, les résultats trouvés pour le champ de blé où étaient placées les chambres automatiques, ont été comparés directement avec les mesures des chambres automatiques. Des résultats encourageants ont été trouvés, notamment pour la méthode LU, montrant un très bon accord avec les mesures obtenues avec les chambres automatiques (10% de différence). Finalement, des cartes originales ont été créées, représentant la variabilité spatiale des flux de N₂O sur un paysage de 1 km de rayon occupé par un mélange de terres cultivées et de forêts.

Cette étude démontre le potentiel de cette méthodologie pour représenter la variabilité spatiale à l'échelle du paysage et pour réduire les incertitudes sur les émissions de N₂O par les sols à l'échelle du paysage. La méthode d'attribution de flux *LU* semble plus adaptée lorsque les pratiques agricoles sont similaires à l'échelle du paysage alors que la méthode *NCLU* semble plus adaptée lorsque les pratiques agricoles sont différentes

5. Conclusions générales

D'un point de vue scientifique, cette recherche appliquée répond à une problématique écologique sur les causes et mécanismes responsables du changement climatique, en apportant des données complémentaires sur les émissions de N₂O sur notre territoire.

Des études ont été développées à différentes échelles, de l'échelle du cylindre pour l'expérimentation sur la température, à l'échelle de la parcelle et du paysage pour la campagne de mesures et la méthode d'attribution des flux. Concernant l'expérimentation en laboratoire, l'originalité de cette expérimentation vient du fait qu'elle a été réalisée avec des températures d'incubations changeantes au cours du temps. Ces conditions étaient en adéquation avec les conditions de terrain et ont été associées avec des conditions plus classiques pour des expérimentations en laboratoire. Cette expérimentation a permis d'obtenir des informations sur le comportement des émissions pendant une augmentation journalière de température. Aucune étude n'avait été menée dans de telles conditions. En ce qui concerne la campagne de mesure et le développement des méthodes d'attribution de flux, la nouveauté a été d'utiliser simultanément 3 types de méthodes de mesures et de les combiner pour créer des cartes originales représentant la variabilité spatiale des flux de N₂O sur une surface de 1 km de rayon, occupée par un mélange de terres cultivées et de forêts.

II. Perspectives

Concernant l'expérimentation sur la température, il serait intéressant de valider ces résultats en refaisant la même expérimentation avec plus d'échantillons, et aussi pendant un temps plus important et ainsi vérifier que les dynamiques observées pendant notre expérimentation se prolongent dans le temps. Pour être encore plus proche des conditions de terrains, la même expérimentation devrait être réalisée, avec cette fois-ci une température qui diminue au cours du temps et qui représenterait la seconde partie de la journée. Ainsi, une dynamique journalière de température serait reproduite entièrement. De plus, cette expérimentation pourrait également être réalisée avec des sols provenant de différents climats.

De plus, cette étude révèle des points d'amélioration dans la modélisation des flux de N₂O. En effet, les modèles prennent l'effet de la température en compte mais cet effet n'évolue pas au cours du temps. Il serait donc intéressant d'appliquer une fonction de température qui varie au cours du temps dans les modèles pour voir si les simulations sont plus proches des mesures réelles. Par ailleurs, nous avons vu que les émissions de N₂O étaient plus importantes pour une température qui augmente au fil du temps que pour une température plus élevée et constante. Cette différence, due à une plus forte réduction du N₂O en N₂ à la température la plus élevée, doit également être prise en compte dans les modèles. Un paramétrage dynamique de la dépendance à la température des différentes étapes enzymatiques pourrait être nécessaire pour les simulations N₂O.

En ce qui concerne la campagne de mesures, les méthodes d'attribution de flux développées à partir des mesures réelles ont montré des résultats encourageants. De nouvelles campagnes de mesures, comme celle présentée dans cette thèse, devraient être réalisées, sur la même période, avec plus de mesures fast-box qui sont les données d'entrée pour les méthodes d'attribution des flux. Plus il y aura de mesures, plus les attributions de flux seront précises et nous verrons alors si ces méthodes peuvent être réellement appliquées. Par ailleurs, avec plus de mesures fast-box et avec une meilleure dispersion des sites de mesures, la variabilité spatiale sera mieux couverte, tout comme les directions du vent et les types de sols et de cultures. Cependant, les mesures de fast-box demandent beaucoup de temps. Elles demandent beaucoup de personnels techniques, du fait des nombreux sites et répétitions, de la combinaison avec la maintenance des 2 systèmes automatiques fonctionnant en même temps, les prélèvements de sols, et le traitement et les analyses en laboratoire des échantillons de sol. Cependant, le protocole que nous avons développé pourrait être appliqué dans des situations différentes, e.g., à travers l'Europe, pour développer des modèles générique d'attribution de flux. Après le développement et la validation des méthodes d'attribution de flux, les réseaux

de mesures de N_2O , qui utilisent déjà des mâts/tours d'eddy covariance, pourraient utiliser ces méthodes pour mieux évaluer les émissions de N_2O dans un écosystème étudié. De plus, ces méthodes pourraient être développées et appliquées pour évaluer les autres émissions de gaz tel que le CH_4 .

Les cultures de pois et de maïs ont été les 2 types de cultures qui ont le plus émis durant la campagne de mesures. Ces 2 cultures suivaient une culture de piège à nitrates cela explique sûrement ces larges flux. Pendant leur période de croissance, les cultures de piège à nitrates avait consommé tout le NO_3^- du sol. Lorsque les pailles ont été enfouies, leur décomposition a probablement entraîné des émissions de N_2O , qu'elles aient été directes ou indirectes. Pour le maïs, un faible apport de fertilisant a été appliqué après le semis, mais rien pour le pois, mais ces 2 cultures ont émis de fortes quantités de N_2O . Les cultures de piège à nitrates doivent être étudiées, tout comme les mécanismes impliqués dans la dégradation des pailles, qui mène visiblement à de fortes émissions de N_2O .

Initialement, nous avions également prévu au cours de cette thèse, de faire tourner les modèles DNDC et CERES-NOE, à partir des données de la campagne de mesures, mais nous n'avons pas eu le temps. Néanmoins, l'ensemble de ces résultats pourra être utilisé pour le développement de modèles de fonctionnement des écosystèmes. Ils vont contribuer à quantifier les émissions de N_2O aux échelles adaptées pour les inventaires et les stratégies d'atténuation.

Conclusions and Overviews

I. Conclusions

1. Objectives

Climatic change and stratospheric ozone layer depletion are currently two of the major ecological problems the most frequently discussed. The increase of the greenhouse gas concentrations in the atmosphere is the main cause (IPCC 2014). Amongst these gases, N₂O is particularly important because it is the 3rd gas responsible for the global warming and now the 1st gas responsible for the stratospheric ozone depletion. Agriculture is the main anthropogenic source of N₂O emissions, due to the use of N fertilizers. Over the last decades, various studies have attempted to determine quantitatively and with increasing precision the different sources of N₂O. The high uncertainties linked to the sources of emissions make that the N₂O concern remains a current problem.

The objectives of our work were (i) to progress on the determinism of N₂O emissions and to improve indirect quantification tools with modeling with a specific work about the effect of a varying temperature on N₂O emissions to be integrated in models, (ii) to progress on the realization of direct measurements at the plot and landscape scale with the application of integrative measurement techniques over time and the development of integrative measurement layout in time and space and (iii) to progress on the source attributions of N₂O emissions with the development of flux attribution approaches from data collected during a measurement campaign.

To do so, a laboratory experiment has been carried out on the effect of daily temperature variations on N₂O emissions. Furthermore, a measurement campaign on the field has taken place in spring 2015, using different measurement techniques at both the plot and landscape scale, to measure N₂O emissions, and to develop flux attribution methods at the landscape scale. Furthermore, we tried to answer to several scientific questions raised.

2. Effect of the temperature variations on N₂O emissions

Several scientific questions were raised about the effect of temperature variations on N₂O emissions:

- Are N₂O emissions higher when temperature increases over time?
- What about denitrification and N₂O reduction processes?
- Do N₂O emission models correctly take into account the effect of temperature?

The experimental study was conducted to assess the effect of daily temperature variations on N₂O emissions by soils. Both total N₂O emissions and denitrification were studied. Results showed that the temperature affected processes involved in N₂O emissions by arable soils in anaerobic conditions. Both denitrification and N₂O reduction were higher at 16°C than at 4°C and 4-16°C, but surprisingly not N₂O emissions. In comparison with CO₂ mineralization, this study reveals the very complex control of N₂O emission by temperature with different responses for the production and reduction processes, also varying over time. Incubations made at changing temperature, relevant to field conditions, suggest that a dynamic parametrization of models need to be investigated to better take into account the effect of temperature.

3. N₂O emission measurements at the plot and landscape scale, using 3 different methods

Several scientific questions were raised about the measurement campaign:

- Can measurements made with 3 different methods and at different scale provide comparable values?
- Can the spatial and temporal variability be totally covered?
- Which type of crop emitted the most N₂O?

The objectives of this study were to assess N₂O fluxes at the landscape scale by coupling results of measurements performed at different scales. Due to their frequencies and their specific characteristics, these methods provided different information on N₂O fluxes and their spatial and temporal variability. It was therefore very interesting to be able to use these methods together and then to cross-check the results. Results showed that the different techniques measuring at different scale could be used simultaneously to measure N₂O fluxes and that values obtained were comparable when running at the same time. Results showed good agreement in magnitude and temporal dynamics. Both the EC system and the automatic chambers were running continuously, covering the temporal variability of the site. However the automatic chambers covered only the temporal variability of a wheat field, and the EC system of an area depending of the wind direction and strength. The spatial variability was covered by the fast-box with measurements made on 16 different sites. However, when comparing both results from the fast-box and the EC mast, the spatial variability does not seem to have been perfectly covered. During the 2-month campaign, the catch crop-pea and the catch crop-corn fields were the crops emitted the highest amount of N₂O. Then came the wheat and rapeseed fields, and finally the forest with the lowest N₂O emitted.

The N₂O fluxes measured by the automatic chambers and the fast-box were positively correlated with soil humidity ($p < 0.01$), water-filled pore space ($p < 0.01$) and nitrate soil content ($p < 0.05$). However, temperature did not appear as a control factor of N₂O emissions. In view of the results obtained during the laboratory experiment dealing with the effect of soil temperature on N₂O emissions, it is not surprising as the relation between N₂O emissions and temperature was not linear. Further investigations are required to test consistencies between field and this specific laboratory experiment.

4. Development of flux attribution methods for mapping N₂O emissions by agricultural soils

Several scientific questions were raised about the development of a flux attribution method:

- Can the origin of the N₂O fluxes be retrieved from the integrated and local measurements?
- Which method would be the best for that, and how to estimate its validity and its uncertainty?
- What is the spatial variability of the N₂O flux over a 1 km radius landscape occupied by a mix of croplands and forests?

During this study, data from the measurement campaign (fast-box and EC measurements) were used to develop 2 flux attribution methods to find the origin of the N₂O fluxes. The 2 flux attribution methods proposed to retrieve both spatial and temporal variability of N₂O emissions over a 1-km radius landscape, one based on land use (*LU*) and the other one based on both land use and NO₃⁻ content (*NCLU*). To test the validity of these flux attribution methods, results found for the wheat field where were placed the automatic chambers were compared directly with the automatic chamber measurements. Some encouraging results were obtained, especially with the *LU* method, showing a close agreement with the results obtained with the automatic chamber method (10% difference). Finally, original maps were created, showing the spatial variability of the N₂O fluxes over a 1 km radius landscape occupied by a mix of croplands and forests.

This study demonstrates the potential of this methodology to represent spatial variability at the landscape scale and to reduce uncertainties on soil N₂O emission at the landscape scale. The *LU* flux attribution method seems more appropriate when agricultural

practices are similar at the landscape scale while *NCLU* flux attribution method seems more appropriate when differ markedly across the landscape.

5. General conclusions

From a scientific point of view, this applied research study answers to an ecological problematic on causes and mechanisms responsible for the climatic change, by bringing complementary data on N₂O emissions in our territory.

Studies were developed at different scales, from the soil cylinder scale for the temperature experiment, to the plot and landscape scale for the measurement campaign and the flux attribution method. Regarding the temperature experiment, the originality of our experiment was to perform soil incubations at varying temperatures. These conditions were defined to be relevant with field conditions and were associated with more classical conditions for laboratories experiment. This experiment made it possible to obtain information on the behavior of emissions during a daily increase in temperature. No studies have been done on such conditions before. Concerning the measurement campaign and the flux attribution methods, the novelty was to use simultaneously 3 types of measurements methods and to combine them to create original maps, showing the spatial variability of the N₂O fluxes over a 1-km radius landscape occupied by a mix of croplands and forests.

II. Overviews

Concerning the temperature experiment, it would be interesting to validate these results by doing this experiment again with more samples, and also during a longer time to see if dynamics observed during our experiment will continue. To get closer to the real conditions

again, the same experiment with a decreasing temperature, representing the second part of the day should be done. An entire daily temperature dynamic would then be reproduced. Moreover, this experiment could also be realized with soils coming from different climate.

Also, this study reveals points of improvement in the modeling of N₂O flux. Indeed, models take the temperature effect into account but this effect does not evolve over time. It would be interesting to apply a temperature function varying over time on models and see if it fits better with the real measurements. Moreover, we saw that N₂O emissions were higher for an increasing temperature than for a constant higher one. This difference, due to a higher N₂O reduction into N₂ at a higher temperature, should also be taken into account in models. A dynamic parametrization of the temperature dependency of the different enzymatic steps might be required for N₂O simulations.

Regarding the measurement campaign, the flux attribution methods developed from field measurements show encouraging results. New measurement campaigns like this one should be carried out, over the same period with more fast-box measurements which are input data for the flux attribution methods. The higher the number of measurements, the more precise the flux attributions will be and we will see if these methods can really be applied. Moreover, with more fast-box measurements and with a better dispersion of the measurement sites, the spatial variability will be better covered, as well as the wind directions, types of soil and culture. However, fast-box measurements are time-consuming. It needs many people due to the number of repetition and the number of sites, and combined with the maintenance of the 2 automatic systems running at the same time, the soil sampling, and the treatment and analyses in the laboratory of the soil samples. Nevertheless, the protocol we have developed could be applied in different situations, e.g., across Europe, to develop generic flux attribution models. After development and validation of the flux attribution methods, N₂O measurement networks, which already use EC mast/tower, could use these methods to better evaluate N₂O

emissions in the studied ecosystem. Furthermore, these methods could be developed and applied to evaluate other gas emissions such as CH₄.

Pea and corn were the 2 crops which emitted the most N₂O during the campaign, although they were not really developed. These 2 crops followed a catch crop and this probably explains large fluxes. During their growing period, catch crops have consumed all the soil NO₃⁻. When straws were buried, their decomposition probably induced, either directly or indirectly, N₂O emissions. For the corn, a little amount of fertilizer was added after seeding, for pea nothing was added, but both emitted large amount of N₂O. So catch crops need to be investigated as well as the mechanisms involved in the soil straw degradation, which obviously leads to high N₂O emissions.

Initially, we planned to make DNDC and CERES-NOE models run with data from the campaign but we ran out of time. Nevertheless, all these results are now available for developing ecosystem models. Both these ecosystems models and the methodologies hereby proposed for upscaling N₂O emissions will help in soil N₂O emission quantification at large scales, relevant to the inventories and mitigation strategies.

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Jordan BUREAU

Emissions de protoxyde d'azote par les sols agricoles : effet des dynamiques de température; mesures à l'échelle de la parcelle et du paysage

Les sols agricoles sont la principale source du gaz à effet de serre N₂O. Ces émissions sont caractérisées par une variabilité spatiale et temporelle considérable, ce qui rend très difficile leur quantification. L'UR SOLS étudie depuis 2008 les émissions de N₂O dans une zone agricole du Centre de la France. Spécifiquement, nous avons étudié au laboratoire l'effet de la température sur ces émissions et développé une méthode permettant l'estimation des émissions de N₂O à l'échelle du paysage. De façon surprenante, nous avons observé que les émissions de N₂O n'augmentent pas systématiquement avec la température. L'indicateur Q₁₀ est apparu, pour les émissions de N₂O, variable avec le temps. L'utilisation de l'acétylène, inhibiteur de la réduction de N₂O, a révélé que les processus biologiques de production et de consommation de N₂O répondent différemment à la température. Les émissions de N₂O mesurées au champ à l'aide de différentes techniques ont permis d'obtenir des résultats cohérents, avec des moyennes de 43 µg N-N₂O m⁻² h⁻¹ pour la méthode par eddy covariance, 37 µg N-N₂O m⁻² h⁻¹ pour la méthode de fast-box et 71 µg N-N₂O m⁻² h⁻¹ pour la méthode des chambres automatiques sur un blé fertilisé. Des méthodes d'attribution des flux ont été développées pour déterminer de façon exhaustive les variations spatiales et temporelles des émissions de N₂O avec élaboration de cartes originales d'émissions à l'échelle du paysage. L'ensemble de ces résultats pourra être utilisé pour le développement de modèles de fonctionnement des écosystèmes. Ils vont contribuer à quantifier les émissions de N₂O aux échelles adaptées pour les inventaires et les stratégies d'atténuation.

Mots clés : N₂O, sols agricoles, changement d'échelle, effet de la température, chambres, eddy covariance

Nitrous oxide emissions by agricultural soils: effect of temperature dynamics; up-scaling measurements from the plot to the landscape

The greenhouse gas N₂O is mainly emitted by soils. Soil emissions are characterized by considerable spatial and temporal variabilities that make their quantification very difficult. While soil N₂O emissions are studied on an agricultural area in the Central France by the UR SOLS since 2008, we specifically studied in the laboratory the effect of temperature on these emissions and also developed a method for upscaling N₂O emissions from the plot to the landscape scales. Surprisingly, N₂O emissions were observed not to increase with temperature. Q₁₀ values, describing N₂O emission sensitivity to temperature, were observed to change over time. The use of acetylene for inhibiting N₂O reduction has revealed that the biological processes involved in the N₂O production and its consumption respond differently to temperature variations. N₂O fluxes measured in the field using several methods covering different scales of the landscape gave consistent results. The mean measured N₂O fluxes were 43 µg N-N₂O m⁻² h⁻¹ for the eddy covariance mast, 37 µg N-N₂O m⁻² h⁻¹ for the fast-box over a similar area, while it was 71 µg N-N₂O m⁻² h⁻¹ by the automatic chambers over a fertilized wheat field. Flux attribution methods were developed to determine both the spatial and temporal variability of the N₂O flux over a 1-km landscape, resulting in original maps of N₂O emissions at the landscape scale. All these results could be further used for developing ecosystem models. Both these ecosystems models and the methodologies hereby proposed for upscaling N₂O emissions will help in soil N₂O emission quantification at large scales, relevant to the inventories and mitigation strategies.

Key-words : N₂O, agriculture soils, up-scaling, temperature effect, chambers, eddy covariance



INRA UR Science du Sol
2163 avenue de la Pomme de Pin
CS 40001 ARDON
45075 ORLEANS Cedex 2

