N$_2$O emission in maize-crops fertilized with pig slurry, matured pig manure or ammonium nitrate in Brittany

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Abstract

N$_2$O is a potent greenhouse gas and solutions have to be sought to reduce its emission from agriculture. This work evaluates N$_2$O emission from maize-crop (Zea mays) fields submitted to different organic or mineral fertilizers (pig slurry, matured pig manure or ammonium nitrate) in Brittany (France). N$_2$O emission was evaluated along a year in two experimental sites receiving 110 or 180 kg N ha$^{-1}$ as ammonium nitrate or pig slurry and 180 or 132 kg N ha$^{-1}$ as ammonium nitrate or matured pig manure at Champ Noel and Le Rheu experimental plots, respectively. N$_2$O emission was evaluated by interpolation method of periodic fluxes on the field scale and by simulation with NOE algorithm using measured soil characteristics such as N content and gravimetric moisture and other soil biological properties determined in a previous study (potential denitrifying activity, N$_2$O/[N$_2$O+N$_2$] ratio during denitrification) or drawn from literature.

On the whole N$_2$O emissions vary between 0.3 kg N ha$^{-1}$ year$^{-1}$ in an unfertilized plot and 2–4 kg N ha$^{-1}$ year$^{-1}$ under ammonium nitrate fertilization. They were higher under N fertilizer application than without N fertilizer but no significant effect of type of N fertilizer was observed on either site. However, N$_2$O losses immediately after fertilizer application were higher under pig slurry and matured pig manure, while measured and predicted fluxes showed that greater N$_2$O losses occurred from summer to winter under ammonium nitrate application. This could be mainly explained by higher mineral N contents at Le Rheu and higher N$_2$O/(N$_2$O+N$_2$) ratio at both sites. The NOE model predicted higher annual N$_2$O emission and emission factor with ammonium nitrate at Champ Noel only and similar emissions for both treatments at Le Rheu. These results suggest that in this climate and soil context the use of pig slurry or matured pig manure did not have a stimulating impact on N$_2$O emissions in comparison with a plot receiving a mineral fertilization.

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Keywords: Soil; Organic fertilizer; Ammonium nitrate; Denitrification; N$_2$O emission; Simulation

1. Introduction

Since the second part of the last century convincing evidence of a change in agents affecting the global climate system has been accumulated. The tropospheric concentration of nitrous oxide (N$_2$O), a potent greenhouse gas also involved in the catalytic degradation of stratospheric ozone (Cicerone, 1987), has increased since the beginning of the Industrial Era, with a rate of 0.8 ppb year$^{-1}$ during the 1990s (IPCC, 2001). According to a recent inventory, approximately 75% of anthropogenic N$_2$O in Europe is produced by agricultural soils and animal husbandries (Freibauer, 2003).

Nitrous oxide mainly originates from biological processes performed by bacteria through nitrification (the oxidation of ammonia to nitrate) and denitrification (the reduction of nitrate to nitrogen gas, N$_2$) (Hutchinson and Davidson, 1993). Although denitrification is usually considered as the major process leading to N$_2$O production in soils (Stevens and Laughlin, 2001; Venterea and Rolston, 2000; Wolf and Russow, 2000), it is well known that nitrification and denitrification can be coupled in soils particularly when ammonium-containing fertilizers are applied, leading to higher N$_2$O production rates than when the two processes are considered independently (Nielsen and Revsbech, 1998).
Table 1

Texture and chemical soil properties (n = 8) of plots at Champ Noëll in October 2002 and at Le Rheu in March 2003

<table>
<thead>
<tr>
<th>Site</th>
<th>Treatment</th>
<th>Clay (%)</th>
<th>Silt (%)</th>
<th>Total C (g C kg⁻¹)</th>
<th>Total N (g N kg⁻¹)</th>
<th>C/N</th>
<th>pH water</th>
<th>CEC° (cmol+ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Champ Noëll</td>
<td>AN</td>
<td>16</td>
<td>70</td>
<td>9.2 b</td>
<td>1.08 b</td>
<td>8.6 b</td>
<td>6.4 b</td>
<td>6.3 b</td>
</tr>
<tr>
<td></td>
<td>PS</td>
<td>16</td>
<td>70</td>
<td>9.8 a</td>
<td>1.12 a</td>
<td>8.8 a</td>
<td>6.9 a</td>
<td>7.0 a</td>
</tr>
<tr>
<td>Le Rheu</td>
<td>AN</td>
<td>14</td>
<td>67</td>
<td>9.4 b</td>
<td>1.04 b</td>
<td>9.0 a</td>
<td>5.9 b</td>
<td>5.4 b</td>
</tr>
<tr>
<td></td>
<td>PS</td>
<td>16</td>
<td>70</td>
<td>10.8 a</td>
<td>1.18 a</td>
<td>9.1 a</td>
<td>6.6 a</td>
<td>6.8 a</td>
</tr>
<tr>
<td></td>
<td>MPM</td>
<td>15</td>
<td>67</td>
<td>10.8 a</td>
<td>1.18 a</td>
<td>9.1 a</td>
<td>6.6 a</td>
<td>6.8 a</td>
</tr>
</tbody>
</table>

AN: ammonium nitrate; PS: pig slurry; MPM: matured pig manure. Values of the same column are significantly different (P < 0.05) if they have different letters. Values of the two experimental sites were analyzed independently.

° Cationic exchange capacity measured by chloride of cobaltihexamine method.

Fertilizer and manure applications may affect N₂O emission in several ways depending more especially on the type of N source (NO₃⁻, NH₄⁺ or organic N) and the applied amount and composition of C substrates in easily biodegradable or recalcitrant C compounds. Organic and mineral fertilizer applications differ in their overall effects on physical, chemical and biological processes and consequently on nitrification and denitrification (Müller et al., 2003; Paul and Beauchamp, 1989) and on N₂O emission as demonstrated by Velthof et al. (2003) in a laboratory experiment on uncropped soil. However, these studies strongly indicate the need for field experiments to confirm the laboratory results and specific determination of emission factors for different fertilizers/manures in order to ensure more accurate assessment of actual N₂O emissions. In addition, the collection of data from different sites, ecosystems, crops and agricultural practices is still considered necessary to improve the accuracy of N₂O emission inventories (Eichner, 1990; Gabrielle et al., 2006). In the absence of a performant, easy-to-apply method for evaluating N₂O emissions in national inventories the IPCC methodology based on a single emission factor of 1.25% of applied N irrespective of fertilizer type and assuming that the amount of N is the sole factor controlling anthropogenic N₂O emission, remains the current reference method.

From a technical point of view, direct measurements of N₂O emission from soils are expensive, time-consuming and labor intensive because of the high levels of spatial and temporal variability of N₂O fluxes (Ambus and Christensen, 1994; Corre et al., 1996). For these reasons and in order to improve estimates of N₂O emission, many attempts to model N₂O production on a field scale in terms of mathematical functions have been presented in the literature (Conen et al., 2000; Hénault et al., 2005; Li et al., 1992; Müller et al., 1997; Ryan et al., 2004) based on the numerous soil and environmental factors controlling denitrification and nitrification such as soil moisture, soil temperature, ammonium and/or nitrate contents.

Our initial objective was to obtain quantitative data on N₂O emissions from plots fertilized with two types of pig manure or ammonium nitrate. Such a study has never before been carried out in France, and certainly not in Brittany, a region of intensive pig farming where land spreading of pig slurries is common practice. Our aim was to collect N₂O emission data in this climatic context and to verify the extent of differences between such emissions in relation to different fertilizer types. The approach adopted was to (i) monitor the N₂O emission rates over a year and (ii) apply the NOE algorithm (Hénault et al., 2005) to simulate N₂O emission rates from the actual field determinations of N₂O fluxes in order to satisfactorily estimate the annual N₂O emission and subsequently define the emission factors for each fertilizer.

2. Materials and methods

2.1. Experimental site

The study was carried out at two experimental sites near Rennes (France, 48°07' N and 1°40' E) on silt loam soils referenced as Luvisol Redoxisol. Some physico-chemical properties of the plots are presented in Table 1. Measurements on the Champ Noëll site, managed by the Institut National de la Recherche Agronomique, were obtained from two 150 m² plots that had been continuously maize-cropped (Zea mays) and fertilized with ammonium nitrate (AN: 110 kg N-NH₄NO₃ year⁻¹) or pig slurry (PS: 35 m³ ha⁻¹ year⁻¹ on average) since 1993. Agricultural practices, except for fertilization type, were similar for both plots with crop residues remaining on the soil surface over winter until plowing at the beginning of spring. N₂O fluxes were monitored between October 2002 and September 2003. During the sampling period maize was sown on 24 April 2003, ammonium nitrate and pig slurry were applied on 13 May, and a sub-plot in each previously fertilized plot was left unfertilized so that fluxes from an unfertilized soil could be measured from 13 May 2003 to the end of the experiment. The soil was harrowed superficially (10 cm) after application of pig slurry to the soil surface. The average characteristics of the pig slurry were pH: 7.7, density: 1.03 g cm⁻³, total organic C content: 29.6 g kg⁻¹, NH₄+−N and organic-N contents: 3.79 g l⁻¹ and 2.10 g l⁻¹, respectively (C/N = 5). The amount of slurry applied during 2003 accounted for 1088 kg ha⁻¹ of organic C, 105 kg ha⁻¹ of NH₄+−N and 75 kg ha⁻¹ of organic-N.

The Le Rheu site, managed by Arvalis-Institut du Végétal, had also been cropped continuously with maize (Zea mays) and fertilized with either organic or mineral fertilizers or left unfertilized (control plot) since 1996.
Measurements were made on experimental plots (6 m × 10 m) amended either with matured pig manure (MPM: 20 t ha⁻¹ year⁻¹) and starter fertilizer (18 kg N ha⁻¹ year⁻¹ and 46 kg P ha⁻¹ year⁻¹) or ammonium nitrate (AN: 162 kg N ha⁻¹ year⁻¹) and starter fertilizer (18 kg N ha⁻¹ year⁻¹ and 46 kg P ha⁻¹ year⁻¹) and on a control plot receiving starter fertilizer only. The MPM used in 2004 was a 4-month matured product with 20.6% dry matter, 72 kg t⁻¹ organic C, 5.7 kg t⁻¹ N 96% as organic nitrogen, C/N 12.6 and pH 7.8. The N₂O fluxes at Le Rheu were monitored between March 2004 and February 2005. MPM was applied on 1 April 2004 and ammonium nitrate on 4 June. All three plots were plowed, amended with starter fertilizer, and sown at the end of April (between 23rd and 26th). The amount of manure applied during 2004 accounted for 1440 kg ha⁻¹ of organic C, 4 kg ha⁻¹ of NH₄⁺-N and 110 kg ha⁻¹ of organic-N. The organic plot then received 132 kg N ha⁻¹, the mineral plot 180 kg N ha⁻¹ for similar crop yields and the control plot 18 kg N ha⁻¹.

At both experimental sites, the ammonium nitrate was in granular form and applied by hand, as was the matured pig manure, whereas the pig slurry was applied with a watering can.

2.2. N₂O flux measurements

N₂O fluxes were measured using the static closed chamber technique (Hutchinson and Livingston, 1993) as described in previous studies (Henault et al., 1998). Cylindrical steel frames (20 cm high and 50 cm diameter) were inserted into the soil to a depth of 8 cm. Eight frames were placed in each plot. The frames remained in the soil and open to the atmosphere between samplings, except when removed for tillage and sowing. During the measurements the frames were covered with gas-tight white lids for 135 min. The atmosphere of the closed chamber was sampled at 0, 45, 90 and 135 min with 3 ml previously purged tubes (Terumo®). N₂O fluxes were calculated from the linear increase of the N₂O concentration in the headspace. Sampling was carried out between 14:00 and 16:00 h, every 2 days for the 2 or 3 weeks following fertilizer application and every 3–4 weeks thereafter. Gas fluxes were measured on 23 different dates at Champ Noël and 24 at Le Rheu.

N₂O concentrations were determined using a Varian® 3400 Cx gas chromatograph (Varian, Walnut Creek, USA) fitted with an ⁶³Ni electron capture detector and an automated sample headspace sampler (HSS 8250 SRA Instruments, Monza, Italy). Daily flux measurements for each treatment were calculated using the arithmetic mean of the eight chambers and are quoted along with standard errors of the mean.

Two approaches were used to calculate the cumulative fluxes. In the first, the annual emissions were estimated by interpolating the fluxes measured over the first weeks following fertilizer application and adding this amount to the quantity estimated for the remaining period as the average daily fluxes times the number of days. In the second approach the daily fluxes simulated from the NOE model were cumulated and completed by emission following immediately manure application and evaluated by interpolation.

2.3. Soil sampling and analysis

Composite soil samples from 10 replicates were taken from 0 to 20 cm depth with a 3-cm diameter auger, at different dates in accordance with the N₂O flux measurements. Total organic nitrogen was determined using the standard method of dry combustion (INRA Laboratory of Soil Analysis, Arras, France). Ammonium content (ammonium, nitrate and nitrite) was measured on three replicates. Fresh soil samples (20 g) were extracted with 100 ml M KCl for 1 h at 20 °C. The extracts were filtered (Whatman n°42), frozen, then subjected to continuous-flow analysis with a Perstorp® analyser, using the Griess–Ilosvay procedure for NO₃⁻ and NO₂⁻ and the blue indophenol method for NH₄⁺ (Keeney and Nelson, 1982).

Gravimetric moisture was determined after 24 h at 105 °C on three replicates. Soil bulk density was evaluated using the core method as previously described (Dambreville et al., 2006b), which permits calculation of the soil water-filled pore space (WFPS) from the soil water content. Soil temperature was measured at 10 cm depth. The means of minimum and maximum daily temperatures were used.

2.4. Use of NOE algorithm for N₂O flux simulation

The NOE algorithm (Hénault et al., 2005) was used to simulate the N₂O fluxes. The model simulates the N₂O fluxes due to nitrification and denitrification and is based on the following biological characteristics of soils: the potential denitrification rate evaluated on undisturbed soil cores (D_p), the fraction of N₂O emitted during denitrification (r_max), the potential nitrification rate defined by two parameters (A and B), and the proportion of N₂O produced per NH₄⁺ nitrified (z). D_p and r_max had been previously evaluated at the Champ Noël site (Dambreville et al., 2006b) and were determined using the same protocol at Le Rheu. For the three other parameters related to nitrification (A, B and z) we used the averages of A and B calculated from Hénault et al. (2005) for five agricultural soils, and a value of 1% for z estimated for a soil with high potential emission by nitrification (Hénault et al., 2005). These parameters are presented in Table 2. The other NOE inputs were soil moisture and nitrogen contents. The STICS model (Brisson et al., 1998) was used to simulate daily gravimetric moisture while the soil nitrate and ammonium contents were extrapolated from measured values using Sigmaplot® software based on the Weibull’s equation (five parameters) to fit our data. The model was used in its initial form without any adjustments to our data except at the Le Rheu site where the water-filled pore space was always lower than 0.70 and generally below 0.62
considered as the threshold for denitrification in this model. Then, at this site, we were brought to establish the threshold of water-filled pore space for denitrification at 0.55 allowing a convenient fit to our measured fluxes.

2.5. Statistical analyses

Statistical analyses were performed with StatView® (SAS Institute Inc.). Average values for the N\textsubscript{2}O emission rates were determined from the individual kinetics of static chambers (eight replicates per treatment). A t-test was applied to compare averages with a significance level of 5%. The arithmetic means and their standard errors are presented in all the tables.

The simulation of gravimetric moisture with the STICS model gave coefficients of determination of 96.8 and 82.8% in all the tables.


ing soil water; \( B \): intercept of nitrification response function to soil water content (Hénauld et al., 2005); \( \varepsilon \): proportion of NH\textsubscript{4}\textsuperscript{+} nitrified as N\textsubscript{2}O (1%); \( r\text{\textsubscript{\text{max}}} \): fraction of denitrified N emitted as N\textsubscript{2}O during denitrification.

Table 2
Soil microbial parameters integrated into NOE (0–20 cm)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>( D_p ) (kg N ha\textsuperscript{-1} day\textsuperscript{-1})</th>
<th>( \varepsilon )</th>
<th>( r\text{\textsubscript{\text{max}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Champ Noël</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AN</td>
<td>5644</td>
<td>0.034</td>
<td>–0.186</td>
</tr>
<tr>
<td>PS</td>
<td>6367</td>
<td>0.034</td>
<td>–0.186</td>
</tr>
<tr>
<td>CT</td>
<td>5644</td>
<td>0.034</td>
<td>–0.186</td>
</tr>
<tr>
<td>Le Rheu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AN</td>
<td>1951</td>
<td>0.034</td>
<td>–0.186</td>
</tr>
<tr>
<td>MPM</td>
<td>2558</td>
<td>0.034</td>
<td>–0.186</td>
</tr>
<tr>
<td>CT</td>
<td>1951</td>
<td>0.034</td>
<td>–0.186</td>
</tr>
</tbody>
</table>

AN: ammonium nitrate; PS: pig slurry; MPM: matured pig manure; CT: control plot; \( D_p \): potential denitrification; \( A \): nitrification rate, depending on soil water; \( B \): intercept of nitrification response function to soil water content (Hénauld et al., 2005); \( \varepsilon \): proportion of NH\textsubscript{4}\textsuperscript{+} nitrified as N\textsubscript{2}O (1%); \( r\text{\textsubscript{\text{max}}} \): fraction of denitrified N emitted as N\textsubscript{2}O during denitrification.

3. Results

3.1. Effect of fertilizer type on soil properties

The soil texture at both experimental sites was similar (Table 1). Applications of pig slurry (PS) and matured pig manure (MPM) for 10 and 7 years at Champ Noël and Le Rheu sites, accounting for 9.3 and 22.4 t C ha\textsuperscript{-1}, respectively, affected the soil properties between 0 and 20 cm depth. At the beginning of our experiment, total C and N were higher (\( P < 0.05 \)) in the PS and MPM plots compared to those fertilized with ammonium nitrate (AN). Microbial biomass was increased by 66% (239 versus 144 mg C kg\textsuperscript{-1} dry soil) under PS (Dambreville et al., 2006b) and 51% (234 versus 154 mg C kg\textsuperscript{-1} ds; results not shown) under MPM fertilization, respectively. The organic amendments also led to higher water pH and cationic exchange capacity (CEC).

3.2. Dynamics of mineral N contents

Soil mineral N content can be a driving parameter of nitrification, denitrification and N\textsubscript{2}O emissions and was monitored throughout the field experiments. The NH\textsubscript{4}\textsuperscript{+} content before the fertilizer applications at Champ Noël and Le Rheu was low (Fig. 1). A few days after the fertilizer application at Champ Noël NH\textsubscript{4}\textsuperscript{+} content peaked at 25 mg N kg\textsuperscript{-1} dry soil under pig slurry and at 15 mg N kg\textsuperscript{-1} ds under ammonium nitrate. This NH\textsubscript{4}\textsuperscript{+} content then declined rapidly and was followed by an increase in NO\textsubscript{3}\textsuperscript{-} content which reached the maximum a few days later under pig slurry. Nitrate and ammonium contents under ammonium nitrate followed the same pattern, attaining the maximum on the same day. The decline in NO\textsubscript{3}\textsuperscript{-} content was longer than that of NH\textsubscript{4}\textsuperscript{+} content under both treatments. By the end of the vegetation period the nitrate and ammonium contents under AN and PS were almost at background level. The mineral N contents under the two treatments were never significantly different (\( P > 0.05 \)).

At Le Rheu, differences in NH\textsubscript{4}\textsuperscript{+} content between MPM and AN were significant (Fig. 1). The NH\textsubscript{4}\textsuperscript{+} content was always lower (<4 mg N kg\textsuperscript{-1} ds) under MPM whereas it increased after AN application to peak at 63 mg N kg\textsuperscript{-1} ds on 1 July. This peak tailed off during the 2 months following AN application. After MPM application, the NO\textsubscript{3}\textsuperscript{-} content increased slowly and reached the maximum (21 mg N kg\textsuperscript{-1} ds) on 18 June. This peak was smaller (\( P < 0.05 \)) than the one under AN which reached 65 mg N kg\textsuperscript{-1} ds on 1 July. The NO\textsubscript{3}\textsuperscript{-} content thereafter declined to background level under both treatments during the maize growth period.

The NH\textsubscript{4}\textsuperscript{+} content in the control was always less than 6 mg N kg\textsuperscript{-1} ds and the NO\textsubscript{3}\textsuperscript{-} content remained below 14 mg N kg\textsuperscript{-1} ds.

3.3. Effect of fertilizer type on measured N\textsubscript{2}O fluxes

The observed N\textsubscript{2}O fluxes did not vary widely over time or between treatments during the year, except for short periods in autumn (Champ Noël) or spring (Le Rheu) (Fig. 2). The N\textsubscript{2}O fluxes were always below 100 g N ha\textsuperscript{-1} day\textsuperscript{-1} on both sites, with a maximum of 66 g N ha\textsuperscript{-1} day\textsuperscript{-1} at Champ Noël under AN treatment and 69 g N ha\textsuperscript{-1} day\textsuperscript{-1} at Le Rheu under MPM treatment. At Champ Noël, the N\textsubscript{2}O fluxes increased (\( P < 0.05 \)) after fertilizer application not immediately but just after a 35 mm rainfall event 5 days after N application. N\textsubscript{2}O losses for 16 days after fertilizer applications were higher (\( P < 0.05 \)) under PS treatment than under AN treatment and cumulative losses attained 81, 27 and 20 g N ha\textsuperscript{-1} under PS, AN fertilization and in the control plot, respectively (Table 3). The maximum flux was not observed directly after this application but in autumn.
(November 2002) under AN treatment: N$_2$O fluxes were higher at three sampling dates in October, November and December, ($P < 0.05$) under AN than under PS (Fig. 2). Moreover, these fluxes were higher than those measured in spring and summer.

The highest fluxes at Le Rheu were observed just after the MPM application (1 April 2004) peaking at 24 h and tailing off over the following days. Another smaller peak was observed on 7 May 2004, after plowing, sowing and starter fertilizer application. From 18 June onwards the N$_2$O fluxes under MPM were not significantly different from those of the control plot, the fluxes always being below 1.5 g N ha$^{-1}$ day$^{-1}$ (Fig. 2). Following the AN fertilizer application (4 June 2004), the N$_2$O fluxes were higher ($P < 0.05$) under AN treatment than under MPM and control treatments until 25 November although the fluxes were always low (<6.5 g N ha$^{-1}$ day$^{-1}$). However, the N$_2$O emissions were much stronger (11×; $P < 0.05$) just after MPM application than after AN application (Table 3).

3.4. Prediction of NOE model

The simulated and measured fluxes at the two sites were approximately within the same range (Fig. 3). The model predicted lower N$_2$O fluxes in average at Le Rheu than at Champ Noël which is in agreement with measured fluxes. At Champ Noël, the model simulates higher fluxes under AN in autumn and winter than under PS, even though there is not a perfect coincidence between simulated and measured fluxes. However, the model was not able to simulate the increase of N$_2$O fluxes after pig slurry or pig manure applications. It predicted the maximum N$_2$O emission at Champ Noël on 9 October 2003, just after rainfall which induced a WFPS increase from 30 to 83% (Fig. 3). This predicted peak was higher under AN than under PS (72 versus 21 g N ha$^{-1}$ day$^{-1}$) and was similarly important in control. The highest N$_2$O losses at Le Rheu occurred in August when the WFPS increased from 20% to fluctuate between 50 and 60%. At this period, fluxes were also higher under AN than under MPM.

3.5. Estimation of the annual emissions

N$_2$O fluxes were measured every 1–3 days following fertilizer applications and every 3–4 weeks thereafter. Three approaches were used to estimate the annual N$_2$O emissions (Table 4). The first estimate was obtained by interpolating the values between sampling dates over 17 and 40 days after fertilizer application and adding this amount to the number of remaining days (348 and 325) times the mean daily fluxes at Champ Noël and Le Rheu, respectively.

This annual emission at Champ Noël appears higher under AN than under PS treatment with respectively 2.17 and 1.03 kg N ha$^{-1}$ year$^{-1}$ (Table 4); however these estimates were not significantly different while the pattern of emission varies over the year. More N$_2$O was emitted under PS after the fertilizer applications ($P < 0.05$) whereas more N$_2$O was emitted under AN treatment ($P < 0.05$).
during the autumn and winter before fertilizer application (Fig. 2 and Table 3). Emissions on the control plot were differentiated with fertilized plots only after the date of fertilizer application: with the mentioned interpolation method emissions on 5 months following this application N$_2$O emissions were 136.5, 120.7 and 88.9 g N ha$^{-1}$ from AN, PS and control plots, respectively.

At Le Rheu, the plots receiving N fertilizers showed higher N$_2$O losses (2.5$\times$, $P < 0.05$) than the control plot.

Table 3
Cumulative N$_2$O emissions from soils for 16 days following the applications of ammonium nitrate (AN), pig slurry (PS) or matured pig manure (MPM) and from the control plots (CT) at Champ Noël and Le Rheu sites ($n = 8$)

<table>
<thead>
<tr>
<th>Period</th>
<th>Treatment</th>
<th>Cumulative N$_2$O emissiona (g N ha$^{-1}$)</th>
<th>Proportion of N applied (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Champ Noël After applications</td>
<td>PS</td>
<td>81 (6) a</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>AN</td>
<td>27 (2) b</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>CT</td>
<td>20 (2) c</td>
<td>–</td>
</tr>
<tr>
<td>Le Rheu* After MPM application</td>
<td>MPM</td>
<td>395 (64) a</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>AN</td>
<td>11 (2) b</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>CT</td>
<td>15 (3) b</td>
<td>–</td>
</tr>
<tr>
<td>After AN application</td>
<td>MPM</td>
<td>36 (2) a</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>AN</td>
<td>35 (3) a</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>CT</td>
<td>18 (2) b</td>
<td>–</td>
</tr>
</tbody>
</table>

* Cumulative N$_2$O emissions are calculated over the 16 days following MPM and AN application separately as the two fertilizers were not applied the same day; values are significantly different ($P < 0.05$) if they have different letters. Values of the two experimental sites were analyzed independently after each fertilizer application.
Table 4. Estimation of N$_2$O emissions for 1 year using different methods and the corresponding emission factors

<table>
<thead>
<tr>
<th>Site</th>
<th>Treatment</th>
<th>Method of calculation</th>
<th>Interpolation$^a$</th>
<th>Modified NOE$^b$</th>
<th>IPCC$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual N$_2$O emission (g N ha$^{-1}$ year$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Champ Noël</td>
<td>AN</td>
<td></td>
<td>2167 (475) a</td>
<td>3750</td>
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<tr>
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<td>CT</td>
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<tr>
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<td>MPM</td>
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<tr>
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<tr>
<td>N$_2$O emission factor (%)</td>
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<td>0.00</td>
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</table>

Numbers in brackets are the standard errors of the emissions (n = 8).

- $^a$ Linear interpolation over the first 17 days for Champ Noël and first 40 days for Le Rheu plus number of days (348 and 325) times mean daily fluxes: values are significantly different ($P < 0.05$) if they have different letters. Values of both experimental sites were analyzed independently.
- $^b$ Modified NOE integrates emissions calculated by interpolation after organic fertilizer application and simulated emissions on the remaining part of the year. N$_2$O emission factor with the NOE method: (emission from the fertilized plot) – (emission from the control plot) divided by (total applied N).
- $^c$ Calculated emissions were obtained by adding anthropic contributions to the natural emissions, such as 1 kg N ha$^{-1}$ + 1.25% of added N according to IPCC method.
- $^d$ We assumed that 1 kg N ha$^{-1}$ was emitted by the unfertilized plot at Champ Noël in accordance with the basic IPCC estimation in unfertilized plots. t-test at $P < 0.05$.

No difference was observed between annual N$_2$O losses under AN and MPM treatments. A large loss of N$_2$O occurred after MPM application whereas more N$_2$O ($P < 0.05$) was emitted under AN from summer to the end of the experiment (Fig. 2) similarly with Champ Noël observations.

As the model was not able to simulate higher fluxes after slurry or manure applications we added emissions after these applications (1 month) calculated by interpolation to the annual emissions predicted by the model. Thus, the cumulative N$_2$O emission estimates increase from 434 and 1318 g N ha$^{-1}$ under MPM and PS, respectively (results non-presented) to 854 and 1399 g N ha$^{-1}$, which is more in agreement with the quantities calculated by interpolation. The NOE model combined with the interpolation method for the period following fertilizer application predicted annual emissions at Le Rheu in very good accordance with the estimates by the interpolation method on the whole year, with similar amounts under AN and MPM treatments (Table 4). The predicted emissions at Champ Noël were higher under AN than under PS treatment, and were lightly higher than estimated ones by the interpolation method. However, an unexpected high emission was predicted for the control plot. The annual emissions evaluated with the emission factor recommended by IPCC, that integrates natural emissions, were higher than the emissions estimated by interpolation and with the NOE model at Le Rheu. Moreover, the IPCC approach, unlike the two other methods, predicted higher N$_2$O losses under the PS treatment at Champ Noël. These losses are the most important under AN treatment at Le Rheu, which received a larger amount of applied N. These annual emissions evaluated by interpolation method or by NOE model application allow evaluating of emission factors taking account of emissions in control plots: at Champ Noël this emission in control plot was estimated at 1 kg N ha$^{-1}$ year$^{-1}$ in accordance with basic IPPC estimation in unfertilized plots. In such conditions, the emission factors are comprised between 0.02 and 1.07% of applied N from results obtained with interpolation method and between –0.63 and 1.10% from NOE simulation. The highest emission factor was observed for the AN treatment at Champ Noël and for the MPM treatment at Le Rheu using both methods.

4. Discussion

As the effect of fertilizers on N$_2$O emission is influenced by climatic conditions and soil characteristics, studies to regulate such emissions need to be performed in many different ecosystems and countries. Most investigations of the effect of different fertilizer types on N$_2$O emission on the field scale have been carried out on grasslands (Clayton et al., 1997; Dobbie and Smith, 2003) and questions remain concerning the effect of this factor on N$_2$O emission in other crops. Thus, our initial aim was to compare the effects of pig slurry, pig manure and ammonium nitrate on N$_2$O emission from a maize-crop, in Brittany, fertilized according to the N requirements based on similar crop-yields.

4.1. Effect of the type of fertilizer on N$_2$O emissions (from measured fluxes)

Firstly, the N$_2$O emission rates were generally low except at the beginning of the measurements in autumn 2002 and just after fertilizer application, especially the organic fertilizers (Fig. 2) during the 2 years of study. These emission rates were within the range reported in previous studies (Clayton et al., 1997; Thornton et al., 1998). However, the emission rates observed in grasslands could attain nearly 5 kg N-N$_2$O ha$^{-1}$ day$^{-1}$ in the days following N fertilizer application in particularly favorable conditions (Ball et al., 2004). The low emission rates in our study could principally be explained by the water-filled pore space being below 45 and 46% at Champ Noël and Le Rheu in late spring and summer when the nitrate and ammonium contents were high and by the low mineral N contents in winter and early spring when the water-filled pore space exceeded 62 and 50% at Champ Noël and Le Rheu. Low WFPS and low
mineral N contents are both known to strongly limit N\textsubscript{2}O fluxes and may each be the main driving factor of emissions at different periods. Thus, Clayton et al. (1997) observed substantial N\textsubscript{2}O emissions only when the WFPS was higher than 65\% and Sehy et al. (2003) measured N\textsubscript{2}O fluxes above 12 g N ha\textsuperscript{-1} day\textsuperscript{-1} when the nitrate contents exceeded 3.5 mg N kg\textsuperscript{-1} dry soil and the WFPS was between 55 and 90\%.

Moreover, this study demonstrates that the pattern of N\textsubscript{2}O emission is affected by fertilizer type: although more N\textsubscript{2}O was emitted just after organic fertilizer application, later N\textsubscript{2}O losses, in the autumn–winter at Champ Noël and during summer and autumn at Le Rheu, were higher in plots fertilized with ammonium nitrate and Fukumoto et al. (2003) measured a high N\textsubscript{2}O emission rate during composting of livestock wastes. On the other hand, N\textsubscript{2}O may originate from hot spots in soils induced by the organic C and N of the manure application when denitrification and nitrification are stimulated (Nielsen and Revsbech, 1994). The denitrification rate was observed to increase exponentially in such hot spots during the first days after liquid manure application could have two origins. First, N\textsubscript{2}O could be produced within the matured manure and remained trapped until release during spreading; thus Monteny et al. (2001) describe favorable conditions for N\textsubscript{2}O production during the aerobic storage as well as land spreading of solid manure and Fukumoto et al. (2003) measured a high N\textsubscript{2}O emission rate during composting of livestock wastes. The on the other hand, N\textsubscript{2}O may originate from hot spots in soils induced by the organic C and N of the manure application when denitrification and nitrification are stimulated (Nielsen and Revsbech, 1994). Also, Paul and Beauchamp (1989) showed that C substrates such as the volatile fatty acids in liquid manure provide a direct C source for denitrifiers. However, the production of N\textsubscript{2}O during anaerobic storage of pig slurry is negligible due to the absence of nitrification (Monteny et al., 2001) which implies that only the second phenomenon would have been involved in N\textsubscript{2}O production with this liquid effluent.

The highest fluxes measured in autumn and winter at Champ Noël (Figs. 2 and 3) were in accordance with a similar emission pattern observed by Gabrielle et al. (2006) and assigned by these authors to the determining effect of residual mineral N content after harvest. The mineral N contents did not differ significantly between fertilizer types at Champ Noël and these different fluxes might be explained by other factors. Several determinants that affect the mechanisms of N\textsubscript{2}O production are modified by the type of fertilizer. Thus, bulk density tends to be higher in AN than in PS treatments (Dambreville et al., 2006b) and may favor denitrification and probably N\textsubscript{2}O emissions. The composition of the denitrifying community differed between soils fertilized with matured pig manure and with ammonium nitrate and could account for the lower amount of N\textsubscript{2}O emitted during denitrification and consequently a lower N\textsubscript{2}O/[N\textsubscript{2}O + N\textsubscript{2}] ratio \(r_{\text{max}}\) in the plot receiving organic fertilizer (Table 2) (Dambreville et al., 2006a,b). At Le Rheu the highest fluxes under AN from summer to winter could be due to the mineral N contents and N\textsubscript{2}O/[N\textsubscript{2}O + N\textsubscript{2}] ratio \(r_{\text{max}}\) which were higher under this treatment. Similarly Dittert et al. (2005) observed a limited N\textsubscript{2}O/N\textsubscript{2} ratio after cattle slurry application compared with mineral N application.

4.2. Simulated fluxes with the NOE model

Our objective was to estimate the annual N\textsubscript{2}O fluxes under different fertilization regimes by (i) measuring the N\textsubscript{2}O fluxes and (ii) using a simulation model, as measuring fluxes is both fastidious and time-consuming. This study confirms that the N\textsubscript{2}O emissions in a given ecosystem may be evaluated and probably forecast with accuracy from a general model such as NOE. However, the model could not predict the response of N\textsubscript{2}O fluxes following application of slurry and manure. But using measurements interpolation on weeks following manure applications combined to prediction of the model on the remaining part of the year allowed a more accurate estimation of annual losses. This lack of prediction of the response of N\textsubscript{2}O fluxes to manure or slurry application is certainly due to N\textsubscript{2}O directly emitted by spread solid manure and the stimulation of denitrification under slurry application what could not be predicted by the model. In fact, NOE model in its present form does not integrate the variation of carbon availability on denitrification but uses a single value of potential denitrification over the year. Moreover, high N\textsubscript{2}O fluxes predicted by the model did not always coincide with high fluxes measured at the fields. This lack of coincidence between measured and estimated fluxes have ever been observed by several authors. Thus, Hénault et al. (2005) mentioned some differences between patterns of simulated and measured N\textsubscript{2}O fluxes but the annual emissions whatever the evaluation method were always in agreement. In our situation the measured and predicted fluxes are in the same magnitude in both sites and the different treatments.

In this study, we reduced of 12\% the threshold of waterfield pore space at which denitrification begins at Le Rheu to improve the success of the NOE model. Such modification could be made for other ecosystems (Sehy et al., 2003; Heinen, 2006) as this threshold is not so precise but depends on climate and soil conditions. In fact, the microbial community from one site to another may respond differently to soil moisture (Bergsma et al., 2002), depending on the environmental and climatic conditions of the site and can support such a modification.

4.3. Evaluation of the annual N\textsubscript{2}O emissions

The annual N\textsubscript{2}O losses estimated both by the rates and percentage of applied N were generally comparable with those reported in other studies (Clayton et al., 1997; Jones et al., 2005; Rochette et al., 2000). Thus, estimations by the interpolation method ranged from 344 g N ha\textsuperscript{-1} for the
control at Le Rheu to 2167 g N ha⁻¹ under ammonium nitrate at Champ Noël. These emissions in fertilized plots are accounting for 0.02–1.07% of the applied N. These values were within the range of the default value of 1.25% (±1%) recommended in the IPCC approach (IPCC, 1997) for three of them, while the value with PS was lower (Table 4). We noted that annual losses were higher under N fertilizer application than without N fertilizer but no effect of type of N fertilizer was observed on either site, suggesting that in this climatic context the use of pig slurry or matured pig manure compared with mineral fertilizer did not have a negative ecological impact due to increased N₂O emissions. Similarly, Jones et al. (2005) did not observe any significant difference between N₂O emissions under cattle slurry or NPK fertilizer in a 2-year study while Ball et al. (2004) reported higher annual N₂O emission under NPK fertilizer than with cattle slurry injected to 5 cm depth. They also observed that N₂O emission was decreased in the following order: NPK fertilizer > cattle slurry = liquid sludge > composted sludge > dried pellets > NPK slow-release fertilizer.

As estimation of the annual N₂O emissions might be affected by the method of assessment, we used several approaches. The cumulative N₂O emission was lower with the interpolation method than with NOE application (2.2 and 3.8 kg N ha⁻¹ year⁻¹, respectively) at Champ Noël but was similar (0.8–0.9 kg N ha⁻¹ year⁻¹) at Le Rheu. These two methods predicted higher N₂O losses under AN than under PS at Champ Noël and similar N₂O losses under AN and MPM treatments at Le Rheu, when N₂O losses estimated by interpolation after manure application were added to that calculated with the model. Unlike the interpolation method the NOE approach takes into account the daily variation in environmental conditions influencing N₂O emission such as water-filled pore space and N contents. Thus, the higher N₂O fluxes at Le Rheu, under AN treatment, were predicted in summer when nitrogen was freely available and rainfall occurred: the field measurements during this period were too interspaced to make such emissions obvious. The unexpected higher emission in the control plot at Champ Noël compared to the slurry treatment had probably two reasons: first, this control was previously a fertilized plot and was differentiated from AN treatment only after fertilizer application in spring, thus mineral N content was probably higher than that in a real control plot unfertilized for several years and induced a similarly overestimated N₂O emission, as suggested by measurements on the last 5 months after N application on fertilized plots; secondly, a significantly lower N₂O/[N₂O + N₂] ratio was observed under the slurry treatment (Table 2). The emission estimates with the IPCC approach gave higher results on the whole and did not allow discrimination of the fertilizer effect on N₂O losses, because it only took N input into consideration and not the type of N. Nor did it consider the variation in climatic conditions from 1 year to another, which is possible with more sensitive models, as demonstrated here. It must also be remembered that annual precipitations may have a stronger effect on annual emission than the amount and type of fertilizer, even though the effect of fertilizer type depends on the annual rainfall pattern (Clayton et al., 1997).

5. Conclusions

The aim of this study was to evaluate the effect of applications of different types of fertilizer on N₂O emissions from maize-crops and more particularly to compare N₂O emissions under mineral and organic fertilizers. On the whole N₂O emissions vary between 0.3 kg N ha⁻¹ year⁻¹ in an unfertilized plot to 2–4 kg N ha⁻¹ year⁻¹ under ammonium nitrate fertilization and were higher under N fertilizer application than without N fertilizer. No significant effect of type of N fertilizer was observed on either site, suggesting that in this climate and soil context the use of pig slurry or matured pig manure did not have a stimulating impact on N₂O emissions. However, field measurements showed that N₂O losses were temporarily greater after organic fertilizer applications, probably due to N₂O trapped in pig solid manure and the stimulation of nitrification and denitrification when pig slurry was applied, while the greatest N₂O losses occurred in plots fertilized with ammonium nitrate in summer, and generally in autumn and winter. This was demonstrated by field measurements and by simulation with the NOE model. This could be explained by the higher proportion of N₂O produced during denitrification (N₂O/[N₂O + N₂] ratio) and the higher residual mineral N contents under ammonium nitrate fertilization. Thus, although the potential denitrifying activity is increased by organic fertilizer applications a positive impact with a reduced N₂O/[N₂O + N₂] ratio and lower nitrogen availability for the same yield apparently produces similar or lower N₂O emission. Finally, the NOE model seems to provide a more sensitive tool than the IPCC method for evaluating annual N₂O emissions, as it takes both climatic conditions and N transformations into consideration.

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References


