Nitrogen oxide emissions from an irrigated maize crop amended with treated pig slurries and composts in a Mediterranean climate

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Abstract

Organic fertilizers may differ greatly in composition and as a result there may also be differences in nitrogen oxides emissions following their application to soils. The aim of this study was to evaluate the influence of mineral and organic N fertilizers on the nitrification and denitrification processes, and consequently on N2O and NO emissions. Therefore, a field experiment was carried out on an irrigated sandy loam soil under Mediterranean conditions during the maize (Zea mays L.) growing season. Untreated pig slurry (UPS) both with and without the nitrification inhibitor dicyandiamide (UPS + DCD), digested thin pig slurry fraction (DTP), composted solid fraction of slurry mixed with urea (CPS + U) and composted municipal solid waste mixed with urea (MSW + U) were applied at a rate of 175 kg available N ha−1. Their emissions were compared with those from urea (U) and a control treatment to which no nitrogen fertilization was administered (Control). Accumulated nitrous oxide losses during the crop season ranged from 6.0 to 9.3 kg N2O-N ha−1 for the Control and CPS + U, respectively, whereas nitric oxide losses ranged from 0.01 to 0.23 kg NO-N ha−1, for the Control and U, respectively. The use of digested slurries mitigated N2O emission by 25% in relation to untreated pig slurry, but NO emissions were similar for both treatments. Dicyandiamide reduced N2O and NO emissions by 64 and 78% with respect to slurry without the inhibitor. An indirect effect of DCD on denitrification was also observed, with a reduction of 32% in denitrification with respect to the slurry without the inhibitor. In this case, the greatest reduction in denitrification losses occurred during the irrigation period. Composts mixed with urea reduced NO emissions by 56% (CPS + U) and 85% (MSW + U) in relation to the urea treatment, but its effect on N2O emission depended on the type of compost involved: CPS + U increased N2O emission by 25%, whereas MSW + U reduced it by 55% in relation to urea. Denitrification was the most important process responsible for N2O emissions when organic fertilizers were applied to the soil, while nitrification was the most important for the inorganic fertilizer. The C:N ratio of fertilizers was a good predictor of their NO emissions, denitrification losses and N2O/N2 ratio. On the other hand, added soluble N was a good predictor for cumulative N2O emissions during the period before irrigation. This work shows that an appropriate selection of organic fertilizers based on their composition could be used to mitigate emissions of the atmospheric pollutants NO and N2O in comparison with urea.

Keywords: Compost; Nitric oxide; Nitrous oxide; Pig slurry; Organic fertilizers

1. Introduction

Nitrous oxide (N2O) and nitric oxide (NO) emissions from soils generally increase with N fertilizer application (Arah et al., 1991). However, fertilizers differ in terms of their N2O and NO emissions suggesting that fertilizer selection could help to reduce emissions of these gasses (Bremmer and Blackmer, 1981; Mosier et al., 1998). Fertilizer and manure type may affect N2O and NO emissions in several ways: (1) the type of N (NO3−, NH4+ or organic N) affects N gas production during nitrification and denitrification; (2) the presence of easily decomposable organic C can both sustain denitrification and induce anaerobic conditions by stimulating biological O2 demand; (3) the addition of other compounds (such as salt...
and water) have effects on biological, chemical and physical soil processes (Velthof et al., 2003).

Land application of untreated livestock manure increases health risks for both animals and people because of the diffusion of pathogens to the soil and air and it also creates unpleasant odours (Burton and Turner, 2003). Composting and anaerobic digestion are treatments which can be used for odour removal and pathogen reduction in manure. These biological processes also change the composition of manure, particularly reducing its content of soluble organic compounds. These changes could have an effect on N\textsubscript{2}O particularly reducing its content of soluble organic nitrogenous compounds after the nitrification and denitrification processes (Velthof et al., 2003).

The application of solid waste composts to soils has also been proposed as a useful source of nitrogen for crops (Diez et al., 2000) and as an amendment for increasing the organic C content of soils containing little organic matter. The labile C content of these materials could promote N immobilization in soils (Azam et al., 1985). It is therefore frequent to add a synthetic N fertilizer to compost in order to increase the availability of N in soils. There is, however, still little available data concerning nitrogen oxide emissions, especially regarding the application of synthetic N to soils accompanied by various other composted wastes (de Wever et al., 2002).

One potentially effective strategy for reducing N\textsubscript{2}O and NO emissions from fertilized fields would be the inhibition of nitrification and denitrification in situations in which these processes could take place at high rates. The nitrification inhibitor dicyandiamide (DCD) has been tested with urea fertilizers (Skiba et al., 1993) and slurries (de Klein et al., 1996; Vallejo et al., 2005) to evaluate its ability to reduce N\textsubscript{2}O and NO emissions. However, DCD is a soluble compound that could be leached under irrigation conditions and this could affect its efficiency. More studies are therefore necessary to establish the best conditions for mitigating the emission of nitrogen gases from soils amended with pig slurry in irrigated crops.

A field experiment was carried out to evaluate the influence of different mineral and organic N fertilizers on N\textsubscript{2}O and NO emissions under irrigation conditions. First, emissions from soils amended with two different composts mixed with urea were quantified. Then, the effects of fertilization with digested thin pig slurry fraction, untreated pig slurry and pig slurry previously mixed with DCD were studied. A mineral fertilizer (in this case urea) and a Control without N fertilizer were included in the experiment for reference.

2. Materials and methods

2.1. Soil characteristics

The field experiment was carried out at “La Poveda” Field Station, in Arganda del Rey. The site is 30 km south-east of Madrid (40°19’N, 3°19’W) and lies in the middle of the Jarama river basin. The soil is a Typic Xerochrept with a sandy loam texture in the upper 0.5 m. Some of the physico-chemical properties of the (0–20 cm) soil were: 14 g total organic matter kg\textsuperscript{-1}; 1.1 g total Kjeldahl N kg\textsuperscript{-1}; pH\textsubscript{H2O} 8.1; 1.47 Mg m\textsuperscript{3} bulk density; 34 g CaCO\textsubscript{3} kg\textsuperscript{-1}; 20.2% (w/w) field capacity; 44.5% porosity; 37% sand, 45% silt; 13% clay. Water soluble organic C was 8.9 mg C kg\textsuperscript{-1} and the NO\textsubscript{3}−-N content was 0.5 mg kg\textsuperscript{-1} at the beginning of the experiment. The mean temperature in this area (for the last 10 years) was 13.5 °C. The mean annual rainfall for the last 10 years was 460 mm.

2.2. Experimental procedure

Twenty-one 40 m\textsuperscript{2} plots were selected and randomly arranged with three replicates per treatment. The treatments were: (i) untreated pig slurry (UPS), (ii) anaerobically digested thin pig slurry fraction (DTP), (iii) pig slurry mixed with dicyandiamide (UPS + DCD), (iv) composted solid fraction of pig slurry plus urea (CPS + U), (v) municipal solid waste plus urea (MSW + U), (vi) urea (U) and (vii) a control without any nitrogen fertilizer. The physico-chemical properties of the different organic fertilizers and the amounts of the different compounds added to the soil together with the organic fertilizers are summarised in Table 1.

The pig manures (UPS, DTP, and CPS) were provided by the pig slurry treatment plant of Almazán (Soria-Spain). The liquid fraction of pig slurry was obtained by the physical separation of slurry using a rotary sieve drum (0.9 mm mesh). This was anaerobically digested in a 50 m\textsuperscript{3} continuous digester with a hydraulic retention time of 32 days. The solid fraction was composted for 3 months and then stored for 9 more months. The treatment with DCD was prepared in situ, mixing the inhibitor with untreated pig slurry in a 100-l tank. The municipal solid waste was collected from the Valdemingomez MSW-plant (Madrid). The material was composted at this plant for 3 months and was then stored in the field for 1 month.

Organic fertilizers were applied on 14 April 2004. The quantities applied were calculated to provide a rate of 175 kg available N ha\textsuperscript{-1}. Total slurry applied was 39.7, 38.8 and 36.3 m\textsuperscript{3} ha\textsuperscript{-1} for UPS, DTP and UPS + DCD, respectively. Available N for CPS and MSW was estimated according to the method described in Sánchez et al. (1997). The percentages for the amounts of organic N mineralised in this soil were 35–37% for CPS and 25–26% for MSW. They were therefore applied at rates of 16.0 Mg ha\textsuperscript{-1} for CPS (250 kg N ha\textsuperscript{-1}) and 28.0 Mg ha\textsuperscript{-1} for MSW (250 kg N ha\textsuperscript{-1}). Urea (50 kg N ha\textsuperscript{-1}) was also applied in combination with both the MSW and CPS.

Liquid manures were applied to the soil using a hosepipe connected to a 100l tank, in order to distribute them uniformly. CPS and MSW were also applied at the surface. Following application, the fertilizers were incorporated into the upper layer of the soil (0–5 cm) with a rotocultivator.
Table 1
Chemical composition of organic fertilizers and amount of different compounds added with fertilizers

<table>
<thead>
<tr>
<th>Property</th>
<th>UPS Composition (g kg⁻¹)</th>
<th>Added (g m⁻²)</th>
<th>DTP Composition (g kg⁻¹)</th>
<th>Added (g m⁻²)</th>
<th>CPS Composition (g kg⁻¹)</th>
<th>Added (g m⁻²)</th>
<th>MSW Composition (g kg⁻¹)</th>
<th>Added (g m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>937</td>
<td>–</td>
<td>970</td>
<td>–</td>
<td>639</td>
<td>–</td>
<td>610</td>
<td>–</td>
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<tr>
<td>Total N</td>
<td>4.4</td>
<td>17.5</td>
<td>4.5</td>
<td>17.5</td>
<td>15.6</td>
<td>25.0</td>
<td>8.9</td>
<td>25.0</td>
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<tr>
<td>Dissolved organic N</td>
<td>0.1</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Non dissolved organic N</td>
<td>0.8</td>
<td>3.2</td>
<td>0.7</td>
<td>3.1</td>
<td>13.0</td>
<td>20.8</td>
<td>6.1</td>
<td>17.0</td>
</tr>
<tr>
<td>NH₃⁺</td>
<td>3.5</td>
<td>14.0</td>
<td>3.7</td>
<td>14.3</td>
<td>2.6</td>
<td>4.2</td>
<td>2.6</td>
<td>7.3</td>
</tr>
<tr>
<td>Total C</td>
<td>30.6</td>
<td>114.7</td>
<td>15.8</td>
<td>61.0</td>
<td>200.1</td>
<td>320.0</td>
<td>226.1</td>
<td>634.0</td>
</tr>
<tr>
<td>Soluble organic C</td>
<td>0.272</td>
<td>1.02</td>
<td>0.181</td>
<td>0.71</td>
<td>0.097</td>
<td>0.155</td>
<td>0.307</td>
<td>0.860</td>
</tr>
<tr>
<td>Soluble carbohydrates</td>
<td>0.004</td>
<td>0.015</td>
<td>0.002</td>
<td>0.009</td>
<td>0.002</td>
<td>0.003</td>
<td>0.015</td>
<td>0.042</td>
</tr>
<tr>
<td>Soluble proteins</td>
<td>0.011</td>
<td>0.042</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.008</td>
<td>0.023</td>
</tr>
<tr>
<td>Soluble phenolic compounds</td>
<td>0.007</td>
<td>0.025</td>
<td>0.021</td>
<td>0.084</td>
<td>0.004</td>
<td>0.006</td>
<td>0.006</td>
<td>0.016</td>
</tr>
<tr>
<td>VFA</td>
<td>0.046</td>
<td>0.170</td>
<td>0.052</td>
<td>0.202</td>
<td>0.073</td>
<td>0.171</td>
<td>0.040</td>
<td>0.112</td>
</tr>
<tr>
<td>C/N</td>
<td>6.5</td>
<td>3.5</td>
<td>12.8⁺</td>
<td></td>
<td>26.3⁺</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculated in the original fertilizer (wt. weight).

* C/N was 10.6 and 21.1 in CPS and MSW mixed with urea, respectively.

On 24 April 2004, maize (Zea mays L. cv Juanita) was sown in rows, with a spacing of 75 cm and at a density of 75,000 plants ha⁻¹. Maize was harvested on 15 September 2004, when the grain was mature. An overhead mobile-line sprinkler irrigation system was used during the maize growing period. Eighteen irrigation sessions took place from 18 June to 1 September 2004, at a frequency of two applications per week. Irrigation was calculated on a weekly basis by measuring soil moisture using time domain reflectometry (TDR) and adding an additional amount of water to obtain drainage rates of close to 5% of irrigation. Each application of irrigation ranged from 20 to 30 mm. The total amount of water applied was 485 mm.

2.3. Sampling and analysis of N₂O and NO

N₂O and NO fluxes were measured using the closed chamber technique, with 19.34 l (diameter 35 cm and height 23 cm) chambers. The insides of the chambers had previously been covered with a Teflon film to prevent the gases from reacting with the plastic of the chamber walls. A three-way Luer fitting tube (4.0 mm internal diameter × 10 cm length) was installed to vent the chamber. A thermometer inserted into the chamber was used to record the temperature when gas samples were taken. The chambers were fitted inside a stainless steel ring, which was inserted into the soil to a depth of 10 cm. Rings were placed in plots after fertiliser application (on 14 April) and remained there throughout the experiment. Two chambers were used on each plot, one within the maize row and the other one in between rows. These chambers were placed in the rings and kept closed for 1 h. To quantify N₂O emissions, duplicate (10 ml) air samples were removed from the headspace atmosphere using a syringe. These samples were extracted via a gas-tight neoprene septum at times 0 and 60 min and were stored in 10 ml blood containers (Vacutainers, Venoject). From 15 to 28 April, additional measurements were taken from all plots at 20 min intervals in order to test the linearity of the emissions from this soil. The increase in N₂O remained linear for up to 1 h (r² > 0.90 for 85% of regressions). Lower correlation coefficients were often associated with low surface emissions that were difficult to detect. To remove NO samples, the lids were opened for a few minutes and then ozone-free air (compressed air) was pumped through the chambers at a flow rate of 10 l min⁻¹ for 3 min to remove most of the initial air. A few seconds before the chamber was closed, 2 l of the air was removed from the chamber by connecting a Teflon gas collection bag to a valve in the chamber (time 0). The chambers were kept closed for 20 min and then 2 l of gas was sampled from the headspace by pumping it (at a flow rate of 3 l min⁻¹) into a Teflon gas collection bag and then transporting it to a chemiluminescence detector (Environment AC31 M) that had been previously placed at the edge of the field (Williams et al., 1998). During gas sampling a charcoal filter was connected to the vent tube to reduce the ozone content of the air that entered the chamber to compensate the differences in pressure. The NO concentration was always determined within 5–10 min of the samples being taken. On several occasions, two bags were filled with 1.0 and 0.1 μl NO-N l⁻¹ standards in the field and analysed for NO following the procedure described above. The relative error was always less than 5%. In this experiment it was not possible to take measurements by directly connecting the equipment to dynamic chambers due to the flooding conditions that were created in the field after irrigation, which made it very difficult to move the NO detector. Under the existing circumstances, an error in measuring the flux would have been possible if the rate of air sample withdrawal had not been compensated by pressure venting (Livingston and Hutchinson, 1995). However, the potential error associated with this is assumed to be small, firstly because of the relatively small sample volume (2 l) compared to the total volume of the inside of the chamber.
I

2.4. Soil analysis

Denitrification was estimated through incubations using the acetylene (C₂H₂) inhibition technique (5%, v/v). N₂O emissions via nitrification and denitrification were estimated using an incubation technique involving different concentrations of C₂H₂ (Müller et al., 1998). Soil cores of 2.5 cm diameter × 10 cm depth were incubated with 0, 5 Pa and 5% (v/v) in 11 hermetic glass jars and buried close to the experimental field for 24 h. After incubation, 10 ml gas samples were removed from the jars headspace using a syringe and then stored in 10 ml blood containers (Vacutainers, Venoject).

The N₂O from the vials was quantified by gas chromatography. A HP-6890, equipped with a 6¹⁴Ni electron-capture detector, a capillary column HP-Plot Q and the capillary precolumn of an HP-Retention Gap were used to remove water vapour from the samples. The temperatures of the injector, oven and detector were 50, 50 and 300 °C, respectively, and the carrier gas flux (N₂) was 30 ml min⁻¹.

Gas samples (N₂O and NO emissions) were taken from the cover boxes everyday for 1 week following the application of fertilizers and then on a weekly basis from April to September. Gas samples were taken from the jars twice a week for the first 2 weeks and thereafter on a weekly basis. Additional samples were taken after each rainfall event. Sampling after rainfall or irrigation was always carried out between 12 and 48 h after each event.

Following the methodology described by Müller et al. (1998), the fraction of N₂O production attributable to denitrification during jar incubation was expressed as the fraction IS₅Ps/IS₀Ps, where IS₅Ps and IS₀Ps were the mean N₂O emissions from incubation with 5 and 0 Pa C₂H₂, respectively. N₂O emissions due to denitrification from cover boxes (Fden) were calculated by multiplying the fraction IS₅Ps/IS₀Ps by the daily N₂O flux (Fday) and assuming that the fraction determined from jar incubation was equal to the average daily fraction for the plots (IS₅Ps/IS₀Ps = Fden/Fday). Denitrification N₂ production (IN₂) was calculated using the equation: IN₂ = I(N₂+N₂O) - IS₅Ps, where I(N₂+N₂O) is the N₂ + N₂O produced from denitrification (incubation with 5% C₂H₂).

2.5. Calculation and statistical analysis

N₂O and NO flux rates were calculated from the slope of the temporal change in concentration within the chamber and corrected for temperature and the ratio between chamber volume and surface area (Mackenzie et al., 1998).

Total N₂O-N emission, NO-N emission, denitrification losses, total N₂ and total N₂O produced from denitrification per plot were estimated by successive linear interpolation of N₂O-N emissions, NO-N emissions, the denitrification rate, IN₂, and IS₅Ps, respectively, based on sampling date and assuming that emissions (or production) followed a linear trend during the periods in which no samples were taken. The N₂O/N₂ ratio in the gases produced from denitrification was calculated by dividing total accumulated IS₅Ps during the experimental period by total IN₂.

Statistical analysis was performed using the STAT-GRAPHICS Plus 5.1 (Manugistics, 2000). One-way ANOVA was used to determine significant differences between treatments with respect to soil denitrification rates, N₂O and NO emissions, DOC, NH₄⁺-N and NO₃⁻-N contents. The L.S.D. test was used for multiple comparisons of means. Step-wise multiple linear regression analyses (P < 0.05) were performed to determine whether daily N₂O and NO emissions and denitrification rates were related to WFPS, NO₃⁻-N content, NH₄⁺-N content, soil temperature and DOC. Simple linear regressions were carried out to assess the relationship between the N₂O, NO and denitrification losses and different fractions of the organic fertilizers.

3. Results

3.1. Environmental conditions, evolution of mineral N and dissolved organic carbon

The WFPS was 46% immediately after the application of fertilizers (Fig. 1). Rainfall events increased WFPS and maintained it at above 70% from 22 April to 27 May. The high evapotranspiration rates of June (5–6 mm H₂O d⁻¹), which are characteristic of Mediterranean climates, together with the lack of rainfall, reduced WFPS to 40% on 15 June. Irrigation was therefore necessary to sustain the crop from 18 June to 31 August. WFPS during the irrigation period was kept at around 70%. Average daily soil temperature ranged

(19.3 l) and secondly because the time required to obtain the sample was about 45 s and the tube vent partially compensated for the difference in pressure during sampling. As the same static approach was used for all chambers, a comparison between the different treatments is valid. We had previously evaluated losses attributable to diffusion through the vent tube and seal by injecting N₂O standards into chambers fixed to the ring but closed at the bottom of ring. The observed losses were generally lower than 5% in 1 h.

Denitrification was estimated through incubations using the acetylene (C₂H₂) inhibition technique (5%, v/v). N₂O emissions via nitrification and denitrification were estimated using an incubation technique involving different concentrations of C₂H₂ (Müller et al., 1998). Soil cores of 2.5 cm diameter × 10 cm depth were incubated with 0, 5 Pa and 5% (v/v) in 11 hermetic glass jars and buried close to the experimental field for 24 h. After incubation, 10 ml gas samples were removed from the jars headspace using a syringe and then stored in 10 ml blood containers (Vacutainers, Venoject).

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2.4. Soil analysis

The core of each jar was mixed to determine soil NO₃⁻ and NH₄⁺. These parameters were determined by extracting 10 g of fresh soil with 100 ml of 1 M KCl. NO₃⁻ and NH₄⁺ were determined colorimetrically using a Technicon AAII Auto-analyser (Technicon Hispania, Spain). Dissolved organic carbon (DOC) was extracted and analysed as described by Mulvaney et al. (1997).

Water filled pore space (WFPS) was estimated by dividing the volumetric water content by the total soil porosity. Rainfall and air temperature data were obtained from a meteorological station located in the same field.

2.5. Calculation and statistical analysis

N₂O and NO flux rates were calculated from the slope of the temporal change in concentration within the chamber and corrected for temperature and the ratio between chamber volume and surface area (Mackenzie et al., 1998).

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from 10 to 20 °C in April and May, and from 20 to 30 °C from June to September (Fig. 1).

The application of fertilizers increased soil NH$_4^+$ content with respect to the Control for 15 days in all treatments (Fig. 2). DTP was the treatment which produced the highest NH$_4^+$ soil content (13.7 mg NH$_4^+$-N kg$^{-1}$ soil) followed by U and MSW + U (12.5 and 9.2 mg NH$_4^+$-N kg$^{-1}$ soil, respectively). From the beginning of May until September the concentration of NH$_4^+$ remained below 0.5 mg NH$_4^+$-N kg$^{-1}$ soil, except in the case of the treatment with DCD, which maintained a significantly ($P < 0.05$) higher soil NH$_4^+$ concentration than UPS until 15 May. Soil NO$_3^-$ content in the upper 10 cm layer (Fig. 2) increased during the 10 days after fertilizer application. DTP was also the treatment that produced the highest soil NO$_3^-$ content (35.2 mg NO$_3^-$-N kg$^{-1}$ soil). When the first important rainfall event (21 mm H$_2$O) occurred (22 April), NO$_3^-$ soil content decreased rapidly in all treatments. With irrigation, a more intensive reduction in NO$_3^-$ was produced, with levels remaining below 1 mg NO$_3^-$-N kg$^{-1}$ soil after 2 July in all treatments.

The application of fertilizers produced differences in dissolved organic carbon (DOC) content in the upper 10 cm of the soil profile (Table 2). The greatest increases in DOC with respect to the control occurred in the first month after fertilizer application for UPS, UPS + DCD and U. For DTP and CPS + U the greatest increase occurred during the third month, whereas for MSW + U this increase occurred during the fifth month. In contrast, we observed a reduction in DOC with respect to the Control in the second month for composted treatments mixed with urea and also for UPS and UPS + DCD.

### 3.2. N$_2$O emission

N$_2$O emissions were influenced by the addition of fertilizers and several peaks were registered for each treatment during the experimental period (Fig. 3). We established two different periods in order to facilitate comparisons of fluxes between treatments. The first period ran from 15 April to 17 June, coinciding with the period before irrigation (BIP), and the second covered the following 3 months, when the soil maintained high WFPS due to irrigation (IP). In the first period, the largest N$_2$O fluxes were produced by the untreated pig slurry (both with and without DCD), DTP and urea treatments, coinciding with the moment when the soil had a WFPS of over 70%. CPS + U also produced large N$_2$O emissions at the end of this period, when the soil had a WFPS of around 40%. In the second period, the largest fluxes of N$_2$O were associated with soils treated with urea and composts mixed with urea.
Total N₂O-N emissions during the 142 days (from April to September) ranged from 6.0 kg N ha⁻¹ (Control) to 9.3 kg N ha⁻¹ (CPS + U) (Table 3). Discounting the N₂O lost in the Control, the percentage of N₂O lost in relation to the available N for the experimental period was 1.30% (UPS), 0.90% (DTP), 0.41% (UPS + DCD), 1.88% (CP + U), 0.66% (MSW + U) and 1.49% (U). In general, the cumulative N₂O emission for each fertilizer was lower for the period before irrigation than during the irrigation period. For the first period, U and UPS had the highest N₂O emissions, whereas during the second period the CPS + U treatment produced the greatest N₂O fluxes.

Step-wise multiple linear regressions showed positive relationships between N₂O flux rates and several different soil variables (Table 4). However, WFPS, soil temperature and NH₄⁺ only explained about 26% of N₂O flux variability during the irrigation period and the first two parameters explained 10% of the N₂O fluxes during the total period.

Denitrification was the process responsible for most of the N₂O emissions, except in plots treated with urea, where emissions were mainly produced by nitrification. With the acetylene inhibition method (Müller et al., 1998), the percentages for N₂O losses via denitrification were 70% (UPS), 75% (DTP), 80% (UPS + DCD), 91% (CPS + U), 89% (MSW + U), 43% (U) and 90% (Control).

### 3.3. NO fluxes

A significant increase in NO occurred during the first 20 days after fertilizer application (Fig. 4). The greatest NO fluxes were measured in mineral fertilizer (1.95 mg NO-N m⁻² d⁻¹ on 28 April). Differences between NO emission rates from DTP and UPS were not significant at any sampling time. The addition of DCD to pig slurry was very efficient for reducing NO emissions: in the majority of samples, NO fluxes were similar to those observed in the Control. The properties of the composted materials had an important effect on NO emissions: significantly (P < 0.05) for the period before irrigation than during the irrigation period.

#### Table 2
Dissolved organic C (DOC) in the 0–10 cm soil layer during the experimental period

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Average DOC (difference between soil sample and Control treatment) (mg C kg⁻¹ soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First month</td>
</tr>
<tr>
<td>Control (C)</td>
<td></td>
</tr>
<tr>
<td>Untreated pig slurry (UPS)</td>
<td>26.8 (17.8)</td>
</tr>
<tr>
<td>Digested thin pig slurry fraction (DTP)</td>
<td>8.9 (0)</td>
</tr>
<tr>
<td>Pig slurry + DCD</td>
<td>20.8 (11.9)</td>
</tr>
<tr>
<td>Composted pig slurry fraction + urea (CPS + U)</td>
<td>14.9 (5.9)</td>
</tr>
<tr>
<td>Municipal solid waste + urea (MSW + U)</td>
<td>16.4 (7.4)</td>
</tr>
<tr>
<td>Urea (U)</td>
<td>35.7 (26.8)</td>
</tr>
</tbody>
</table>

Different letters within each column indicate significant differences between fertilizer treatment (P < 0.05) according to the least significant significance (L.S.D.) test.

* Mean value of accumulated N₂O emission from three plots ± standard deviation.

#### Table 3
Cumulative N₂O emissions over different periods during the maize growing season

<table>
<thead>
<tr>
<th>Treatment</th>
<th>N₂O emission (kg N ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before irrigation</td>
</tr>
<tr>
<td>Control</td>
<td>2.03 ± 0.16 a</td>
</tr>
<tr>
<td>Untreated pig slurry (UPS)</td>
<td>3.23 ± 0.58 b</td>
</tr>
<tr>
<td>Digested thin pig slurry fraction (DTP)</td>
<td>2.79 ± 0.81 ab</td>
</tr>
<tr>
<td>Pig slurry + DCD</td>
<td>2.72 ± 0.79 ab</td>
</tr>
<tr>
<td>Composted pig slurry fraction + urea (CPS + U)</td>
<td>3.17 ± 0.71 b</td>
</tr>
<tr>
<td>Municipal solid waste + urea (MSW + U)</td>
<td>2.82 ± 0.55 ab</td>
</tr>
<tr>
<td>Urea (U)</td>
<td>3.71 ± 0.82 b</td>
</tr>
</tbody>
</table>

Different letters within each column indicate significant differences between fertilizer treatment (P < 0.05) according to the least significant significance (L.S.D.) test.

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**Fig. 3.** Emissions of N₂O from soil during the maize growing season. The vertical bars indicate L.S.D. at 0.05 between treatments for each sample time. The single arrow indicates the date of fertilizer application; the double-headed arrow indicates the first irrigation.

**Fig. 4.** Emissions of NO from soil during the maize growing season. The vertical bars indicate L.S.D. at 0.05 between treatments for each sample time. The single arrow indicates the date of fertilizer application; the double-headed arrow indicates the first irrigation.
higher NO fluxes occurred from CPS + U than from MSW + U. During the irrigation period, nitric oxide fluxes were lower than 0.1 mg NO-N m$^{-2}$ d$^{-1}$ in all treatments and differences between treatments were not significant at $P < 0.05$.

Step-wise multiple linear regressions showed positive relationships between NO fluxes and NH$_4^+$ and NO$_3^-$ during the first period and negative relationships with soil temperature and WFPS, explaining 57% of variability for these parameters (Table 4). For the total study period, NH$_4^+$, NO$_3^-$ and soil temperature explained 50% of variability.

Cumulative NO emissions have been included in Table 5. Discounting the NO lost in the Control, the percentages of N lost as NO compared with total N applied were 0.128 (U), 0.071 (DTP), 0.068 (UPS), 0.051 (CPS + U), 0.015 (UPS + DCD) and 0.012% (MSW + U).

Under these experimental conditions, emissions of N$_2$O were greater than those of NO for all sampling times. For the whole experimental period, the molar NO/N$_2$O ratios were 0.007 (Control), 0.019 (MSW + U), 0.021 (UPS + DCD), 0.043 (CPS + U), 0.062 (UPS), 0.070 (DTP) and 0.109 (U). The NO/N$_2$O ratio was strongly correlated with the percentage of N$_2$O produced by nitrification ($%N_2O-N$) ($r = 0.89$, $P < 0.01$). The correlation equation was

$$%N_2O-N = 3.0 + 421.5 \frac{NO}{N_2O}. \quad (1)$$

3.4. $N_2O+N_2$ production from denitrification

Irrigation increased denitrification activity and a peak occurred in all treatments except the Control and UPS + DCD on 2 July (Fig. 5). The values of these peaks were 226, 213, 242, 273 and 289 mg N m$^{-2}$ d$^{-1}$ for the UPS, DTP, CPS + U, MSW + U and U treatments, respectively, and coincided with a WFPS value of 71%.

![Fig. 4. Emissions of NO from soil during the maize growing season. The vertical bars indicate L.S.D. at 0.05 between treatments for each sample time. The single arrow indicates the date of fertilizer application; the double-headed arrow indicates the first irrigation.](image)

![Fig. 5. Denitrification rate (DR) in the 0–10 cm soil layer during the maize growing season. The vertical bars indicate L.S.D. at 0.05 between treatments for each sample time. The single arrow indicates the date of fertilizer application; the double-headed arrow indicates the first irrigation.](image)
Cumulative denitrification losses from the upper soil layer (0–10 cm) varied greatly between treatments (Table 6). The maximum losses were associated with the MSW + U treatment (48.0 kg N ha$^{-1}$). Digested thin pig slurry fraction produced similar denitrification losses to untreated pig slurry (26.90 and 27.33 kg N$_2$O-N ha$^{-1}$ for UPS and DTP, respectively), whereas the nitrification inhibitor reduced denitrification losses (18.15 kg N$_2$O-N ha$^{-1}$) with respect to UPS. Depending on the treatment, losses during the irrigation period ranged from 60 to 88% of total denitrification losses.

The evolution of the denitrification rate for each treatment over the experimental period was related to the DOC evolution, although this only explained about 16% of the effect (Table 4). Before irrigation, environmental properties (WFPS and soil temperature, $P < 0.05$) explained 15% of variability in the denitrification rate, while in the second period, DOC of soil and NO$_3^-$ soil content explained 40% of variability.

Cumulative N$_2$O production from denitrification was much lower than cumulative N$_2$ production for all treatments. The N$_2$O/N$_2$ ratio was influenced by fertilizer type. The addition of compost plus urea reduced this ratio (0.21 and 0.30 for MSW + U and CPS + U, respectively) with respect to urea (0.54). Digested pig slurry increased this ratio in comparison with UPS both with and without DCD (Fig. 5). The N$_2$O/N$_2$ ratio was higher before rather than during the irrigation period for all treatments (Fig. 6).

3.5. Denitrification losses, N$_2$O and NO emissions associated with fertilizer composition

As fertilizer composition has an influence on nitrogen gas emissions, we studied correlations between these parameters and several compounds added with fertilizers (Table 7). Results for UPS + DCD were excluded because of the characteristic effect of DCD. Urea and the Control were also discarded when relationships between these gases and C:N were calculated. Our results indicated that the C:N ratio of fertilizer was a good predictor of its associated NO and denitrification losses. Denitrification was positively correlated with fertilizer C:N, whereas total NO and NO in the period before irrigation were negatively correlated. Nitrous oxide linearly increased until a value of C:N = 10, but diminished with C:N for compost. There was a strong correlation between NO emissions and the C:N of fertilizer, the effect of DCD (Fig. 5). The N$_2$O/N$_2$ ratio was higher before rather than during the irrigation period for all treatments (Fig. 6).
negative correlation between N\(_2\)/N\(_2\) ratio and the inverse of C:N for the first and the total period. Total C was also a good predictor of denitrification losses and N\(_2\)/N\(_2\) ratio during both the first and the whole experimental period. The N\(_2\)/N\(_2\) ratio was also positively correlated with added ammonium. Nitrous oxide emission was only correlated with added soluble N in the period before irrigation.

4. Discussion

4.1. NO and N\(_2\)O emissions from treated liquid manure

Upon field application, manure and inorganic fertilizers significantly contribute to anthropogenic emissions of N\(_2\)O and NO. Understanding the impact of fertilizer composition on these emissions remains an important goal. Pig slurry usually contains high concentrations of NH\(_4^+\)-N, which is rapidly nitrified when mixed with aerated soils and supplies easily decomposable organic C that can sustain denitrification (Rochette et al., 2000). The large emissions of N\(_2\)O and NO measured in this experiment, and associated with slurry application, are in line with reports from other authors (Yamulki et al., 1998; Chadwick et al., 2000; Rochette et al., 2000; Vallejo et al., 2005). However, the peaks were observed from 20 to 30 days after its application instead 12–15 days, which was observed by these above referred authors. This different behaviour could be explained because in the experiments carried out by these authors conditions favoured nitrification, whereas in this experiment a high WFPS (\(>75\%\)) maintained in the soil during the first 30 days as consequence of rainfall, reduced nitrification rate in that period.

The application of liquid slurry to the field also supposes a major environmental problem for areas close to farms because of the production of odours and the diffusion of pathogens to both the soil and the air. A useful and common treatment to reduce this problem is the anaerobic digestion of the thin fraction of slurry (Burton and Turner, 2003). The separation of solid fraction from slurry using mechanical separators and the anaerobic digestion of the liquid fraction subsequently obtained reduces the overall organic load in terms of total organic C and reduces the non soluble component of slurry (Burton and Turner, 2003). These changes in slurry composition produce a beneficial effect and help to mitigate N\(_2\)O emissions: in this experiment, they reduced their production by 25\% with respect to untreated pig slurry. Petersen (1999) and Vallejo et al. (2006) measured a reduction in N\(_2\)O emissions of from 20 to 40\% when applying anaerobically treated pig slurry as opposed to untreated slurry. In this study, we have only evaluated emissions resulting from the application of fertilizers to the soil. Emissions produced before the application of these products have not been taken into account.

Furthermore, previous slurry treatment stabilizes and homogenizes the product and the separation of the solid fraction before anaerobic digestion reduces its viscosity and therefore facilitates a better distribution and infiltration into the soil. This effect also reduces NH\(_3\) volatilization and the potential for the anaerobic processes within soil (Petersen, 1999). Although this experiment did not measure NH\(_3\) volatilization, we suppose this was a possible explanation for the higher NO\(_3^-\) and NH\(_4^+\) soil content in the DTP than in the UPS treatment in the 30 days following slurry application.

The NO fluxes correlated with the NH\(_4^+\) content of the soil, indicating that nitrification is the main source of NO (Skiba et al., 1993). In spite of differences in soil NH\(_4^+\) content between UPS and DTP, differences between their NO emissions were not significant at \(P < 0.05\). Denitrification losses were also similar for the two treatments. We had expected less denitrification in DTP than in UPS because of the smaller quantity of added DOC with DTP. However, in this soil, the lower DOC content found in plots treated with DTP than in those treated with UPS was only maintained for the first month, when the denitrification rate was still relatively low.

Using DCD was effective for mitigating N\(_2\)O and NO emissions from pig slurry in this agroecosystem because the inhibitor reduced N\(_2\)O and NO emissions by 64 and 78\% respectively compared with results for untreated slurry.

Table 7

<table>
<thead>
<tr>
<th>Added carbohydrates</th>
<th>Added organic N</th>
<th>Added soluble N</th>
<th>Non dissolved organic N</th>
<th>NH(_4^+)</th>
<th>N/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)O</td>
<td>0.82* (BIP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>0.99** (BIP)(^a)</td>
<td>0.99** (total)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DR</td>
<td>0.95** (BIP)</td>
<td>0.95* (BIP)</td>
<td>0.94** (BIP)</td>
<td>0.82* (IP)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.98* (total)</td>
<td>0.80* (total)</td>
<td>0.94* (total)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(_2)/N(_2)</td>
<td>0.99** (BIP)</td>
<td>0.81* (total)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.88** (BIP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) \(n = 4\).

\(^b\) In parenthesis, period: BIP is before irrigation period (from 14 April to 17 June), IP the irrigation period (from 18 June to 3 September) and total is the whole period (from 14 April to 3 September). Correlations significant at \(P \leq 0.001, 0.01\) and 0.05 indicated with ***/**/* respectively.
During the 30–40 days after its application, the inhibitor was very efficient at reducing N₂O and NO from nitrification. In temperate climates, with lower temperatures than the Mediterranean area, a persistence period of more than 1–2 months has been reported (Cookson and Cornforth, 2002). The inhibition of the nitrification process explained the increased efficiency for mitigating NO rather than N₂O. The frequent rainfall events in this period, favoured the production of N₂O and the consumption of NO through the process of denitrification. In the irrigation period, DCD also significantly reduced (P < 0.05) N₂O with respect to the untreated slurry. This reduction could have been associated with a 32% mitigation of denitrification losses promoted by DCD (Table 5). Although DCD did not inhibit N₂O emission under wet conditions (Skiba et al., 1993) or reduce denitrification losses (Vallejo et al., 2005), other authors observed important reductions in N₂O + N₂ production by denitrification after the application of DCD to slurry (Pain et al., 1990; Merino et al., 2001). In these cases, the inhibitor probably had an indirect effect on denitrification because a reduced quantity of NH₄⁺ was transformed into NO₃⁻, the substrate of the denitrification process. In our experiment, we observed smaller amounts of NO₃⁻ in UPS + DCD than in UPS when conditions favoured denitrification, during the irrigation period.

### 4.2. NO and N₂O emissions from composts

The incorporation of local organic residues provides a source of readily available C and N in soils and constitutes a practical way of improving soil fertility, especially in semiarid climates, where soil fertility is highly dependent on soil C content. The incorporation of urea with the compost maintained a higher NO₃⁻ soil content than in the Control during the days after application, thereby reducing the negative effect of soil N immobilization on available N. The C:N ratio of compost might play an important role in N gas emissions and in denitrification losses (Table 7). Huang et al. (2004) found that cumulative emissions of N₂O were negatively correlated with the C:N ratio in plant residues. This effect was only observed in our experiment when we compared the composted materials (CPS + U and MSW + U). This behaviour was not therefore generalised for all organic fertilizers: the C:N ratio was not correlated with N₂O emissions during any period in which both liquid manures and composts were included for calculation. For liquid manure the highest emissions corresponded to the highest C:N ratios. The effect of C:N on nitrogen oxide emissions may have been associated with changes in mineral N and DOC during the decomposition of these materials in soils that affected the nitrification and denitrification processes. The C:N ratio and DOC are sometimes used as indicators of compost stability. A very stable compost often has a low C:N ratio (10–14) in combination with a low DOC. A product with a final C:N ratio of above 20 may not readily release nitrogen because N microbial immobilization increases when these types of compost are applied to soil (Azam et al., 1985). The addition of greater amounts of soluble organic compounds with municipal organic compost increased the DOC of soil during the first month with respect to the CPS + U treatment. The positive ΔDOC observed in the MSW + U treatment during July and August, which favoured denitrification, may have been associated with insoluble organic compounds that had decomposed 4–5 months after application. As environmental conditions favoured denitrification during the first month, NO may be used by denitrifiers, in combination with soluble organic compounds, to reduce emissions of this gas. MSW + U produced a four-fold reduction in emissions of NO with respect to CPS + U. The application of urea without compost significantly increased DOC during the first month, as also reported by Huang et al. (2004) and Vallejo et al. (2006). When urea is hydrolyzed, it locally increases soil pH and causes DOC mobilization (Shand et al., 2000). Nevertheless, in this case, the concentration of NH₄⁺ during the first month was greater than in the compost treatments, which were responsible of the highest NO emissions (9.7 times greater than MSW + U). The larger amount of N₂O emitted from soils treated with U in relation to those treated with MSW may also have been a consequence of the additional organic C, which favoured the consumption of this gas by denitrifiers during the irrigation period (Vallejo et al., 2006). One exception to this general tendency was the CPS + U treatment, which emitted greater amounts of N₂O than the U treatment, despite the incorporation of soluble organic compounds.

In this experiment, significant differences were observed between fertilizer plots and the Control (11,900 kg ha⁻¹) at P < 0.05 in maize yield. Treated organic fertilizers were effective in maintaining maize yield (which ranged from 13,100 kg ha⁻¹ for UPS + DCD to 16,700 kg ha⁻¹ for MSW), as were urea (15,700 kg ha⁻¹) and untreated pig slurry (15,500 kg ha⁻¹). The mitigation of emissions using treated organic waste is therefore a suitable option for farmers as it allows them to reduce nitrogen gas emissions while still maintaining crop yield.

### 4.3. Origins of NO and N₂O emissions

Under these environmental conditions, denitrification was the main process responsible for N₂O emissions from the organic fertilizer treatments whereas nitrification was the most important process on plots treated with urea. The addition of organic C compounds present in organic fertilizers probably promoted oxygen consumption by microbial growth, creating temporary anaerobic microsites (Cannavo et al., 2003) which, in turn, favoured denitrification.

Williams et al. (1998) used relative emissions of NO and N₂O as a potential methodology for distinguishing between soil nitrification and denitrification in situ. According to the criteria of these authors, it could be
argued that denitrification rather than nitrification was the dominant process throughout the whole period. A high correlation was found between the NO/N₂O ratio and the percentage of N₂O produced by nitrification measured with the methodology proposed by Müller et al. (1998). Therefore, measurement of the NO/N₂O ratio constitutes a rapid method for distinguishing between nitrification and denitrification. However, the condition of a NO/N₂O ratio > 1 proposed by Anderson and Levine (1986) for the predominance of nitrification did not correspond with the data obtained in this experiment. Taking Eq. (1) into account, the predominance of nitrification (%N₂O-N > 50) occurred when NO/N₂O > 0.11. Laboratory studies have shown that denitrifiers produce a ratio of 0.01, while during nitrification the ratio is > 1. Under field conditions, this ratio probably diminished. Denitrifiers have a very high affinity for NO and can consume it as a substrate even in well-aerated soils (Conrad, 1996). Furthermore, denitrifying bacteria tend to utilise oxidised forms of N such as NO₃⁻ before utilising N₂O, and similarly tend to utilise NO in preference to N₂O (Yamulki and Jarvis, 2002). It is therefore to be expected that residence time and the physical characteristics of the soil will have a major impact on NO as opposed to N₂O emissions.

N₂O production from nitrification was not measured directly; values were calculated from differences between total N₂O production rates and N₂O production from denitrification (Müller et al., 1998). An atmosphere of 5–10 Pa acetylene was required to inhibit nitrification without blocking N₂O reductase. Under these conditions nitrifier denitrification is also inhibited (Wragg and Velthof, 2001). There is an important limitation with this method, as the nitrification fraction would also include nitrifier denitrification (Webster and Hopkins, 1996).

4.4. N₂O/N₂

Fertilizer composition had an influence on the N₂O/N₂ ratio of gases emitted through denitrification. An interesting reduction in this ratio occurred for compost mixed with urea as opposed to urea alone. The reduction was more effective in MSW + U than in CPS + U. In a field experiment carried out in a clay loam soil with a low level of organic matter, Vallejo et al. (2006) observed a negative correlation between this N₂O/N₂ ratio and soluble organic C added with fertilizers. In this sandy loam soil, a high positive correlation was found between this ratio and the inverse of the fertilizer C:N ratio, as well as with ammonium content. Negative correlations were found with total C and added organic N. As consequence, these correlations indicated that the addition of organic C might have favoured the production of N₂ whereas the addition of NH₄⁺ might have promoted the production of N₂O. A higher N₂O/N₂ ratio was therefore observed for DTP than for UPS. Evaluation of the N₂O/N₂ ratio was carried out with the methodology proposed by Müller et al. (1998), based on the inhibition of nitrification in the presence of 5–10 Pa C₂H₂. N₂ was calculated from differences between measured denitrification rates and N₂O production from denitrification. The results obtained from the application of this method could not therefore be taken as absolute values, but could be used for making comparisons between treatments (Estavillo et al., 2002; Vallejo et al., 2006).

5. Conclusions

This study demonstrated that the composition of organic fertilizers applied to soils had a great influence on NO and N₂O emissions. The addition of organic fertilizers temporarily modified DOC and mineral N in soil, which affected denitrification and nitrification rates. Under irrigation conditions, the application of organic fertilizers produced a reduction in NO and N₂O in comparison with emissions from urea at the same available N rate in soils with a low organic C content. The C:N ratio of organic fertilizers constituted a good predictor for NO emissions and denitrification losses. When this ratio was increased, NO emissions were reduced and denitrification increased.

The application of treated pig slurry to agricultural soils is an efficient alternative for mitigating N₂O and NO emissions. Anaerobic digestion of pig slurry reduced N₂O emissions with respect to untreated pig slurry. The incorporation of the nitrification inhibitor DCD mixed with untreated slurry was an efficient alternative to mitigate N₂O and NO emissions in irrigated soils. It was also very effective in reducing denitrification during the irrigation period. The incorporation of urea into stabilised compost with a low C:N enhanced N₂O emission. Nevertheless in the case of compost that was not well-stabilised and had high DOC and C:N, this addition mitigated emissions with respect to urea.

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