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Comparison of N losses (NO_3^-, N_2O, NO) from surface applied, injected or amended (DCD) pig slurry of an irrigated soil in a Mediterranean climate

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Abstract

Nitrous oxide (N_2O), nitric oxide (NO), denitrification losses and NO_3^- leaching from an irrigated sward were quantified under Mediterranean conditions. The effect of injected pig slurry (IPS) with and without the nitrification inhibitor dicyandiamide (DCD) was evaluated and also compared with that of a surface pig slurry application (SPS) and a control treatment (Control) without fertiliser. After application, fluxes of NO and N_2O peaked from SPS (3.06 mg NO-N m^{-2} d^{-1} and 108 mg N_2O-N m^{-2} d^{-1}) and IPS (3.50 mg NO-N m^{-2} d^{-1} and 105 mg N_2O-N m^{-2} d^{-1}). However, when irrigation was applied, N_2O and NO emissions declined. The total N_2O and denitrification losses were slightly large from IPS than from SPS, although the differences were not significant ($P < 0.05$). Emission of NO was not affected by the method of pig slurry application. DCD inhibited nitrification during the first 20–30 days and reduced N_2O and NO emissions from pig slurry by at least 46% and 37%, respectively. Considering the 215 days following pig slurry application, the emission factor of N_2O based on N fertiliser was 1.60% (SPS), 2.95% (IPS), and 0.50% (IPS + DCD). The emission factor for NO was 0.14% (SPS), 0.12% (IPS), and 0.02% (IPS + DCD). Environmental conditions of the crop favoured the denitrification process as the most important source of N_2O during the experimental period. The differences in the denitrification rate between treatments could be explained by the pattern of water soluble carbon (WSC), that was the highest value in injected pig slurry (with and without DCD). Due to low drainage (5% of water applied), leaching losses of NO_3^- were lower than those of denitrification from the upper soil layer (0–10 cm) in all treatments and especially with IPS + DCD, where the nitrification inhibitor was very efficient in reducing leaching losses.

Introduction

Soils contribute about 65% of the total nitrous oxide (N_2O) produced by the terrestrial ecosystem (IPCC, 1997) and between 24% and 62% of the total nitric oxide (NO) production (Skiba et al., 1997). These gases are directly or indirectly involved in global warming, the destruction of stratospheric ozone and the photochemical formation of nitric acid (Bouwman, 1990).

In soil, NO and N_2O are primarily produced biologically, by nitrification and denitrification (Firestone and Davidson, 1989). The balance between the two processes contributing to N_2O and NO emission varies with the climate, soil

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conditions and soil management (Skiba et al., 1997). High rainfall, poor drainage and high organic carbon content promote denitrification and associated N_2O and NO production. Low rainfall, good drainage and aeration promote nitrification and associated N_2O and NO production. However, both gases have been rarely measured in irrigated crops of Southern European countries (Teira-Esmatges et al., 1998) despite the large surface areas covered by this land use. Conditions of these soils favour denitrification as high moisture contents due to irrigation coincide with high soil temperatures, another factor affecting the denitrification (Maag and Vinther, 1999).

The application of manure to such irrigated soils is useful to maintain its fertility. The organic matter content of the soil is frequently less than 2%, with low fertility and high risk of erosion. As the second pig producer in the EU, Spain generates 2×10^{10} kg y^{-1} pig slurry, half of which is directly used as fertiliser. Pig slurry usually contains high concentrations of NH_4^+–N, which is rapidly nitrified when mixed with aerated soils. Slurries also supply easily decomposable organic C that can both sustain denitrification and induce anaerobiosis by stimulating biological O_2 demand (Rochette et al., 2000). Several authors have reported increases in N_2O and NO emission following application of slurry to soils (Gut et al., 1999; Maag and Vinther, 1999), but little is known about the emission from pig slurry applied in irrigated fields, especially under Mediterranean conditions. Traditionally, in these areas pig slurry is surface-applied to soils, with a high risk of NH_3 loss by volatilization. Recommendations based on injecting pig slurry into the soil or immediate incorporation after surface application were followed to reduce NH_3 loss (Klarenbeek and Bruins, 1991). However, these practices can appreciably increase the denitrification losses (Pain et al., 1989; Thompson et al., 1987). According to Díez et al. (2001) NO_3^- leaching after the application of pig slurry is another environmental problem in these agroecosystems. Dicyandiamide (DCD), a nitrification inhibitor, mixed with NH_4^+–N or ureic-N fertilisers could be efficient in mitigating NO_3^- leaching losses (McCarty and Bremner, 1990) and N_2O emission from arable soils (McTaggart et al., 1994; Skiba et al., 1993). DCD has also been used with cattle slurry (de Klein et al., 1996), although more studies on its efficiency of diminishing gas emissions and leaching losses are necessary, depending on climatic conditions.

The aims of this study were: (1) to quantify N_2O, NO emission and NO_3^- leaching from irrigated crop lands in a Mediterranean climate; (2) to compare the effect of the injected pig slurry with the traditional application of pig slurry to the land surface and (3) to evaluate the effect of the DCD nitrification inhibitor to reduce N_2O, NO emission and NO_3^- leaching.

Materials and methods

Experimental site and lysimeters

The study was conducted in a Typic Xerofluvent soil at a field in Arganda del Rey (Madrid) (40°19′ N, 3°19′ W) in 2002. Some relevant soil properties (0–20 cm) were: total organic matter, 1.4%; pH_{H_2O}, 8.1; bulk density, 1.47 Mg m^{-3}; $CaCO_3$, 3.4%; field capacity, 20.2% (w/w); porosity, 46%; sand, 37%; silt, 45%; and clay, 13%. The average annual temperature in this area (in the last 10 years) was 13.5 °C. Average annual rainfall was 460 mm (in the last 10 years).

In January 2002, 12 plots (3.3 × 3.3 m) were selected in the experimental field. In each plot a lysimeter (1.0 × 1.0 × 0.75 m deep) was installed to measure drainage and leaching losses. Lysimeters consisted of concrete containers which were fitted with a polyethylene pipe at the base connecting the outlet to an underground 20-L bottle. In the central surface area (2.5 × 2.5 m) of each plot, a hole was made to set up the lysimeter. A total of seven soil layers (10 cm thick) were removed from the soil and separately stored until the installation of lysimeters. A layer of gravel was first placed at the base when lysimeters were filled. Layers of un-sieved soil were carefully packed down and irrigated at field capacity to give as closely as possible conditions of the unaltered soil. The space surrounding the lysimeter was also filled with the different soil layers as well as lysimeter so that the upper part of each lysimeter was at ground level. The water colleted in the underground bottle is evacuated by suction with a vacuum pump. A TDR-probe was set up in each lysimeter. Tall fescue (*Festuca* *arundinacea*) was planted in February 2002. At the beginning of the experiment (20 May), soil bulk density in the upper soil layer (0–10 cm depth) of the lysimeters was close to the unaltered soil, and significant differences at $P < 0.05$ were not found.

Pig slurry

The slurry was collected from the underground storage tank of a pig farm at the ETSI Agrónomos in Madrid, Spain. Before slurry application, N content was determined to calculate the application rate. The main characteristics of the slurry were: pH, 7.1; dry matter, 97 g kg^{-1}; organic matter, 85.9 g kg^{-1}; total N, 4.07 g N kg^{-1}; NH_4^+–N, 3.79 g N kg^{-1}; total P, 0.27 g P kg^{-1}; and total K, 0.92 g K kg^{-1}.

Experimental procedure

Four treatments were applied to the experimental plots on 20th May. The treatments were: surface-applied pig slurry (SPS, 200 kg N ha^{-1}), injected pig slurry (IPS, 200 kg N ha^{-1}), injected pig slurry + dicyandiamide (IPS + DCD, 200 kg N ha^{-1}) and a control treatment without any fertiliser (Control). Each treatment was replicated 3 times using a random plots design.

In the IPS treatment, 4.9 L m^{-1} pig slurry was injected using a shallow injector system in the area surrounding the lysimeter surface. The spacing between the injection slots was 200 mm. In order to inject the slurry into the lysimeters, shaped knives were used to cut vertical slots in the grass sward to a depth of 5 cm. Slurry was released into each slot. After releasing the slurry, the slots were closed by a small press wheel. In the plots receiving the IPS + DCD treatment, 4.9 L of pig slurry mixed with 1 g DCD-N per m^2 was also injected into the soil. In the plots receiving the SPS treatment, pig slurry was applied to the soil using a watering can connected to a 10 L tank with a hosepipe to produce an uniforme distribution on the surface. In order to maintain the same soil water content in all plots Control plots were also irrigated with 4.9 L m^{-2} of water on 20th May.

Watering by using a sprinkler system was used and daily irrigations took place from 5th June to 31st August, and twice a week in September. Irrigation was calculated weekly by measuring soil moisture by Time Domain Reflectometry (TDR) and adding an additional amount of water to obtain drainage close to 5% of irrigation. Figure 1 includes the weekly irrigation amount and rainfall. The total amount of water applied as irrigation was 403 mm. The grassland was cut six times in the experimental period.

Sampling and analysis of N_2O and NO

Fluxes of N_2O and NO from the soil surface were measured using closed chambers, 30 cm in diameter and 30 cm in height, inserted into the soil to a depth of 3 cm. Each chamber had a head space volume of 19.06 L and covered a surface area of 0.0706 m^2. The chambers used in this study were coated inside with a Teflon film to minimize losses of NO on the walls of the chambers. The lids to the chambers were closed and 20 min later an approximate 2 L gas sample was pumped for *in situ* NO determination in a chemiluminescence detector (Environment AC31 M). NO was determined when a stable concentration reading was obtained. Immediately, the chambers were opened during 5 min and shut again for 30 min. After that, two 10 mL gas samples were removed from the headspace atmosphere with a syringe via a gas-tight neoprene septum in 10 mL evacuated blood containers (Vacutainers, Venoject) for N_2O analysis. A sample of air from near the experimental field was also taken to determine NO and N_2O. Assuming that the concentration of NO and N_2O in the headspace after 20 or 30 min, respectively, was the equilibrium concentration, fluxes of these gases were calculated from the concentrations measured (Williams et al., 1998). The chambers were always placed in the central area of each plot (altered soil).

Denitrification was estimated in the field through incubations using the acetylene (C_2H_2) inhibition technique (5% v/v). N_2O emission via nitrification and denitrification were also estimated with an in-field incubation technique in the presence of varying concentrations of C_2H_2 (Müller et al., 1998). Incubation of 6 soil cores (2.5 × 10 cm deep) with the 3 C_2H_2 concentrations (0, 5 Pa, and 5% v/v) were performed in 1-L glass jars inserted in holes made near the experimental field. For each jar, the

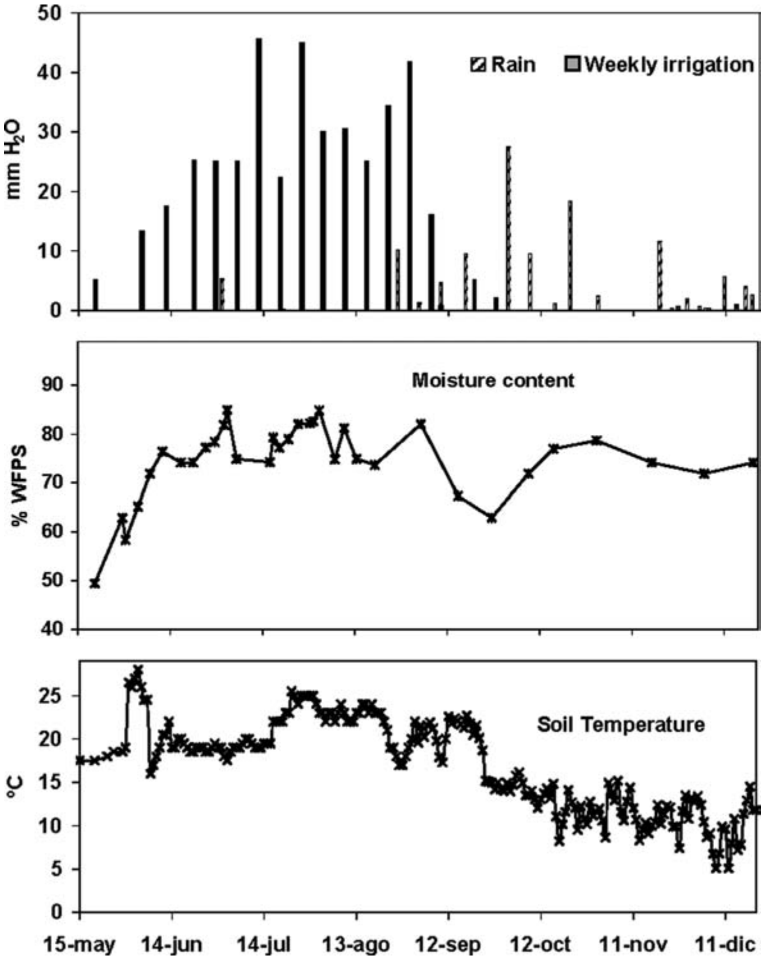

Figure 1. Rainfall and irrigation, water filled pore space (WFPS) and soil temperature during the experimental period.

5 Pa C_2H_2 concentration in the jar atmosphere was adjusted by exchanging, an exact calculated headspace volume with a 1000 Pa C_2H_2 standard, freshly prepared (Müller et al., 1998). After 24 h, a 10 mL gas sample was taken from each jar with a syringe and eventually stored in a 10 mL evacuated blood container (Venojets). Soil cores were usually taken from the central area of the plots (altered soil).

The N_2O content in the vials was analysed by gas chromatography (HP6890), using a ^{63}Ni electron-capture detector. A capillary column HP-Plot Q was used, incorporating a capillary precolum of an HP-Retention Gap to remove the water vapour from the sample. The injector, oven and detector temperatures were 50, 50 and 300 °C, respectively, and the carrier gas flux (N_2) was 30 mL min^{-1}.

Gas samples from cover boxes (N_2O and NO) were taken twice a day for 1, 2, 3 and 4 days after the slurry application (May 20th), every 2–3 days from 7 to 40 days after application, once a week during July and August and every fortnight from September to December. Gas samples were also taken once a week in the month before the application of pig slurry. Gas samples from 1 L jars were also sampled in the same dates as from cover boxes but only once a day.

Following the methodology described by Müller et al. (1998), the fraction of N_2O production due to denitrification in the jar incubation was expressed as the fraction I_{5Pa}/I_{0Pa}, where I_{5Pa} and I_{0Pa} were the geometrical mean of N_2O emission from incubation with 5 and 0 Pa C_2H_2, respectively. The N_2O emission due to denitrification from cover boxes (F_{den}) was calculated by multiplying the fraction I_{5Pa}/I_{0Pa} by daily N_2O flux (F_{day}), assuming that the fraction determined from the jar incubation was equal to the average daily fraction in the plots ($I_{5Pa}/I_{0Pa} = F_{den}/F_{day}$). Total N_2O-N emission due to denitrification, NO-N emission and denitrification losses per plot were estimated by successive linear interpolation of N_2O-N emissions, N_2O-N emissions due to denitrification (F_{den}), NO-N emission and denitrification rate, respectively, on the sampling days assuming that emissions followed a linear trend during the periods when no sample was taken. To estimate the total N_2O emission via denitrification (cover boxes) from denitrification losses (jar incubations) a factor for each treatment was calculated by dividing the N_2O emission due to denitrification by the denitrification losses in the whole experimental period in each treatment.

Analysis of soil and leaching

After sampling the headspace, the soil from each jar was thoroughly mixed and soil NO_3^- and NH_4^+ were determined by extracting 10 g of fresh soil with 100 mL 0.01 M $CaCl_2$; NO_3^- and NH_4^+ were determined colorimetrically using a Technicon AAII Auto-analyser (Technicon Hispania, Spain). To determine water-soluble organic carbon (WSC), extracts of soil were obtained and analysed as described by Mulvaney et al. (1997).

Water filled pore space (WFPS) (Figure 1) was calculated by dividing the volumetric water content by total soil porosity. Total soil porosity was calculated by measuring the bulk density of soil, according to the relationship: soil porosity = (1−soil bulk density/2.65); and assuming a particle density of 2.65 Mg m^{-3}. Soil temperature was monitored in the field using a temperature probe inserted 10 cm into the soil and connected with to a data logger. Rainfall data were obtained from the meteorological station located in the field. Drainage water was collected from the lysimeters every 2–3 days and stored in a refrigerator at 4 °C. NO_3^- N content in leachates was measured weekly by ion chromatograph using a HPLC (HP 1050) with an ionic conductivity detector (Metrohm 690 Ion Chromatograph). Leaching losses were calculated by multiplying the weekly drainage water by the NO_3^-–N concentration in the leachates.

Statistical methods

The statistical analysis was performed by using the STATGRAPHICS Plus 5.1. One-way ANOVA also served to establish the effect of fertiliser treatment with regard to the denitrification rate, N_2O, NO emissions, WSC and NO_3^-–N content in soil and leachates. The LSD test was used for multiple comparisons of means. Simple correlation analyses were performed to determine whether the N_2O, NO emission and denitrification rate were related in each of the treatments with WFPS, NO_3^-–N content, soil temperature and WSC.

Results

Environmental conditions, evolution of mineral N and soluble organic carbon

Water filled pore space was smaller than 50% before the irrigation period (Figure 1), but during the irrigation period WFPS values were often higher than 72%, especially from June 12th to September 1st due to daily irrigations during that period. After the irrigation period (September–December), WFPS ranged from 50% to 75%. The average daily soil temperature in the 0–10 cm soil layer (Figure 1) varied between 17 and 28 °C from June to September and between 5 and 16 °C from October to January.

The concentration of NH_4^+ declined rapidly after the application of fertilisers (Figure 2), although the IPS + DCD treatment maintained higher concentration than the IPS treatment between 7 and 20 days after the application. The soil NO_3^- content in the 10 cm upper layer was generally higher in the IPS treatment than in the other treatments during the first 30 days (Figure 2). In IPS + DCD treatment NO_3^- concentration was lower than the Control during the first 20–30 days, due to nitrification inhibition.

The application of pig slurry increased the WSC content, maintaining significant differences with Control during 40 days after irrigation (Figure 2). In the upper soil layer (0–10 cm), the average of the WSC content from the fertiliser application to the end of the irrigation period was 36 mg C kg^{-1} (SPS), 40.5 mg C kg^{-1} (IPS), 40.5 mg C kg^{-1} (IPS + DCD) and

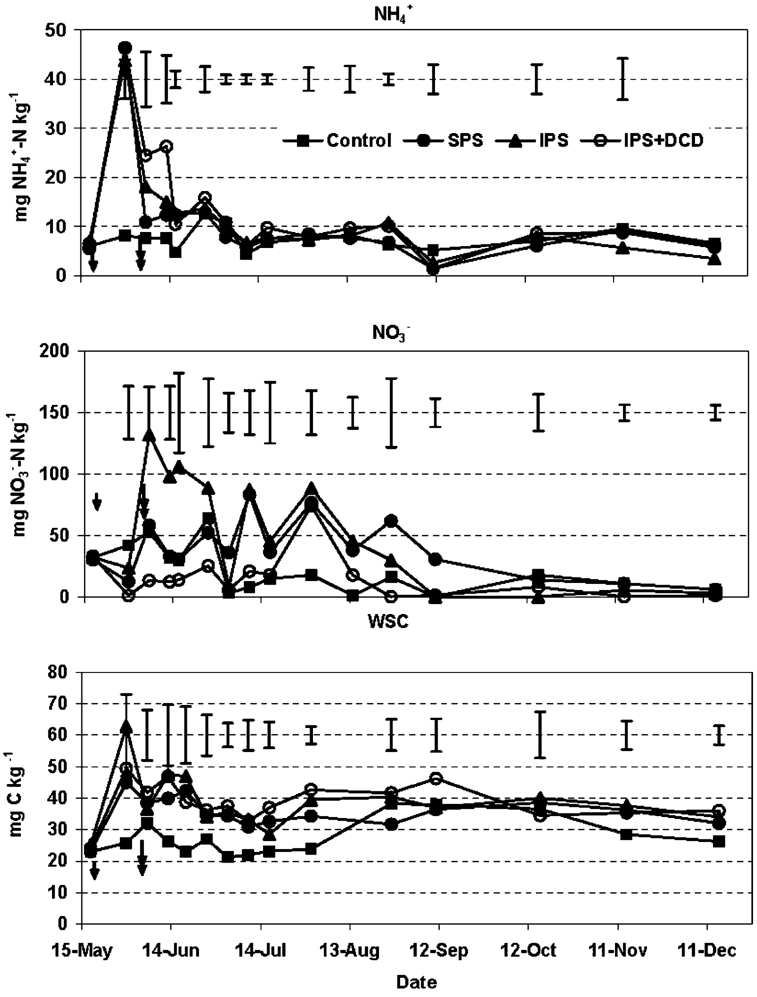

Figure 2. NO_3^- concentration, NH_4^+ and water soluble organic carbon (WSC) in the 0–10 cm soil layer during the experimental period. The single arrow indicates the date of pig slurry application; double-headed arrow, first irrigation. The vertical bars indicate LSD at 0.05 between treatments for each sample time.

28.0 mg C kg^{-1} (Control). After irrigation, the WSC content increased in all treatments.

Leached NO_3^-

The experiment took place in low drainage conditions. Mean drainage was 20.5 mm during the irrigation period, representing 5.1% of the total water applied as irrigation. The mean NO_3^- (Table 1) concentration in the leachates was 22.2 (SPS), 54.1 (IPS), 19.1 (IPS + DCD) and 7.3 mg NO_3^-–N L^{-1} (Control). Losses of N by leaching during the experimental period (215 days) were 0.78, 2.03, 0.45 and 0.11 g NO_3^- m^{-2} for SPS, IPS, IPS + DCD and the Control, respectively (Table 1). The percentage of N losses by leaching with respect to N applied, discounting the leached N in the Control, was 3.3% (SPS), 9.6% (IPS) and 1.7% (IPS + DCD). The nitrification inhibitor was efficient in reducing NO_3^- leaching (Figure 3).

$N_2O + N_2$ production from denitrification

Ten days after fertiliser application a first peak in denitrification rate (DR) was observed (Figure 4), but after 14 days the DR decreased very considerably due to the fact that WFPS diminished. The peak DR values were 291, 247 and 192 mg N m^{-2} d^{-1} for IPS, SPS and IPS + DCD, respectively. The first irrigation increased denitrification activity, and a second peak occurred 6 days

Table 1. Mean NO_3^- concentration in leachates, leached NO_3^--N, NO and N_2O emissions, N denitrification losses integrated over the experimental period

	Mean NO_3^- concentration in leachates (mg NO_3^- -N L^{-1})	Leached NO_3^--N (g N m^{-2})	Denitrification losses* (g N m^{-2})	Total N_2O emission (g N m^{-2})	Total NO emission (g N m^{-2})
Control	7.3 (2.3)a*	0.11 (0.02)a	1.77 (0.28)a	0.46 (0.05)a	0.028 (0.08)a
SPS	22.2 (5.9)b	0.78 (0.19)b	4.27 (0.85)b	0.78 (0.13)ab	0.056 (0.010)b
IPS	54.1 (6.7)c	2.03 (0.37)c	5.66 (0.65)b	1.05 (0.30)b	0.052 (0.015)b
IPS + DCD	19.1 (4.3)b	0.45 (0.10)ab	5.59 (0.89)b	0.56 (0.12)a	0.033 (0.019)a

*Denitrification from the upper (0–10 cm) soil layer.

**SDs are given in parentheses. Different letters within each column indicate significant differences between fertilizer treatment ($P < 0.05$) according to LSD test.

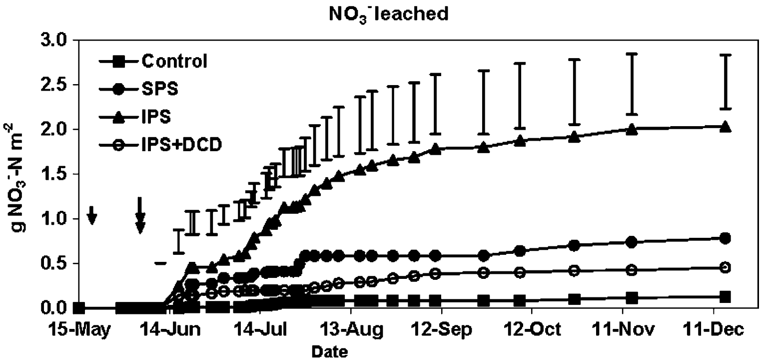

Figure 3. Nitrate leaching during the experimental period. The single arrow indicates the date of pig slurry application; double-headed arrow, first irrigation. The vertical bars indicate LSD at 0.05 between treatments for each sample time.

after the beginning of irrigation for the SPS (263 mg N m^{-2} d^{-1}) treatment and 12 days for the IPS (252 mg N m^{-2} d^{-1}), IPS + DCD (148 mg N m^{-2} d^{-1}) and Control (42 mg N m^{-2} d^{-1}) treatments. Twenty days after the first irrigation (2 July), there were no significant differences ($P < 0.05$) in DR between the treatments. In the October–December period, DR was lower than 10 mg N m^{-2} d^{-1} for all the treatments. The DR was significantly correlated with the WSC content ($r = 0.507^{***}$, $n = 60$) and with soil temperature ($r = 0.301^{*}$, $n = 60$) (Table 2). Nitrate in soil solution and WFPS were not correlated with DR.

The accumulated denitrification losses of the upper soil layer (0–10 cm) were significantly higher in pig slurry treatments than in the Control (Table 1). The nitrification inhibitor and the method of pig slurry application did not affect denitrification although values of SPS were slightly lower than ISP, but not significant at $P < 0.05$. Between 70% and 81% of the losses occurred in the 2 months following fertiliser application. After the irrigation period (from September to December), denitrification production was lower than 6% of the total denitrification losses, although WFPS was higher than 70% in November and December due to rain.

Under these conditions (low drainage), N losses by denitrification were higher than N losses by leaching: 2.8 times higher for IPS, 5.5 times for SPS, 12.4 times for IPS + DCD and 16.1 times for the Control.

N_2O fluxes

With the pig slurry treatments, the N_2O emission peaked ten days after the application reaching 105, 108, and 78 mg N m^{-2} d^{-1} for IPS, SPS, and IPS + DCD, respectively (Figure 4). No peak was found during the irrigation period (from June to September). Significant differences ($P < 0.05$) in N_2O emissions between plots with

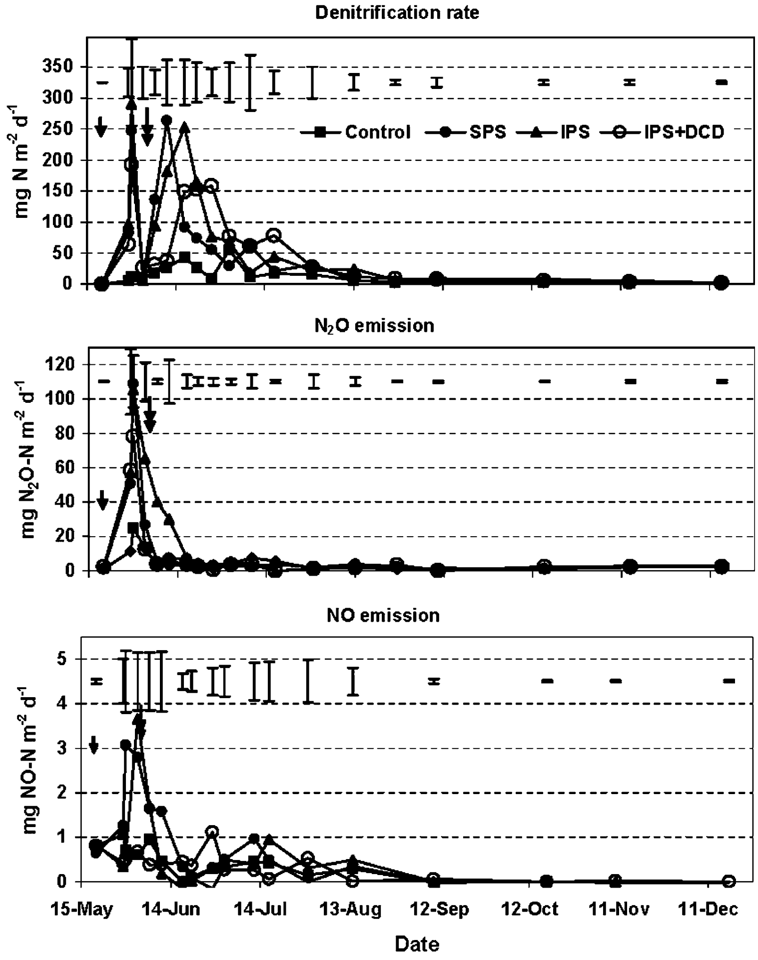

Figure 4. Denitrification rate, N_2O emission and NO emission during the experimental period. The single arrow indicates the date of pig slurry application; double-headed arrow, first irrigation. Vertical bars indicate LSD at 0.05 between treatments for each sample time.

injected and surface applied pig slurry were only detected from day 13 to 21 after pig slurry application. The incorporation of DCD in pig slurry was quite efficient at diminishing N_2O emissions, which reached similar emissions as the Control treatment. The N_2O emission was significantly correlated with the WSC content ($r = 0.484^{***}$, $n = 60$), NH_4^+ ($r = 0.834^{***}$, $n = 60$), soil temperature (0.433^{***}, $n = 60$) and denitrification ($r = 0.542^{***}$, $n = 60$), but not with WFPS and soil NO_3^- content (Table 2).

Total N_2O-N emissions during the 215 days ranged from 0.46 to 1.05 g N m^{-2} (Table 1). Discounting the N_2O lost in the Control, the percentage of N_2O lost in relation to the N applied during the experimental period was 1.60% (SPS), 2.95% (IPS) and 0.50% (IPS + DCD).

Denitrification was the main process responsible for N_2O emission, especially during the irrigation period. Following the method proposed by Müller et al. (1998), the percentage of total N_2O losses via the denitrification process was: 72%, 79%, 70% and 93% for the Control, SPS, IPS and IPS + DCD, respectively. Only before the irrigation period (from 20th May to 5th June), was N_2O emission via the nitrification process more important than via denitrification for the Control, SPS and IPS treatments. Obviously, nitrification rate was very low in IPS + DCD treatment during this first period. The factors to estimate the total N_2O emission via denitrification

Table 2. Correlation coefficients ($n = 60$) between NO emission, N_2O emissions and denitrification rate with some soil parameters

Soil parameter	Denitrification rate	N_2O emission	NO emission
WSC	0.507***	0.484***	NS
Soil NO_3^-	NS	NS	0.340**
Soil NH_4^+	NS	0.834***	0.396***
WFPS	NS	NS	NS
Soil Temperature	0.301*	0.433***	0.422**
Denitrification rate		0.542***	0.271*
N_2O emission			0.586***

Correlations significant at $P \leqslant 0.001$, 0.01 and 0.05 indicated with ***/**/* respectively.
NS is not significant at $P \leqslant 0.05$

(cover boxes) from denitrification losses (jar incubations) were 0.18 (Control), 0.13 (SPS), 0.12 (IPS) and 0.10 (IPS + DCD).

NO fluxes

In general, evolution of NO was similar to the pattern of N_2O (Figure 4). Pig slurry treatments had maximum emission between 10 and 15 days after slurry application (3.06 and 3.50 mg NO m^{-2} d^{-1} for SPS and IPS, respectively) and no significant differences ($P < 0.05$) were found between them. When irrigation took place, NO emission decreased and after the 21st of June emission was lower than 1.1 mg NO-N m^{-2} d^{-1} in all treatments. The nitrification inhibitor was very efficient at diminishing fluxes of NO, as these losses were similar to the Control from the first day after application. NO emission was correlated with denitrification ($r = 0.271^{*}$, $n = 60$), N_2O emission (0.586^{***}, $n = 60$), NO_3^- ($r = 0.340^{**}$, $n = 60$) NH_4^+ ($r = 0.396^{***}$, $n = 60$) and soil temperature (0.422^{**}, $n = 60$), but not correlated with the WSC content and moisture content.

In some samples from August to December, soil and/or cannopy consumed NO from the atmosphere and emission was below zero. This behaviour often occurred in the Control when soil conditions favoured denitrification.The total NO losses during the experimental period (Table 1) were slightly higher in SSP treatment than ISP, although these differences were not significant at $P < 0.05$. The nitrification inhibitor had an important effect in reducing NO losses.

The NO/N_2O ratio was lower than 1 in all sampling times. The mean value was 0.11, 0.06, 0.21 and 0.06 for SPS, IPS, IPS + DCD and Control, respectively.

Discussion

Effect of water availability on gas emissions

Soil moisture has an important effect on denitrification and nitrification processes and consequently on the emission of NO and N_2O. In irrigated agroecosystems the availability of water and the management of N fertilizer and manures are factors which have an important effect over the control of these emissions.

In the days following pig-slurry application, soil conditions (moisture and temperature) favoured nitrification instead of denitrification and most of the NO and N_2O emissions were due to this process. Nitrification is generally considered the main source of NO emission from soil and peaks of NO emission are often observed in the days following NH_4-N fertiliser application (Skiba et al., 1993). In the present experiment, a large amount of NO was also emitted in the days following fertiliser application (0–16 days). As a result, NO emission rates were significantly correlated with the soil NH_4^+ content. Although the amount of N_2O coming from nitrification is generally small (Sahrawat and Keeny, 1986), it can be large when pig-slurry is applied as it contains large quantities of NH_4^+. Within the experiment, the soil NH_4^+ content was correlated with the amount of N_2O, confirming that a fraction of N_2O was produced through nitrification. The large and rapid emission of N_2O after slurry application is in accordance with reports from other authors (Chadwick et al., 2000; Rochette et al., 2000; Stevens and Laughin, 2001; Yamulki et al., 1998).

Denitrification was the main source of the N_2O and NO emitted during the irrigation period, a behaviour that was also confirmed by the significant correlation of N_2O and NO emissions with the denitrification rate. The high soil moisture content after each irrigation and the high soil temperature favoured this process. However, in this experiment it has been proved that the application of water a few days after pig-slurry application decreased the nitrogen oxides emission in relation with the previous period, especially the NO emission, which diminished dramatically after the first irrigation. Under very wet conditions the NO and N_2O has low diffusivity to the atmosphere (Cárdenas et al., 1993). As nitrification is very limited after irrigation, a part of the NO and N_2O produced by denitrification could be consumed by denitrifier microorganisms resulting in little NO emission from soil (McKenney et al., 1982). The magnitude of N_2O emission depends on the N_2O:N_2 ratio, which generally decreases with increasing water filled pore space (WFPS) (Scholefield et al., 1997). From an environmental point of view, the low emission of NO from irrigated soils is important, because it reduces the risk of an increase in NO emission (and the associated increase in tropospheric ozone concentration) as a consequence of manure applications under irrigation conditions when denitrification dominates. Besides, when the soil NH_4^+ content is low, as frequently occurs in Mediterranean soils, the emission of NO from nitrification could only be important in the days following application of animal slurries or NH_4^+–N fertilizer. If the first irrigation is immediately applied after pig slurry application, it could result in a decrease of gaseous N emissions, especially NO. In this hypothetical scenario, ammonia volatilization could be also reduced.

Generally, NO_3^- leaching is considered to be one of the most important environmental problems in irrigated agroecosystems. A good management of irrigation is necessary for reducing drainage and consequently NO_3^- leaching losses. When evapotranspiration (ET) is high, as occurs during the summer in Mediterranean soils, a long period of time between two consecutive irrigations is not convenient because the risk of drainage increases when a great amount of water per application is used (Díez et al., 2001). Even when irrigation was spaced in the time, denitrification was very intense during the 5–6 days following water application (Vallejo et al., 2004). Results of this experiment indicated that when irrigation was controlled and low drainage was produced, loss of N due to denitrification was higher than by leaching. Because of this and from an agricultural point of view, denitrification losses must be taken into account in these farming systems in order to obtain an accurate assessment of the N balance.

The application of pig slurry markedly increased denitrification losses during the irrigation period because the water soluble carbon (WSC) content was also increased in soil with the pig-slurry application (Figure 2). In most Mediterranean-climate soils, organic matter is low ($<2\%$) and WSC is also frequently low. As water-soluble organic compounds are used by denitrifier microorganisms, an increase in the WSC content promotes denitrification (Rochette et al., 2000). WSC is a limiting parameter for denitrification in this soil and because of this denitrification rate (DR) was significantly correlated with the WSC content (Table 2).

Despite some evidence that denitrification can be greater by injection rather than by surface application of slurry (Pain et al., 1989; Thompson et al., 1987), in this study, no such effect was observed. This could be explained by the fact that there were no differences in WSC between the injected pig slurry (IPS) and surface-applied pig slurry (SPS) treatments during the whole experimental period. The dicyandiamide (DCD) application did not affect denitrification, because in this case the WSC content variations were neither observed between IPS nor IPS + DCD. In contrast, other authors (Merino et al., 2001; Pain et al., 1989) found a lower $N_2O + N_2$ production by denitrification when DCD was applied to slurry.

The percentage of applied N that was lost as N_2O during the experimental period (215 days) was 2.95% for IPS. The percentage lost with SPS was smaller (1.60%) because a large part of N was probably lost through ammonia volatilization. Although in this study ammonia volatilization was not measured, it can be assumed that N losses due to this process could be large when slurry was surface-applied (SPS) (Thompson et al., 1987), whereas if pig slurry was injected in the soil (IPS), losses could be low (Klarenbeek and Bruins, 1991). On the other hand, because the soil of the experimental plots was altered to install lysimeters, the NO and N_2O proportion could be slightly different than that from the unaltered soil, and absolute values must be viewed cautiously.

In the current IPCC methodology, the total amount of N applied is considered as the major factor controlling N_2O emission from agricultural soils. A single N_2O emission factor of 1.25% of total N applied is used for all types of fertilisers, manures and application techniques. If the results reported here are confirmed for other irrigated crops, it will be necessary to revise the factor used for the N_2O inventory in Mediterranean areas treated with pig-slurry. The estimated NO-N losses into the atmosphere during the experimental period were 0.14% of the N applied as fertiliser for the SPS and 0.12% for the IPS. These values agree with those measured by Gut et al. (1999) in cattle manure (0.14%) applied to wheat, but were lower than the measurements of Veldkamp and Keller (1997), who estimated that about 0.5% of fertiliser N applied to agricultural fields was emitted into the atmosphere as NO.

The methodology used to distinguish N_2O emission from nitrification and denitrification was based on the inhibition of the nitrification properties in the presence of 5–10 Pa C_2H_2 without blocking N_2O reductase in the denitrification pathway (Müller et al., 1998). We have used a 24 h incubation time, like Estavillo et al. (2002), in order to account for the effect of the temperature-dependent diurnal variation in nitrification and denitrification (Sánchez et al., 2001). Due to high spatial variability among cores distributed in the different jars and when denitrification predominated, in some samples the N_2O production without C_2H_2 ($I_{0\mathrm{Pa}}$) was lower than the N_2O production with 5 Pa C_2H_2 ($I_{5\mathrm{Pa}}$). In these cases, the N_2O production from nitrification ($I_{0\mathrm{Pa}}-I_{5\mathrm{Pa}}$) was considered zero, therefore the N_2O production came from denitrification. Estavillo et al. (2002) also criticised this method, but they concluded that it is useful for comparative purposes between treatments, although the absolute values obtained should be considered cautiously.

Williams et al. (1998) used the relative emission of NO and N_2O as a potential method to distinguish between soil nitrification and denitrification *in situ*. With the criteria of these authors, it can be said that denitrification rather than nitrification was also the dominant process in the period former to irrigation because the average molar ratio of NO-N–N_2O-N ranged from 0.007 to 0.026. The significant correlation between NO emission and denitrification agrees with this conclusion.

Effect of DCD on N_2O and NO emissions

Dicyandiamide was very efficient in reducing NO_3^- leaching, because these losses decreased more than 80% in relation with the IPS treatment. This behaviour was a consequence of an efficient inhibition of nitrification during the first 20–30 days. This short-term inhibitory effect of DCD could be explained by the drainage conditions and the high temperature observed after the application. A part of the DCD could have leached under drainage conditions (Abdel-Sabour et al., 1990) and according with Guiraud and Marol (1992) the persistence of DCD in soil was inversely related to the soil temperature. In temperate climates with lower temperatures than the Mediterranean climate, a persistence period higher than 1–2 months has been observed (Cookson and Cornforth, 2002). In spite of this difference, we think that in this type of agroecosystem, with both high temperature and moisture due to irrigation, the nitrification inhibitor is useful to reduce nitrate leaching when drainage is produced in the days following the application of animal slurries.

Dicyandiamide did not entirely prevent nitrification, partly due to the uneven distribution of the inhibitor, resulting in some nitrification of NH_4^+ derived from organic matter in microsites not penetrated by the DCD (Skiba et al., 1993). In the present experiment, the efficiency of DCD to reduce the N_2O and NO emissions from pig-slurry was lower than that reported by McTaggart et al. (1994), for N_2O emission from a grassland soil, and by Skiba et al. (1993) for NO in $(NH_4)_2SO_4$ treated with DCD in a greenhouse experiment. As DCD did not inhibit denitrification it can be assumed that a large amount of these gases came from denitrification when pig-slurry was treated with DCD. In fact, the NO-N to N_2O-N ratio was also the lowest for the IPC + DCD treatment during the non-irrigated period, and this also occurred when $(NH_4)_2SO_4$ was treated with DCD (Skiba et al., 1993).

In spite of the short persistence period of DCD in irrigated soils during the summer, we think DCD could be efficient in reducing NO and N_2O fluxes in the following days of animal-slurry application.

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