



# Management of pig manure to mitigate NO and yield-scaled N<sub>2</sub>O emissions in an irrigated Mediterranean crop



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## ABSTRACT

Substitution of conventional mineral fertilizers with organic sources can avoid the environmental problems associated with high concentrations of intensive livestock production in some Mediterranean areas. Some management practices, such as the use of nitrification inhibitors or more efficient irrigation techniques (e.g., drip irrigation), have been suggested as effective alternatives to mitigate nitrous oxide (N<sub>2</sub>O) and nitric oxide (NO) emissions released from soils amended with synthetic and organic fertilizers. In this experiment, we aimed to assess the effect of different organic amendments derived from pig manure (control without N fertilization (C); liquid fraction of pig slurry (LFPS); pig urine with the nitrification inhibitor 3,4 dimethylpyrazolephosphate (DMPP) (LFPSI); compost from the solid phase of pig slurry (COM)) compared to urea (U) and two different irrigation systems (the widespread sprinkler and alternative drip irrigation systems) on greenhouse gas (N<sub>2</sub>O, methane, CH<sub>4</sub>, and carbon dioxide, CO<sub>2</sub>) and NO emissions in a maize (*Zea mays* L.) crop. The effect of these treatments on crop yields and yield-scaled N<sub>2</sub>O emissions were also evaluated. The use of DMPP with LFPS was an effective practice to reduce N<sub>2</sub>O and NO losses (40 and 32% mitigation, respectively, compared to LFPS alone), and was also associated with the highest rates of CH<sub>4</sub> oxidation. Drip irrigation significantly reduced the global warming potential (in spite of a lower CH<sub>4</sub> sink) but increased the NO losses by 58%, as opposed to sprinkler irrigation. The higher biomass production and similar grain yields observed with drip irrigation resulted in lower yield-scaled N<sub>2</sub>O emissions in this treatment than in sprinkler irrigation. The use of organic fertilizers penalized grain yields compared to U (16–33%), although the differences were not significant in the case of LFPSI. Consequently, LFPSI in drip irrigation was (together with U applied by drip-fertigation) the treatment that led to the lowest yield-scaled N<sub>2</sub>O emissions. The use of organic N sources in irrigated maize is an environmentally advisable strategy in Mediterranean cropping systems, but an optimum balance between N oxides and greenhouse gas losses, N efficiency and crop yields requires the use of nitrification inhibitors (e.g., DMPP) with liquid organic sources.

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## 1. Introduction

Some Mediterranean countries, such as Spain, France or Italy, belong to the 10 world-leading countries in number of pigs (FAO, 2014). Certain regions of these countries have dense concentrations of intensive fattening pigs per unit of utilized agricultural area, so the management of pig manure is a problem of crucial environmental and economic interest. In these areas, with the implementation of strategies such as *in situ* separation of the solid

and liquid fractions of pig slurry, it is possible to obtain solid manure that can be composted and consequently transported, stored and applied less expensively as organic fertilizer (Alonso et al., 2010).

The use of both the solid and liquid phases of slurries as nitrogen (N) fertilizers has been reported as a major source of ammonia (NH<sub>3</sub>) emissions (Sanz-Cobena et al., 2010) and also has the potential risk of increasing the emission of nitrous oxide (N<sub>2</sub>O) (Chadwick et al., 2011) and nitric oxide (NO) (Sanchez-Martín et al., 2010). Some effective NH<sub>3</sub> mitigation strategies, such as the incorporation of manures/slurries (Sanz-Cobena et al., 2014a), have shown the trade-offs of increasing N<sub>2</sub>O emissions under favourable soil conditions (Chadwick et al., 2011). Nitrous oxide

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contributes to ozone depletion and accounts for 6.2% of the anthropogenic greenhouse effect (IPCC, 2014). Nitric oxide, a highly reactive constituent of the troposphere, is produced mainly through fossil fuel combustion and biomass burning. However, agricultural soils are major sources of this reactive N form in rural areas, reaching almost  $9 \text{ N Tg y}^{-1}$  (Medinets et al., 2015). Therefore, it is important to find management strategies to provide the best balance between the mitigation of all N emission forms.

Nitrogen oxides are by-products of soil biochemical processes in agricultural soils, mainly nitrification and denitrification (Firestone and Davidson, 1989), which are directly related to soil moisture, with low values of water-filled pore space (WFPS) favouring nitrification (WFPS <60%). Although denitrification has been described as the process leading to the highest  $\text{N}_2\text{O}$  emissions (Williams et al., 1992), nitrification has been described as a major contributor of  $\text{N}_2\text{O}$  emissions, and particularly of NO emissions (Skiba et al., 1997), in semi-arid areas and low C-content soils, e.g., in the Mediterranean (Aguilera et al., 2013). Several studies reported that mixing nitrification inhibitors (NIs) with liquid manure can prevent large  $\text{N}_2\text{O}$  losses from nitrification (due to the inhibition of the oxidation of ammonium ( $\text{NH}_4^+$ ) to nitrate ( $\text{NO}_3^-$ )) (Pereira et al., 2010; Misselbrook et al., 2014). The vast majority of experiments reporting N emissions abatement with NIs have evaluated the use of dicyandiamide (DCD), particularly with sheep/cattle liquid manures in humid climates. To date, few studies have evaluated the use of the NI 3,4-dimethyl pyrazole phosphate (DMPP) with liquid manure, particularly with pig urine/slurry, as a potential tool to mitigate both  $\text{N}_2\text{O}$  and NO emissions in Mediterranean areas.

Due to the influence of soil N and WFPS in the processes leading to N oxide emissions, an integrated assessment of the best mitigation strategies requires the evaluation of different fertilizer and irrigation treatments and their interactions. Irrigation systems that lead to water saving (e.g., drip irrigation) are pivotal strategies to improve the sustainability of Mediterranean agro-ecosystems, characterized by water scarcity (Vallejo et al., 2014). Moreover, some studies have reported a lower amount of  $\text{N}_2\text{O}$  release from drip-irrigated soils, as opposed to conventional furrow irrigation (Sánchez-Martín et al., 2008; Kallenbach et al., 2010), as the low amount of water applied creates less favourable conditions for denitrification. Although sprinkler is a widely adopted irrigation system in summer Mediterranean crops, e.g. maize (MAGRAMA, 2013), the area of this crop under drip irrigation is expected to increase due to the higher water use efficiency, similar yields and technical viability, as reported by Couto et al. (2013). This system could also allow the implementation of split applications of fertilizer N dissolved in the irrigation water (drip fertigation). Potential side effects of drip irrigation on N oxide emissions, as opposed to sprinkler, are still poorly understood.

In some Mediterranean regions with intensive pig production, the use of manures at seeding complemented with the application of synthetic fertilizers at dressing, is a widespread fertilization strategy in summer irrigated crops (e.g. maize). Some management strategies can be implemented in addition to this practice to mitigate N oxides losses such as (i) the use of NIs with liquid manures, (ii) the use of a compost from the solid manure, due to the lower rate of N mineralization (Aguilera et al., 2013) or (iii) the use of irrigation systems which lead to lower soil water contents (e.g. drip), decreasing large  $\text{N}_2\text{O}$  losses from denitrification.

To identify the most effective GHG mitigation strategies, the side effects on methane ( $\text{CH}_4$ ) uptake, which is affected by soil water content and mineral N (Tate, 2015) and carbon dioxide ( $\text{CO}_2$ ) emission from the soils, need to be considered. Moreover, the effect of irrigation and fertilization techniques on crop yields and N efficiency should also be considered to find strategies potentially acceptable to farmers. In this context, a field experiment was

carried out evaluating the effect of the irrigation system (sprinkler versus drip) and fertilization (partially replacing urea at dressing with organic fertilizers derived from pig manure at seeding) on GHG and NO emissions and crop yields. As the type (liquid/solid) of organic fertilizers has been demonstrated to affect  $\text{N}_2\text{O}$  emissions (Aguilera et al., 2013), both the liquid fraction of pig slurry (with and without DMPP) and a compost from the solid fraction were evaluated. We hypothesized that (i) splitting N fertilizer application, using organic fertilizers at seeding (2 months before the start of irrigation) and urea at dressing (during the irrigation period), would reduce total N oxides emissions in comparison to a single application of urea at dressing; (ii) the use of DMPP with liquid organic sources would mitigate N oxide emissions and increase N efficiency and crop yields, in agreement with Abalos et al. (2014a) and Qiao et al. (2015); and (iii) the drip irrigation system would also mitigate  $\text{N}_2\text{O}$  fluxes, with possible side effects enhancing NO emissions.

## 2. Materials and methods

### 2.1. Site description

The study was carried out at “El Encín” field station in Madrid (latitude  $40^\circ 32' \text{N}$ , longitude  $3^\circ 17' \text{W}$ ). The soil was a *Calcic Haploxerept* (Soil Survey Staff, 1992) with a sandy clay loam texture (clay, 28%; silt, 17%; sand, 55%) in the upper horizon (0–28 cm) with vermiculite as a dominant clay mineral. Some relevant characteristics of the top 0–28 cm soil layer are as follows: total organic C,  $8.1 \pm 0.3 \text{ g kg}^{-1}$ ;  $\text{pH}_{\text{H}_2\text{O}}$ , 7.6; bulk density,  $1.4 \pm 0.1 \text{ g cm}^{-3}$ ; and  $\text{CaCO}_3$ ,  $13.2 \pm 0.4 \text{ g kg}^{-1}$ . At the beginning of the experimental period, the  $\text{NH}_4^+$  content was  $1.0 \text{ mg NH}_4^+ \text{--N kg soil}^{-1}$ ; the  $\text{NO}_3^-$  content was  $15.9 \text{ mg NO}_3^- \text{--N kg soil}^{-1}$ ; and the dissolved organic C (DOC) content was  $50.8 \text{ mg C kg soil}^{-1}$ . The site has a semi-arid Mediterranean climate with a dry and hot summer period, and the mean annual temperature and rainfall (over the last 10 years) in this area are  $13.2^\circ \text{C}$  and 460 mm, respectively.

Rainfall and temperature data were obtained from a meteorological station located at the field site (CR23X micro logger, Campbell Scientific, Shepshed, UK, equipped with a Young<sup>®</sup> tipping bucket rain gauge (RM Young Company, Michigan, USA)). The soil temperature was monitored using a temperature probe (SKTS 200, Skye Instruments Ltd., Llandrindod Wells, UK) inserted 10 cm into the soil. The mean hourly data were stored on a data logger (DataHog, Skye Instruments Ltd., Llandrindod Wells, UK).

### 2.2. Experimental design and management

A total of 30 subplots ( $7 \text{ m} \times 6.5 \text{ m}$ ) were established in a three-replicated *split plot* design with two irrigation treatments (Sprinkler, S, and Drip, D) and 5 fertilization treatments: (i) compost from pig manure at seeding + urea at dressing (COM); (ii) liquid fraction of pig slurry at seeding + urea at dressing (LFPS); (iii) liquid fraction of pig slurry with NI 3,4 dimethylpyrazolephosphate (DMPP) at seeding + urea at dressing (LFPSI); (iv) urea (U) applied at dressing on the soil surface (in the S plots) and by drip-fertigation (in the D plots) as two contrasting synthetic fertilization techniques; and (v) a control (C) with no N fertilizer application. The N source, application date and N rate for each treatment are specified in Table 1. All treatments (except the control) received  $180 \text{ kg N ha}^{-1}$ . The DMPP was applied at a rate of 0.8% of  $\text{NH}_4^+ \text{--N}$  content in LFPS.

The LFPS was mechanically separated (Alonso et al., 2010) and collected from an experimental farm of the Technical University of Madrid. The compost was made (during 4 months) of the solid fraction of pig slurry and a mix of stover and pruning of different

**Table 1**

Source and rate of organic and synthetic N fertilizers in each fertilization event for the evaluated treatments (C, control, U, urea, COM, compost, LFPS, liquid fraction of pig slurry, LFPSI, liquid fraction of pig slurry + DMPP, S, sprinkler irrigation, D, drip irrigation).

Treatment	Amount of N applied (kg ha <sup>-1</sup> )			
	Seeding fertilization 5th May	Dressing fertilization 17th June	Fertigation 7th July <sup>a</sup>	Fertigation 23th July <sup>a</sup>
	Organic	Urea	Urea	Urea
C-D, C-S	–	–	–	–
U-S	–	180	–	–
U-D	–	–	90	90
COM-S, COM-D	120	60	–	–
LFPS-S, LFPS-D	120	60	–	–
LFPSI-S, LFPSI-D	120	60	–	–

<sup>a</sup> And next irrigation events.

crops. The main physico-chemical properties of COM and LFPS are summarized in Table 2.

A cultivator pass was performed on 11th April 2014. A basal fertilization was applied on 30th April 2014, spreading by hand 50 kg P ha<sup>-1</sup> and 150 kg K ha<sup>-1</sup> as Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> and K<sub>2</sub>SO<sub>4</sub>, respectively, in all the plots. In the case of the organic amendments, the P and K content was analysed and taken into account to re-calculate the amount of synthetic P and K added.

All the organic fertilizers were spread over the plots' surface before maize sowing, and a cultivator pass was subsequently performed on 6th May 2014. The maize (*Zea mays* L. FAO class 600) was seeded on 7th May 2014 in a plant population density of 7.50 plants m<sup>-2</sup>. The urea applied at dressing was also spread by hand in all treatments except C-S, C-D (with no N-fertilizer applied) and U-D, in which the urea was applied by fertigation. The fertigation was split into two applications (Table 1), starting on 7th July 2014 (at 6 pair of leaves stage, applying 90 kg ha<sup>-1</sup> during three irrigation events) and 23th July 2014 (at 10–12 pair of leaves stage, applying the remaining 90 kg ha<sup>-1</sup> in two irrigation events). A non-electric proportional dispenser (Dosatron DI16-11GPM, Dosatron International Inc., Bordeaux, France) was used to inject the correct rate of N fertilizer in each fertigation event. This system used water pressure (0.3–6 bar) as the driving force to suck up the fertilizers from the tank and mix them homogeneously with the irrigation water. This process took place in a mixer section to assure the correct application rate, independent of the water flow or pressure variations.

Irrigation, which occurred from 26th May to 19th September, was applied in the D plots by a surface drip irrigation system that included one pressure-compensated drip irrigation line for each two maize lines. Consequently, each subplot had half of the surface between rows with drip lines ("wet area") and without drip lines ("dry area"). Each line had 0.33-m-apart emitters (nominal discharge of 4 L h<sup>-1</sup>), 0.33 m apart. In the S plots, irrigation was performed by an installed 12 m × 12 m sprinkler irrigation system at a height of 2.5 m. A net amount of 688 mm of water was applied

**Table 2**

Chemical composition (g kg<sup>-1</sup>) of organic fertilizers (COM, compost, LFPS, liquid fraction of pig slurry).

Parameter	Concentration (g kg <sup>-1</sup> )	
	LFPS	COM
Total N	4.62	9.10
N-NH <sub>4</sub> <sup>+</sup>	4.22	1.70
N-NO <sub>3</sub> <sup>-</sup>	–	0.02
P <sub>2</sub> O <sub>5</sub>	–	0.08
DOC	4.30	13.31
K	4.80	20.35
Zn	0.01	0.23
Cu	–	0.12

through 32 and 48 irrigation events for the sprinkler and drip irrigation, respectively (Fig. S3).

The water doses to be applied were estimated from the crop evapotranspiration (ET<sub>c</sub>) of the previous week (net water requirements). This was calculated daily as ET<sub>c</sub> = K<sub>c</sub> × ET<sub>o</sub>, where ET<sub>o</sub> is the reference evapotranspiration calculated by the FAO Penman-Monteith method (Allen et al., 1998) using data from a meteorological station located in the experimental field. The crop coefficient (K<sub>c</sub>) was obtained for the maize crop following the method of Allen et al. (1998). The field was kept free of weeds, pests and diseases, following local practices (i.e., herbicides). The maize was harvested on 24th October 2014, and the maize stover was left on the ground and subsequently incorporated by a cultivator pass.

### 2.3. GHG and NO sampling and analyses

The fluxes of N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> were measured from April 2014 to May 2015 using opaque manual circular static chambers as described in detail by Sanz-Cobena et al. (2014b). One chamber (diameter 35.6 cm, height 19.3 cm) was located in each sub-plot in the S plots. In the D plots, two chambers (one in the wet and one in the dry areas) were established. The chambers were hermetically closed (during 1 h) by fitting them into stainless steel rings, which were inserted at the beginning of the study into the soil to a depth of 5 cm to minimize the lateral diffusion of gases and avoid the soil disturbance associated with the insertion of the chambers in the soil. The rings were only removed during management practices.

Gas samples were taken twice per week during the first month after all fertilization events (Table 1). Then, the gas sampling frequency was gradually decreased until the end of the experiment (May 2015). To minimize any effects of diurnal variation in emissions, the samples were taken at the same time of day (10–12 a.m.) (Reeves and Wang, 2015). Measurements of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> emissions were made at 0, 30 and 60 min to test the linearity of gas accumulation in each chamber. The increases in N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> concentrations within the chamber headspace were generally (>80% of cases) linear (R<sup>2</sup> > 0.90) during the sampling period (1 h).

The concentrations of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> were quantified by gas chromatography, using a HP-6890 gas chromatograph (GC) equipped with a headspace autoanalyzer (HT3), both from Agilent Technologies (Barcelona, Spain). HP Plot-Q capillary columns transported the gas samples to a <sup>63</sup>Ni electron-capture detector (ECD) to analyse the N<sub>2</sub>O concentrations and to a flame-ionization detector (FID) fitted with a methanizer for the CH<sub>4</sub> and CO<sub>2</sub> concentrations. Helium was used as the carrier gas. The ECD was run with Ar-CH<sub>4</sub> as the make-up gas. The temperatures for the column and ECD detector were maintained at 40 °C and 300 °C, respectively. The oven and FID were operated at 50 °C and 300 °C, respectively. The precision of the gas chromatographic data at ambient GHG concentrations was ± 1% or better. Two gas standards

comprising a mixture of gases (high standard with  $1500 \pm 7.50$  ppm CO<sub>2</sub>,  $10 \pm 0.25$  ppm CH<sub>4</sub> and  $2 \pm 0.05$  ppm N<sub>2</sub>O and low standard with  $200 \pm 1.00$  ppm CO<sub>2</sub>,  $2 \pm 0.10$  ppm CH<sub>4</sub> and  $200 \pm 6.00$  ppb N<sub>2</sub>O) were provided by Carbueros Metalicos S.A. and Air Products SA/NV, respectively, and used to produce a calibration curve for each gas. The response of the GC was linear within 200–1500 ppm for CO<sub>2</sub> and 2–10 ppm CH<sub>4</sub> and quadratic within 200–2000 ppb for N<sub>2</sub>O.

A gas flow-through system was used to measure the NO fluxes. One chamber per plot was used for this analysis (volume 22 L, diameter 35 cm and height 23 cm). In this case, the interior of the chamber was covered with Teflon<sup>®</sup> to minimize the reactions of NO<sub>x</sub> with the walls and provided with inlet and outlet holes (Abalos et al., 2014b). The nitric oxide was analysed using a chemiluminescence detector (AC31M-LCD, Environnement S.A., Poissy, France). During this measurement, air (filtered through a charcoal and aluminium/KMnO<sub>4</sub> column to remove O<sub>3</sub> and NO<sub>x</sub>) was passed through the headspace of the chamber, and the gas samples were pumped from the chambers at a constant flow rate to the detection instruments through Teflon<sup>®</sup> tubing. An ambient air sample was measured between each gas sampling. As proposed by Kim et al. (1994), the NO flux was calculated from a mass balance equation, considering the flow rate of the air through the chamber and the increase in NO concentration with respect to the control (empty chamber) when the steady state was reached.

#### 2.4. Soil and crop analyses

To relate the gas emissions to the soil properties, soil samples were collected from the 0–10 cm depth during the experimental period on almost all gas-sampling occasions, particularly after each fertilization event. Three soil cores (2.5 cm diameter and 15 cm length) were randomly sampled close to the ring in each plot and then mixed and homogenized in the laboratory. The soil NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N concentrations were analysed using 8 g of soil extracted with 50 mL of KCl (1 M) and measured by automated colorimetric determination using a flow injection analyzer (FIAS 400 PerkinElmer) provided with a UV-vis spectrophotometer detector. The soil DOC was determined by extracting 8 g of homogeneously mixed soil with 50 mL of deionized water and then analysing the result with a total organic C analyzer (multi N/C 3100 Analytik Jena) equipped with an IR detector. The WFPS was calculated by dividing the volumetric water content by the total soil porosity. The total soil porosity was calculated according to the following relationship: soil porosity =  $(1 - \text{soil bulk density}/2.65)$ , assuming a particle density of  $2.65 \text{ g cm}^{-3}$  (Danielson et al., 1986). The gravimetric water content was determined by oven-drying soil samples at 105 °C with a MA30 Sartorius<sup>®</sup> moisture analyzer.

The maize was harvested at physiological maturity (black-layer stage). One sample in each plot, consisting of 5 Lm, was collected to determine the total grain (at 14% moisture level) and above-ground biomass yields. The total C and N content of the maize grain and above-ground biomass were determined by elemental analysis with a LECO TruMac CN analyzer<sup>®</sup>.

#### 2.5. Calculations and statistical methods

The cumulative N<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub> and NO fluxes were estimated by successive linear interpolations between the sampling dates. Three different periods were considered for soil and GHG data reporting and analysis: Period I (from maize sowing to the beginning of dressing fertilization), Period II (from dressing fertilization to September -end of the irrigation period-) and Period III (from September to the end of the experiment). The cumulative fluxes of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> in the drip-irrigated plots were calculated considering the weighted average, taking into account the surface

area of each zone (wet: with drip irrigation line and dry: without drip irrigation line) within the plot (Abalos et al., 2014b). In addition, the cumulative fluxes of the wet and dry areas were also compared. The yield-scaled N<sub>2</sub>O emissions (YSNE) were expressed as the ratio between the amount of N emitted as N<sub>2</sub>O and the above-ground N uptake, while the N surplus was calculated as the N application minus the above-ground N uptake (van Groenigen et al., 2010). The global warming potential (GWP) of the N<sub>2</sub>O and CH<sub>4</sub> emissions was calculated in units of CO<sub>2</sub> equivalents over a 100-year time horizon. A radiative forcing potential relative to CO<sub>2</sub> of 265 was used for N<sub>2</sub>O and 28 for CH<sub>4</sub> (Myhre et al., 2013).

The analysis of data was performed using the *Statgraphics Plus v. 5.1*. Analyses of variance were performed for all variables throughout the experiment. Data distribution normality and variance uniformity were previously assessed by Shapiro-Wilk test and Levene's statistic, respectively, and log-transformed before analysis when necessary. The means were separated by Tukey's honest significance test at  $P < 0.05$ . For non-normally distributed data, the Kruskal-Wallis test was used on non-transformed data to evaluate the differences at  $P < 0.05$ . Linear correlations were carried out to determine the relationships between the gas fluxes and WFPS, soil temperature, DOC, NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N. These analyses were performed using the mean/cumulative data of the replicates of all the fertilizer-irrigation treatments ( $n = 45$ , including both dry and wet areas of the D plots), and also for all the dates when the soil and GHG were simultaneously sampled ( $n = 32$ ).

### 3. Results

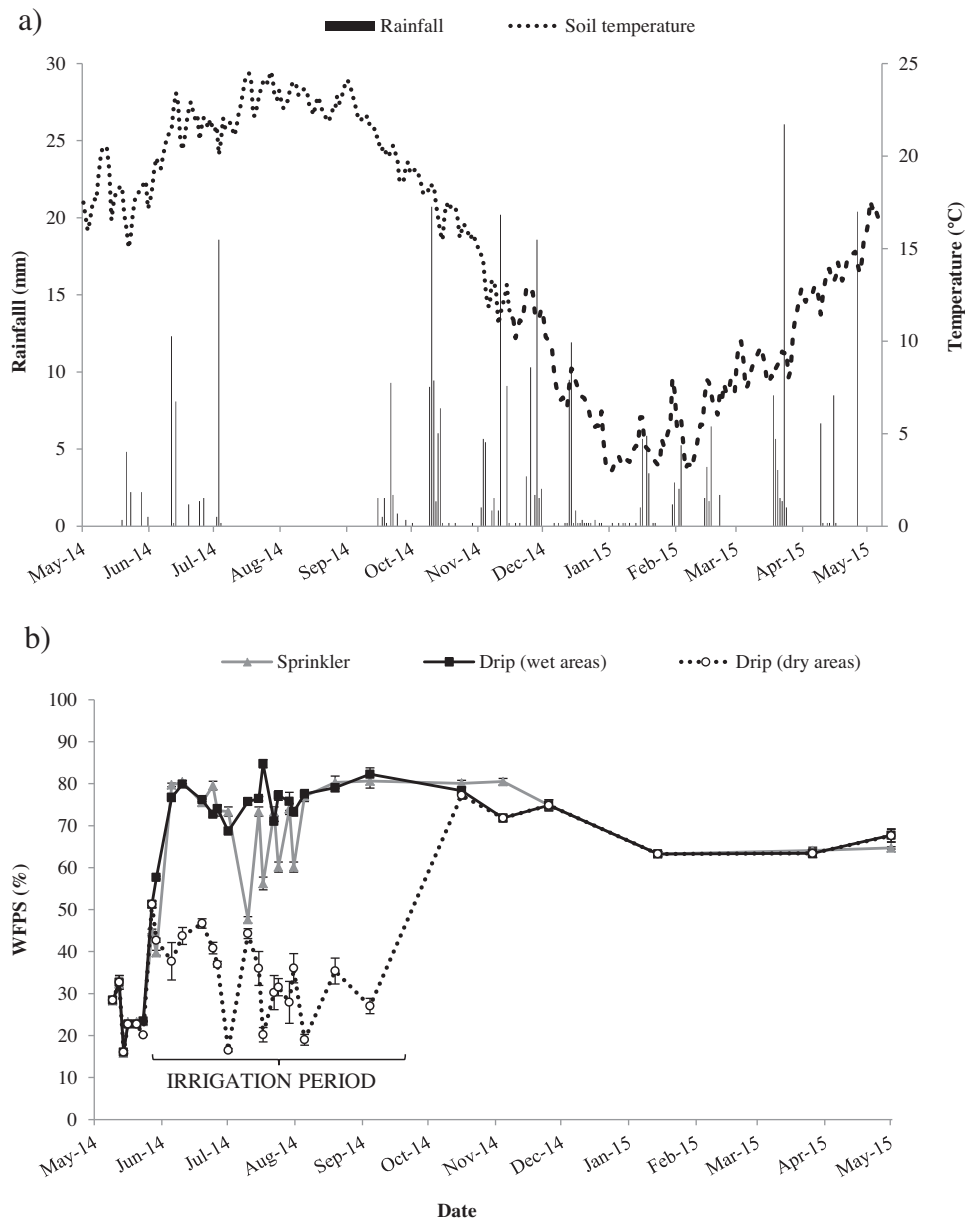
#### 3.1. Environmental conditions and WFPS

The mean soil temperature during the maize crop period was 20.7 °C, ranging from 15.0 to 24.6 °C (Fig. 1a), which were typical values in the experimental area. During Period III, the mean soil temperature was 9.2 °C. The accumulated rainfall was 127 and 241 mm during the maize and intercrop periods, respectively. The evolution of WFPS in the S and D plots is shown in Fig. 1b. The values ranged from 16 to 84% during the maize cropping period. The WFPS fluctuated more in the S plots (two irrigation events per week) than in the D plots (three irrigation events per week) during the irrigation period. The dry areas in the D plots maintained significantly lower WFPS values than the wet areas or the S plots ( $P < 0.05$ ), except after rainfall events (e.g., the first week of July) or when irrigation was not carried out (Fig. 1b).

#### 3.2. Mineral N and DOC

The topsoil NH<sub>4</sub><sup>+</sup> content increased rapidly after seeding (in the organic treatments) and dressing with N fertilization (in the organic treatments and U) (Fig. 2a, b). The NI DMPP significantly increased the NH<sub>4</sub><sup>+</sup> concentration during Period I in the LPSI treatment compared to the LFPS treatment, particularly after the beginning of the irrigation period (Fig. 2a, b). When the synthetic fertilizer (urea) was added at dressing, the LFPSI treatment also showed higher NH<sub>4</sub><sup>+</sup> levels than those in LFPS on some sampling dates, particularly in the dry areas of the D plots (Fig. S1b). In the S plots, the NH<sub>4</sub><sup>+</sup> concentrations decreased to values below 10 mg N kg soil<sup>-1</sup> from one week after dressing fertilization until the end of the experimental period, although an increment (17.6 mg N kg soil<sup>-1</sup>) was observed in the COM-S subplots 1–2 months after dressing fertilization (Fig. 2a). In the D plots, the NH<sub>4</sub><sup>+</sup> concentrations remained above 10 mg N kg soil<sup>-1</sup> for a longer period of time in some fertilizer treatments, (Fig. 2b), particularly in the dry areas (Fig. S1a, b). In the U treatment, a large and transitory increment was observed in the S plot (2 days after dressing





**Fig. 1.** (a) Daily mean soil temperature ( $^{\circ}\text{C}$ ) and rainfall (mm) and b soil WFPS (%) in the sprinkler and drip irrigation plots (wet and dry areas). The maize was seeded on 7th May 2014 and harvested on 24th October 2014. Vertical bars indicate the standard errors.

fertilization, reaching  $151.2 \text{ mg N kg soil}^{-1}$ ), while in the D plots (U applied by fertigation), these increments were much lower (Fig. 2b) because they were not observed in the dry areas (Fig. S2b).

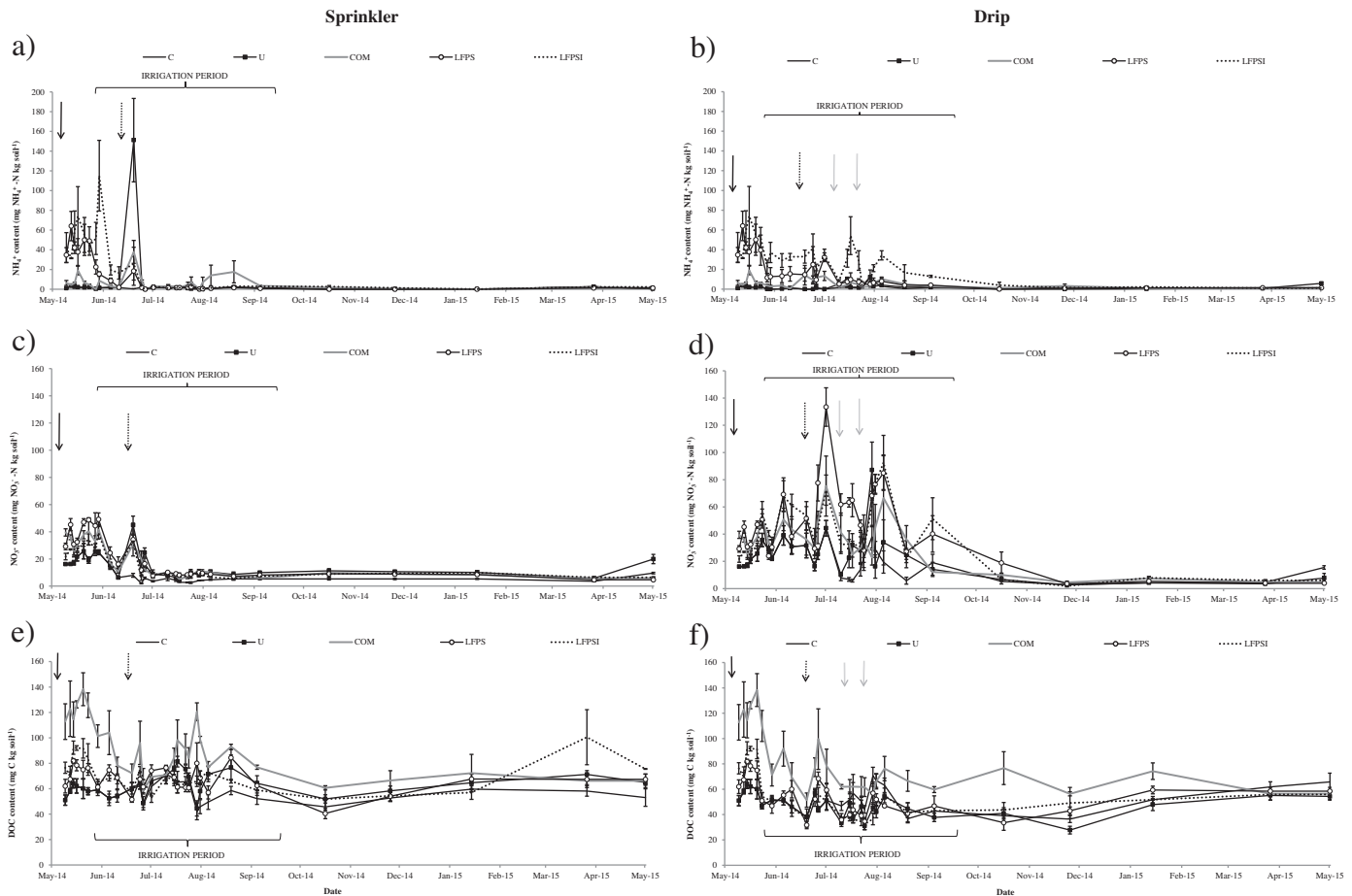
The  $\text{NO}_3^-$  concentrations peaked after both fertilization events (Fig. 2c, d). The topsoil  $\text{NO}_3^-$  content was significantly lower ( $P < 0.05$ ) in LFPSI than in LFPS on some sampling dates and on average. This effect was persistent even after dressing fertilization in the D plots (Fig. 2d). A significant effect of the irrigation system on the  $\text{NO}_3^-$  evolution pattern was observed. In the S plots and the wet areas of the D plots, the  $\text{NO}_3^-$  topsoil concentrations remained below  $15 \text{ mg N kg soil}^{-1}$  from mid-August until the end of the experimental period (Fig. 2c, S1c), while in the dry areas of the D plots, the concentrations were maintained at a higher level until mid-November (Fig. S1d). On average, the  $\text{NO}_3^-$  concentrations were significantly lower ( $P < 0.01$ ) in the S than in the D plots and in the dry areas than in the wet areas of the D plots ( $P < 0.05$ ). As observed for  $\text{NH}_4^+$ , the highest  $\text{NO}_3^-$  peak in the S plots after

dressing fertilization ( $44.9 \text{ mg N kg soil}^{-1}$ ) was observed in the U treatment (Fig. 2c). In the D plots, increments in U were noticed after the fertigation events (reaching  $87.1 \text{ mg N kg soil}^{-1}$ ) and were also higher in the wet areas because the urea was applied with the irrigation water. The evolution of the DOC topsoil concentration is shown in Figs. 2e and f, ranging from 28 to  $138 \text{ mg C kg soil}^{-1}$ . The average values were significantly higher in the COM subplots than in the other fertilizer treatments ( $P < 0.05$ ).

### 3.3. Gaseous emissions

#### 3.3.1. Nitrous oxide emissions

The daily  $\text{N}_2\text{O}$  fluxes of the different fertilizer and irrigation treatments, from May to mid-August (to improve the ease of visualization), are shown in Fig. 3a and b. Thereafter, the fluxes were always below  $0.2 \text{ mg N m}^{-2} \text{ d}^{-1}$ , and small differences were observed among the fertilizer/irrigation treatments (Period III,



**Fig. 2.** (a, b)  $\text{NH}_4^+\text{-N}$ ; c, d  $\text{NO}_3^-\text{-N}$ ; and e, f dissolved organic C (DOC) concentrations in the 0–10 cm soil layer during the experimental period for the different fertilizers (C, control, U, urea, COM, compost, LFPS, liquid fraction of pig slurry, LFPSI, liquid fraction of pig slurry + DMPP) treatments. Data are provided separately for sprinkler (left) and drip (right) irrigation. The black, dotted and grey arrows indicate the time of seeding, fertilization and the start of irrigation. The maize was seeded on 7th May 2014 and harvested on 24th October 2014. Vertical lines indicate standard errors.

Table 3). The nitrous oxide fluxes ranged from  $-0.08$  (LFPSI-S on 14th January) to  $9.78$  (U-S on 24th June)  $\text{mg N m}^{-2} \text{d}^{-1}$  during the experimental period.

The addition of the NI DMPP to the LFPS treatment significantly influenced the  $\text{N}_2\text{O}$  losses. Although the fluxes were low during Period I, particularly before the start of the irrigation period, LFPSI resulted in a 49% abatement of  $\text{N}_2\text{O}$  emissions (Table 3). After dressing fertilization, LFPSI also reduced daily  $\text{N}_2\text{O}$  emissions on some sampling dates (Fig. 3a), resulting in a significant 45% abatement in the S plots ( $P < 0.05$ ) (Table S1). The reduction of the  $\text{N}_2\text{O}$  losses in the NI treatment (LFPSI) could be observed during the  $\text{N}_2\text{O}$  peaks in both irrigation systems (Fig. 3a, b) and in both areas of the D plots (Fig. S2a, b). At the end of the experimental period, LFPSI resulted in a significant ( $P < 0.05$ ) 40% abatement of cumulative losses, as opposed to LFPS. The type of organic fertilizer (liquid versus solid) did not have a significant influence on the  $\text{N}_2\text{O}$  emissions in any of the three periods and the cumulative losses, although these tended to be higher in COM than in LFPS.

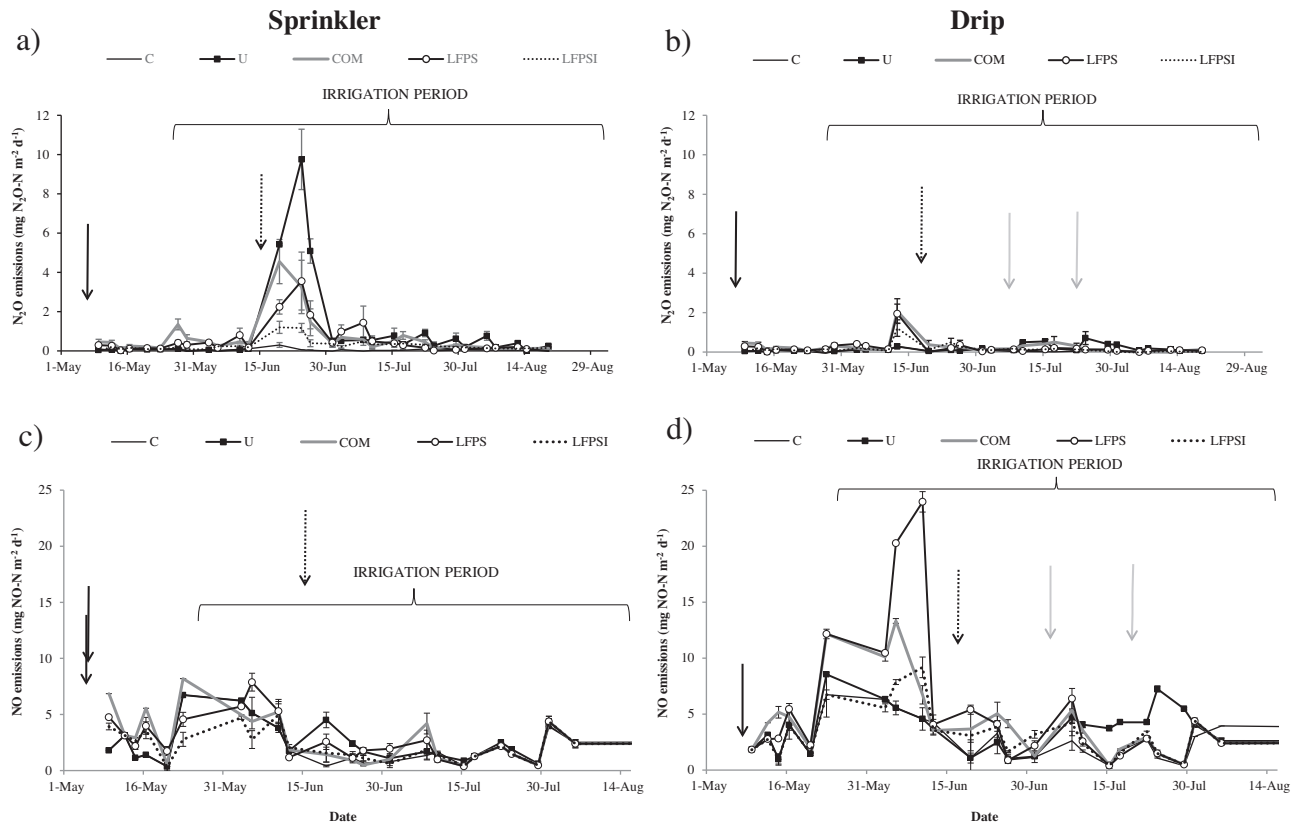
A significant 'fertilizer-irrigation' interaction ( $P < 0.05$ ) was observed (Table 3) during Period II (which was the most influential) and the total emissions (Table S1): the  $\text{N}_2\text{O}$  fluxes were higher in the S plots in COM, LFPS and – particularly – in the U treatments (1321 and  $240 \text{ g N ha}^{-1}$  in U-S and U-D, respectively), although both irrigation systems were similar in LFPSI and C. Although the daily fluxes after N fertilization were generally higher in the wet than in the dry areas of the D plots, a notable  $\text{N}_2\text{O}$  burst

( $2.0\text{--}3.9 \text{ mg N m}^{-2} \text{d}^{-1}$ ) was reported after the rainfall on 11th June in the dry areas (Fig. 1a, Fig. S2b), causing the cumulative  $\text{N}_2\text{O}$  losses to be similar in both areas by the end of the experimental period. Similarly, an increment in  $\text{N}_2\text{O}$  emissions ( $0.31$  and  $0.25 \text{ mg N m}^{-2} \text{d}^{-1}$  in LFPS and COM, respectively) was observed after rainfall events reported in mid-October in the dry areas of the D plots (Fig. S2b). The nitrous oxide fluxes were significantly correlated with the DOC ( $P < 0.001$ ,  $n = 45$ ,  $r = 0.57$ ) and  $\text{NO}_3^-$  ( $P < 0.05$ ,  $n = 32$ ,  $r = 0.42$ ) contents,  $\text{CO}_2$  emissions ( $P < 0.001$ ,  $n = 45$ ,  $r = 0.63$ ), and soil temperature ( $P < 0.001$ ,  $n = 32$ ,  $r = 0.63$ ).

### 3.3.2. Nitric oxide emissions

The daily NO fluxes of the different fertilizer and irrigation treatments, from May to mid-August, are shown in Fig. 3c and d. The highest emission peaks were reported before dressing fertilization, reaching  $24.0 \text{ mg N m}^{-2} \text{d}^{-1}$  in LFPS-D and  $8.2 \text{ mg N m}^{-2} \text{d}^{-1}$  in COM-S. After mid-August, the emissions decreased progressively and remained below  $1 \text{ mg N m}^{-2} \text{d}^{-1}$  throughout the remainder of the experiment.

As observed for the  $\text{N}_2\text{O}$  losses, LFPSI significantly reduced the NO emissions during some sampling dates (particularly before dressing fertilization) and the cumulative NO losses (32% reduction) in both irrigation systems, in comparison with LFPS. After dressing fertilization, the effect of DMPP on the NO losses was not significant. Regarding the irrigation effect, the cumulative NO emissions (Table 3) were significantly higher in D than in S ( $P < 0.001$ ). A significant interaction was observed (Table S1): LFPS



**Fig. 3.** Daily  $N_2O$  (a, b) and  $NO$  (c, d) emissions until mid-August for the different fertilizers (C, control, U, urea, COM, compost, LFPS, liquid fraction of pig slurry, LFPSI, liquid fraction of pig slurry + DMPP) treatments. Data are provided separately for sprinkler (left) and drip (right) irrigation. The black, dotted and grey arrows indicate the time of seeding fertilization, dressing fertilization and the start of fertigation. The maize was seeded on 7th May 2014. Vertical lines indicate standard errors.

led to the highest fluxes in D but emitted a similar amount of  $NO$  as COM in the S plots. The fertigation events in the U subplots also led to increments of  $NO$  emissions (Fig. 3d). The daily  $NO$  emission was negatively correlated with WFPS ( $P < 0.001$ ,  $n = 32$ ,  $r = -0.72$ ) and positively correlated with  $NO_3^-$  ( $P < 0.001$ ,  $n = 32$ ,  $r = 0.73$ ).

### 3.3.3. Methane and carbon dioxide emissions

All the fertilizer-irrigation alternatives were net  $CH_4$  sinks, although the daily fluxes ranged from  $-0.74$  to  $0.64$   $mg\ C\ m^{-2}\ d^{-1}$  (data not shown). The cumulative  $CH_4$  uptake (Table 3) was significantly higher in S than in the D plots ( $P < 0.001$ ), and in U and

LFPSI than in the COM subplots ( $P < 0.05$ ). Although LFPSI numerically increased  $CH_4$  uptake compared to LFPS (55%), the differences were not statistically significant (Table 3). The highest  $CO_2$  fluxes were reported during the maize crop cycle, reaching  $12\ g\ C\ m^{-2}\ d^{-1}$ . The cumulative respiration rates (Table 3) were significantly higher in the COM ( $P < 0.05$ ) and S ( $P < 0.001$ ) treatments for the fertilizer and irrigation effects, respectively. The  $CO_2$  cumulative fluxes were also greater ( $P < 0.05$ ) in the wet than in the dry areas in the D plots, while  $CH_4$  oxidation tended to be lower in the wet areas than in the dry areas during the irrigation period (data not shown). The carbon dioxide emissions

**Table 3**

Cumulative  $N_2O-N$  emissions over the different periods of field experiment and total cumulative  $NO-N$ ,  $CH_4-C$  and  $CO_2-C$  fluxes in the different fertilizer (C, control, U, urea, COM, compost, LFPS, liquid fraction of pig slurry, LFPSI, liquid fraction of pig slurry + DMPP) and irrigation (S, sprinkler, D, drip) treatments.

Effect	$N_2O$ cumulative emission ( $g\ N_2O-N\ ha^{-1}$ )			Total $N_2O-N$ ( $g\ N_2O-N\ ha^{-1}\ y^{-1}$ )	$NO$ cumulative emission ( $kg\ NO-N\ ha^{-1}\ y^{-1}$ )	$CH_4$ cumulative emission ( $g\ CH_4-C\ ha^{-1}\ y^{-1}$ )	$CO_2$ cumulative emission ( $Mg\ CO_2-C\ ha^{-1}\ y^{-1}$ )
	Period I	Period II	Period III				
Irrigation x fertilizer	$P = 0.200$	$P = 0.042$	$P = 0.238$	$P = 0.026$	$P = 0.03$	$P = 0.652$	$P = 0.32$
S.E.	13.7	80.8	31.0	91.1	0.3	102.6	0.1
Irrigation	$P = 0.867$	$P = 0.000$	$P = 0.032$	$P = 0.000$	$P = 0.000$	$P = 0.000$	$P = 0.000$
S	69.5	517.7 b	123.7 b	710.8 b	2.4 a	-358.3 a	0.69 b
D	53.9	130.6 a	65.5 a	261.2 a	3.8 b	-96.0 b	0.25 a
S.E.	6.2	36.1	13.8	40.7	0.1	45.9	0.03
Fertilizer	$P = 0.000$	$P = 0.001$	$P = 0.157$	$P = 0.000$	$P = 0.000$	$P = 0.070$	$P = 0.006$
C	21.5 a	53.3 a	60.9	138.6 a	2.4 a	-163.8 ab	0.44 a
U	20.6 a	634.1 c	126.6	781.9 c	3.1 bc	-332.1 a	0.43 a
COM	122.7 c	421.1 bc	113.9	664.7 bc	3.5 c	-112.1 b	0.61 b
LFPS	95.3 c	327.2 bc	104.7	529.1 b	3.9 c	-163.1 ab	0.37 a
LFPSI	48.2 b	198.7 ab	66.8	315.9 a	2.6 ab	-365.1 a	0.50 a
S.E.	9.7	57.1	21.9	64.4	0.2	72.5	0.04

Different letters within columns indicate significant differences by applying the Tukey's honest significance test at  $P < 0.05$ . Standard Error (S.E.) is given for each effect. The variables  $N_2O$  (Period II), total  $N_2O$ ,  $NO$  and  $CO_2$  were log-transformed before the ANOVA.

significantly correlated with the topsoil DOC concentrations ( $P < 0.001$ ,  $n = 45$ ,  $r = 0.65$ ).

### 3.4. Yield parameters, YSNE and N surplus

The grain and biomass yields and N uptake are shown in Table 4. No significant differences were found between the irrigation systems in grain yield or N uptake, while LFPSI was the only organic treatment to reach similar grain production and N uptake as U. In contrast, COM and LFPS decreased the grain yields by 33 and 26%, respectively, compared with U ( $P < 0.001$ ), but resulting in higher yield than unfertilized C. Urea and D were the fertilizer and irrigation treatments that led to the highest biomass yield, respectively ( $P < 0.05$ ). The use of NI (DMPP) tended to increase the grain yield and N uptake (15 and 8%, respectively) compared to LFPS alone, but the differences were not statistically significant. Regarding biomass production, LFPSI led to a 21% increment with respect to LFPS ( $P < 0.05$ ).

The YSNE (Table 4) ranged from 1.0 to 5.9 g N<sub>2</sub>O-N kg above-ground N uptake<sup>-1</sup>. The LFPSI led to a 43% mitigation of YSNE compared to LFPS ( $P < 0.05$ ), whereas COM resulted in the highest values (Table 4). The drip irrigation system also abated YSNE compared to S ( $P < 0.001$ ), especially in the case of U, where the YSNEs were almost 5 times higher in S than in the D plots. The irrigation effect did not influence the N surplus (Table 4), whereas COM and LFPS significantly increased the N surplus compared to U ( $P < 0.001$ ). Except in the case of COM and LFPS-S, negative values were observed for the N surpluses.

## 4. Discussion

### 4.1. Mitigation of N oxides emissions

#### 4.1.1. Effect of DMPP on N fluxes

The use of DMPP with LFPS reduced the nitrification activity in the soil. As indicated above, this effect can be observed in the evolution of the NH<sub>4</sub><sup>+</sup> (higher contents in LFPSI than LFPS) (Figs. 2a, b, S1a, b) and NO<sub>3</sub><sup>-</sup> content (higher concentrations in LFPS than in LFPSI) (Figs. 2c, d, S1c, d) during Period I (after seeding application). An interesting finding was that the inhibition effect persisted when U (without inhibitor) was applied as dressing fertilization, leading to higher NH<sub>4</sub><sup>+</sup> and lower NO<sub>3</sub><sup>-</sup> concentrations in LFPSI, although this effect was less noticeable and persistent in S than in the D plots (with higher inhibition efficacy in the dry areas than in the wet areas). Considering the whole period (crop and intercrop), the

partial inhibition of NH<sub>4</sub><sup>+</sup> oxidation due to the use of DMPP with LFPS in these short periods of time had important consequences on the N oxide fluxes, reducing by 40% and 32% the cumulative N<sub>2</sub>O and NO losses, respectively ( $P < 0.05$ ). The mitigation efficacy was slightly lower than that reported by the meta-analysis of Akiyama et al. (2010), which obtained a 50% and 36% mitigation (on average) for N<sub>2</sub>O and NO, respectively. The effect of DMPP on the N<sub>2</sub>O fluxes was also observed after dressing fertilization, although the differences in the cumulative fluxes in Period II were only significant in the S plots (Table 3, S1).

Previous studies by Di and Cameron (2011) and Dong et al. (2013) have reported medium- and long-term effects of DMPP on the abundance of NH<sub>3</sub>-oxidizing bacteria (AOB). Although in our study the AOB population was not quantified, we speculated that a reduction of the AOB population could have caused the lower N oxide emissions on some sampling dates after dressing fertilization.

#### 4.1.2. Influence of N fertilization

The application of organic N sources at seeding at a rate of 120 kg N ha<sup>-1</sup> significantly increased the N<sub>2</sub>O emissions during Period I. Conversely, the emission factors (EF) during this period were low (below 0.10% in all organic treatments, including those without DMPP). Consequently, the N<sub>2</sub>O emissions during Period I represented only 15–19% of the total cumulative losses in the N-fertilized treatments (COM, LFPS and LFPSI), showing that applying organic fertilizers under low soil moisture conditions can be considered as a promising mitigation technique (Chadwick et al., 2011). The WFPS values (<50%) during the first three weeks after fertilization (before the start of irrigation) were not favourable for denitrification, which has been reported to be the dominant process at WFPS >60% (Bateman and Baggs, 2005). The molar ratio of NO/N<sub>2</sub>O before dressing fertilization was higher than 1, suggesting that nitrification was apparently the most important source of these gases (Akiyama et al., 2004). The negative correlation of the NO fluxes with soil WFPS and the positive with mean NO<sub>3</sub><sup>-</sup> concentration (showing that the replicates with higher NO<sub>3</sub><sup>-</sup> content generated through nitrification were associated with those with the highest NO emissions) also support this statement. In fact, this correlation was also observed by Abalos et al. (2012).

At the beginning of Period II only 60 kg N ha<sup>-1</sup> (1/3 of the total N rate) were applied as urea in COM, LFPS and LFPSI, but the highest N<sub>2</sub>O increments were observed during this period. These findings suggested that soil moisture and its interaction with N fertilization are limiting factors (more important than even NO<sub>3</sub><sup>-</sup> availability)

**Table 4**

Grain and biomass yield, N uptake, yield-scaled N<sub>2</sub>O emissions (YSNE) and N surplus in the different fertilizer (C, control, U, urea, COM, compost, LFPS, liquid fraction of pig slurry, LFPSI, liquid fraction of pig slurry + DMPP) and irrigation (S, sprinkler, D, drip) treatments.

Effect	Yield (kg ha <sup>-1</sup> )		N uptake (kg N ha <sup>-1</sup> )	YSNE (g N <sub>2</sub> O-N kg aboveground N uptake <sup>-1</sup> )	N surplus (kg N ha <sup>-1</sup> )
	Grain	Biomass			
Irrigation x fertilizer	P = 0.099	P = 0.063	P = 0.683	P = 0.217	P = 0.683
S.E.	1144.5	1653.8	22.9	0.6	22.9
Irrigation	P = 0.760	P = 0.000	P = 0.907	P = 0.002	P = 0.907
S	9300.1	18177.8 a	175.9	4.0 b	-31.9
D	9075.7	23911.1 b	177.6	1.5 a	-33.6
S.E.	511.1	739.6	10.3	0.3	10.2
Fertilizer	P = 0.000	P = 0.000	P = 0.000	P = 0.000	P = 0.000
C	4042.3 a	11955.5 a	103.6 a	1.9 a	-
U	12913.3 c	29644.4 d	263.1 c	3.0 b	-83.1 a
COM	8600.5 b	20600.0 bc	155.1 ab	4.2 c	24.9 b
LFPS	9500.8 b	19466.7 b	180.2 b	3.0 b	-0.2 b
LFPSI	10882.5 bc	23555.6 c	195.2 bc	1.7 a	-15.2 ab
S.E.	9.7	57.1	16.2	0.3	16.3

Different letters within columns indicate significant differences by applying the Tukey's honest significance test at  $P < 0.05$ . Standard Error (S.E.) is given for each effect. The variable YSNE was log-transformed before the ANOVA.



(García-Marco et al., 2014) affecting  $N_2O$  emissions, and this fact is of major relevance in Mediterranean areas. In the U treatment, all N ( $180 \text{ kg ha}^{-1}$ ) was applied during Period II. That caused U to be the treatment with the highest emissions during this period ( $P < 0.05$ ) in the S plots (whereas no differences were observed in the D plots, in which U was applied by drip-fertigation). Under S irrigation, which is the most widespread system in Mediterranean maize cropping areas, the partial replacement of U at dressing by organic fertilizers at seeding resulted in 28, 47 and 70% mitigation of the cumulative  $N_2O$  emissions in COM, LFPS and LFPSI, respectively.

Our results showed that the type of organic fertilizer (solid versus liquid) did not significantly influence the  $N_2O$  or NO emissions, as opposed to the review study of Aguilera et al. (2013) in Mediterranean areas, which found lower  $N_2O$  emissions from solid than liquid sources. These authors explained this effect by the lower concentrations of  $NH_4^+$  in solid organic sources and their low rate of organic N mineralization, in comparison with liquid manure. In our study, lower  $NH_4^+$  contents in the COM-amended subplots than in LFPS were also measured (Table 2, Fig. 2a, b), but this did not result in lower emissions than those of LFPS. That could be explained by the higher C content of COM (Table 2), which significantly increased the DOC topsoil concentrations (see Section 3.2) in this treatment, favouring  $N_2O$  denitrification losses (Vallejo et al., 2006), especially after the beginning of irrigation and during Period II. Regarding NO emissions, the highest peak was observed in the LFPS-D treatment and was higher than that observed in COM-D. This is consistent with the findings of Pereira et al. (2010) comparing liquid and solid fractions of cattle slurry in a laboratory study. This finding could be caused by the higher  $NH_4^+$  content in LFPS than in COM, and this fact would have increased NO production through nitrification. Moreover, the higher soluble C content in COM resulted in higher topsoil DOC levels (Fig. 2 e, f), increasing soil respiration (Table 3) and thereby providing the anaerobic conditions that led to NO consumption (Vallejo et al., 2006).

In addition to the effect of the different fertilizer treatments on  $N_2O$  emissions, indirect  $N_2O$  losses (i.e. after deposition of  $NH_3$ , which is largely volatilised when  $NH_4^+$ -based fertilizers are applied) should be also considered. In this sense, using the methodology developed by Sanz-Cobena et al. (2014a) and the emission factor for indirect  $N_2O$  losses (from  $NH_3$  volatilization) (IPCC, 2014), these could be mitigated in the case of incorporated LFPS ( $0.20 \text{ kg ha}^{-1}$ ) with respect to U ( $0.36 \text{ kg ha}^{-1}$ ) under our experimental conditions. Moreover, low indirect  $N_2O$  emissions from COM (Bittman et al., 2014) and enhanced indirect losses from LFPSI (with respect to LFPS) could be expected (Qiao et al., 2015). For an accurate and non-speculative calculation of these emissions,  $NH_3$  volatilisation should be measured in further studies using, if possible, micrometeorological techniques (Sanz-Cobena et al., 2010).

#### 4.1.3. Effect of the irrigation system on N fluxes

The majority of cumulative  $N_2O$  fluxes in N-fertilized treatments (63–85% of total emissions) occurred during the irrigation period (26th May to 19th September). Regarding NO emissions, the importance of the irrigation period was much lower (19–35% of total emissions). Both N oxide emissions were significantly influenced by the interaction of the irrigation system with the N fertilization (Table 3).

On average,  $N_2O$  fluxes were 63% lower in D compared to S. The different soil wetting pattern associated with D and the type of N applied were the key drivers of these results, influencing the dominant soil processes leading to  $N_2O$  losses. Ammonium was the principal N-source in the fertilizer plots, so nitrifying microorganisms require suitable WFPS conditions (35–60%) (Bateman and Baggs, 2005) to oxidize  $NH_4^+$  in a process that may trigger  $N_2O$

losses both directly and indirectly (when favourable WFPS contents for denitrification are present in the soil). Both moisture requirements (for nitrification and denitrification) were observed, particularly in the S plots. In this system, the irrigation events were less frequent, and the drying-rewetting conditions were more favourable for the coupled-nitrification-denitrification (Wrage et al., 2004) (Fig. 1b), thus increasing the  $N_2O$  emissions. In the D plots, two contrasting areas were observed: wet areas – where WFPS maintained consistently (due to higher irrigation frequency) favourable values for denitrification (favouring the uptake of  $NH_4^+$ -N from the applied fertilizers by the maize plants) (Fig. 1b) – and dry areas – where WFPS values were frequently even below the nitrification threshold (except after rainfall events, which led to a remarkable  $N_2O$  peak in mid-June, as observed in Fig. S2b) and did not reach the threshold for denitrification, therefore showing higher  $NO_3^-$  contents than the wet areas or S plots (Figs. 2c, 1Sc, d). Our results are in agreement with Jamali et al. (2015), who found a significant  $N_2O$  mitigation when irrigation frequency increased. They suggested that avoiding the high magnitude pulses associated with higher amounts of applied water was the reason for the lower  $N_2O$  emissions. The relevance of the denitrification process in the cumulative  $N_2O$  emissions was confirmed by the positive correlations with DOC and  $NO_3^-$  (MacKenzie et al., 1998) and by the NO/ $N_2O$  ratio  $< 1$  when the emission peak was observed (15th June to 30th June in the S plots) (Davidson et al., 1991). The significant irrigation\*fertilizer interaction (Table 2, S1) showed that the differences between the irrigation systems were not significant ( $P > 0.05$ ) in the C and LFPSI subplots (which were the fertilizer treatments with the lowest  $N_2O$  fluxes due to the absence of N fertilizer and the addition of the NI, respectively). However, the differences between both irrigation systems were highest in the case of U (see Section 3.3.1), highlighting the high mitigation potential of drip-fertigation (Kennedy et al., 2013).

The NO fluxes were also affected by the irrigation system. Significantly higher fluxes were observed in the D plots, in which the wet and dry areas were distinguished. In an acid Savannah soil in Venezuela, Cárdenas et al. (1993) suggested that the optimum soil moisture for NO pulses was between 30 and 60% WFPS, reporting higher fluxes during the dry season. Pilegaard (2013) noted that the optimal soil moisture for NO emission differed significantly between soils, ranging from 15 to 65% WFPS, with an average value of approximately 45%. During the NO burst in the D plots, the WFPS values were in these ranges in the dry areas (Fig. 1b), possibly as a consequence of the rainfall events after seeding fertilization (Fig. 1a) and the beginning of the irrigation period. This pulsing effect, which was also observed in the dry areas of the D plots after the June rainfall events, is caused by the accumulation of mineral N in dry soils and reactivation of water-stressed bacteria after rainfall events (Skiba et al., 1997; Sanchez-Martin et al., 2009). During Period II, the WFPS values were above the optimum range in S and in the wet areas of the D plots and decreased below 30% in the dry areas, so that low NO emissions were reported (Fig. 3c, d). In agreement, Vallejo et al. (2005) observed a depletion of NO fluxes when irrigation was applied in a *Festuca* sward. A NO increment (not as high as that observed in LFPSI and COM) was observed in the U-D plots during fertigation (Fig. 3d). At the closest point to the drip irrigation row, WFPS was above the optimum for nitrification, while the low horizontal movement of  $NH_4^+$  ions, together with WFPS  $< 30\%$  in the farthest points from the drip irrigation row, may have been below the lower NO emission from this treatment than from any organic treatment.

The  $N_2O$  emission factors (EF) ranged from 0.10% (U-D, LFPSI-D) to 0.64% (U-S). The average EFs were 0.30 and 0.10% for S and D, respectively, which were below the EFs proposed by Aguilera et al. (2013) for high- and low-water irrigation systems (1.01 and 0.66%, respectively) and below the IPCC default value (1%). The results

also showed the potential of U-fertigation systems to minimize  $N_2O$  losses so that they provide the N in split applications (Kennedy et al., 2013), when plant demand is highest and under high-WFPS conditions (which prevent  $NH_4^+$ -N oxidation). The NO emission factor ranged from 0.4 to 3.5%, with an average value of 1.2%, which is at the lower end of the range of 0.5–10% proposed by Stehfest and Bouwman (2006).

#### 4.2. $CH_4$ and $CO_2$ emissions

The cumulative  $CH_4$  uptake was in the range of the study of Sanz-Cobena et al. (2014b) in a field experiment with irrigated maize performing under similar climatic conditions. Although all the treatments were net  $CH_4$  sinks, some pulses of  $CH_4$  emissions were reported during all the experimental period (data not shown). Several studies have noted the variable effects of N-addition on methanotrophy: small additions ( $<100 \text{ kg ha}^{-1}$ ) tend to stimulate  $CH_4$  oxidation, whereas large additions are inhibitory (Aronson and Helliker, 2010; Veraart et al., 2015). In our study, in which  $180 \text{ kg N ha}^{-1}$  were applied, the inhibitory effect was not observed in the daily  $CH_4$  fluxes, and the cumulative oxidation rates were significantly higher in LFPSI (which maintained higher  $NH_4^+$  concentrations due to the presence of DMPP) and U (a fertilizer that quickly releases  $NH_4^+$ ) than in COM. The LFPS and C results were intermediate (Table 3). Some authors have suggested an inhibitory effect on  $CH_4$  oxidation due to high concentrations of  $NO_3^-$  (Hütsch, 1996; Rigler and Zechmeister-Boltenstern, 1999) because these concentrations are an indicator of high nitrification rates and a possible increase in osmotic potential (Meijide et al., 2010). That could explain the higher rates of  $CH_4$  uptake in LFPSI and U, which were the treatments with the lowest  $NO_3^-$  concentrations (see Section 3.2, Fig. 2c, d). Moreover, the lower  $CH_4$  uptake in the high C-content organic amendment (COM) could be related to changes in soil porosity and enhancement of soil respiration, promoting anaerobic microsites and consequently reducing methanotrophy (Le Mer and Roger, 2001).

The irrigation factor also affected the  $CH_4$  sink, which was almost four times higher in the S plots (Table 3). Le Mer and Roger (2001) noted that methanotrophy increases with values of soil water content close to field capacity; therefore, higher uptake could be expected during the drying cycles in the S plots than in the dry areas of the D plots (Fig. 1b). In the wet areas of the D plots or in the S plot after irrigation events, decreasing  $CH_4$  uptake could be expected. In agreement, Banger et al. (2012) found that continuous irrigation (which could be closer to the wet areas in the D plots) in rice fields increases  $CH_4$  emissions compared to intermittent drainage (which could be closer to the S plots). On average,  $CH_4$  uptake only compensated for 1–12% (average 5.3%) of the  $N_2O$  losses in the N-fertilized treatments, considering a 100-year time horizon (data not shown).

The  $CO_2$  emissions increased during the maize cropping period. The effect of the activation of soil microbial communities after the addition of N, suggested by Chadwick et al. (1998), was not observed in our study, as no differences between the C and N-fertilized treatments were observed. However, the highest peak, which was reported after dressing fertilization, was lower in the C treatment (data not shown) and may be partially caused by the hydrolysis of urea, releasing  $CO_2$ . The increase in plant growth and subsequent root respiration rates appears to be the key driver in the pattern of daily  $CO_2$  emissions. The addition of a C-rich organic amendment (COM) significantly increased  $CO_2$  emissions, as observed by Meijide et al. (2010). These authors also observed a correlation between the DOC and  $CO_2$  fluxes, suggesting that the excess of C could be lost via respiration or increase microbial activity. An irrigation effect was also observed, with lower respiration rates in the D plots. Higher surface under the dry

conditions could explain these results, as indicated by the significantly higher fluxes in the wet areas than in the dry areas (see Section 3.3.3).

#### 4.3. Best management practices in an irrigated maize field amended with organic fertilizers

The most advisable management practices for farmers must link economically acceptable crop yields and the potential impacts of these practices on the environment, e.g., through the release of N oxides and GHGs (Sanz-Cobena et al., 2014a,b). Therefore, these best alternatives should meet the following statements: (i) minimize GWP (taking into account the low importance of  $CH_4$  uptake) and NO losses and (ii) minimize YSNE without decreasing consistent crop (particularly grain) yields, leading to an optimum use of resources.

The partial replacement of U at dressing by organic fertilizers lowered the N uptake and consequently the grain and biomass yields. Sieling et al. (2014) argued that crops generally utilize nitrogen (N) from organic amendments less efficiently than from mineral fertilizers. That may have occurred in our trial, in which the N rate ( $180 \text{ kg N ha}^{-1}$ ) was adjusted on estimated residual soil N and other inputs during the crop cycle. The low  $NH_4^+$  contents observed in COM and LFPS after fertilization (compared to U) (Fig. 2a, b) and the high contents at the end of the maize season (particularly in the dry areas of D), may have caused the lower N uptake and higher N surplus in the organic treatments, in comparison with U, thus affecting maize production. Consequently, some practices could be adopted aiming to avoid substantial yield losses, if most of the N rate is applied as organic amendments at seeding: (1) an accurate calculation (and monitoring) of the availability of N when the organic sources are applied, particularly during the times of highest crop demand; (2) increasing the amount of urea applied at dressing, if necessary -with potential increase of  $NH_3$  volatilization unless some mitigation strategies, e.g. the use of urease inhibitors, are adopted (Sanz-Cobena et al., 2014a)-; and/or (3) using NIs (e.g., DMPP) with organic liquid fertilizers. In this sense, we observed that only LFPSI resulted in a statistically similar grain yield and N uptake as U (Table 4). Compared to LFPS alone, the use of DMPP tended to increase grain yield and N uptake, significantly increasing biomass production. These results are consistent with the meta-analysis of Abalos et al. (2014a), who found that DMPP significantly increased biomass but not grain yields. They also reported that the effect of inhibitors on increasing yields and N uptake was higher in biomass production and irrigated crops, as a result of the reduction of N leaching and denitrification losses.

Finding mitigation techniques that maintain or enhance crop yields is essential in a context of global change and increasing food demand, so YSNE is a valuable index to assess the most 'N<sub>2</sub>O-efficient' alternatives (van Groenigen et al., 2010). The values of YSNE in this field experiment were below those reported by these authors ( $\approx 10 \text{ g N}_2\text{O-N kg above-ground N uptake}^{-1}$ ) for the N rate employed ( $180 \text{ kg ha}^{-1}$ ), which was suggested as the N rate that results in minimal YSNE. As observed by van Groenigen et al. (2010), the treatment with the highest surplus (COM, whose mean N surplus was above the threshold of  $11 \text{ kg N ha}^{-1}$  for enhancing YSNE) was the less "N<sub>2</sub>O-efficient" treatment with the highest YSNE (Table 4). In contrast, LFPSI and U-D were the treatments that led to the lesser amount of  $N_2O$  emitted per kilogram of N up taken, whereas D irrigation also showed lower values of this ratio than S.

Areas with high concentration of animals (e.g., NE, SE and centre of Spain) produce large amounts of manure and slurries, whose utilization in cropping areas provide valuable environmental (i.e., rational use of potential water and soil polluting residues, mitigating  $N_2O$  emissions) and economical (i.e., reducing the use of

synthetic fertilizers) benefits. Conversely, the use of NIs can strengthen the potential advantages (e.g., mitigating N oxide emissions) without substantially penalizing crop yields, particularly when adjusted N rates are employed.

## 5. Conclusions

Our results highlighted that the use of DMPP with LFPS under drip irrigation was the management option involving the use of organic fertilizers that most decreased N<sub>2</sub>O, NO and YSNE, enhancing CH<sub>4</sub> oxidation and leading to similar grain yields as conventional U in S irrigation. Considering the two treatments with only synthetic fertilizer application (U-S and U-D), the latter also showed promising results and an optimum balance between reducing emissions of pollutants and maintaining crop yields.

High water-efficient irrigation systems (e.g., D) are increasing in Mediterranean areas. As opposed to S, D irrigation significantly reduced GWP in spite of the lower CH<sub>4</sub> sink, which had a small contribution to this parameter. Drip irrigation also abated the YSNE and increased biomass yield without decreasing grain production. However, NO emissions were enhanced in this treatment. Furthermore, although the grain yields, N uptake and N surplus were apparently not affected by this innovative irrigation system, the high mineral N contents remaining in the dry areas at the end of the maize cropping period (in the organic treatments) suggest that this system could potentially decrease the optimum N use efficiency by the maize crop when organic fertilizers are applied.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.agee.2016.09.022>.

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