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The effect of nitrification inhibitors on NH_3 and N_2O emissions in highly N fertilized irrigated Mediterranean cropping systems

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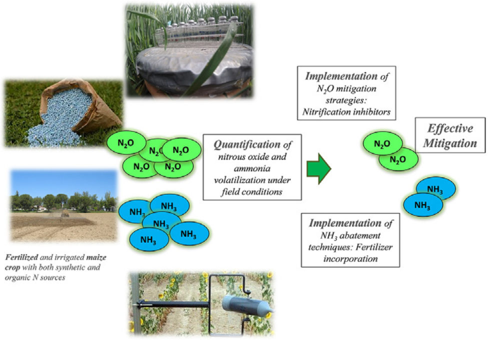
HIGHLIGHTS

- The N_2O abating effect of two nitrification inhibitors (NIs) was assessed.
- Effect of NI over NH_3 and N_2O emissions were simultaneously measured.
- The Integrated Horizontal Flux was used for measuring NH_3 volatilization.
- Cumulative NH_3 losses were not significantly affected by NIs.
- NH_3 and N_2O losses from synthetic and organic fertilizers were controlled by the use of two NIs.

GRAPHICAL ABSTRACT



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ABSTRACT

There is an increasing concern about the negative impacts associated to the release of reactive nitrogen (N) from highly fertilized agro-ecosystems. Ammonia (NH_3) and nitrous oxide (N_2O) are harmful N pollutants that may contribute both directly and indirectly to global warming. Surface applied manure, urea and ammonium (NH_4^+) based fertilizers are important anthropogenic sources of these emissions. Nitrification inhibitors (NIs) have been proposed as a useful technological approach to reduce N_2O emission although they can lead to large NH_3 losses due to increasing NH_4^+ pool in soils. In this context, a field experiment was carried out in a maize field with aiming to simultaneously quantify NH_3 volatilization and N_2O emission, assessing the effect of two NIs 3,4 dimethilpyrazol phosphate (DMPP) and 3,4 dimethylpyrazole succinic acid (DMPSA). The first treatment was pig slurry (PS) before seeding (50 kg N ha^{-1}) and calcium ammonium nitrate (CAN) at top-dressing (150 kg N ha^{-1}), and the second was DMPP diluted in PS (PS + DMPP) (50 kg N ha^{-1}) and CAN + DMPSA (150 kg N ha^{-1}) also before seeding and at top-dressing, respectively. Ammonia emissions were quantified by a micrometeorological method during 20 days after fertilization and N_2O emissions were assessed using manual static chambers during all crop period. The treatment with NIs was effective in reducing c. 30% cumulative N_2O losses. However, considering only direct N_2O emissions after second fertilization event, a significant reduction was not observed using CAN+DMPSA, probably because high WFPS of soil, driven by irrigation, favored denitrification. Cumulative NH_3 losses were not significantly affected by NIs. Indeed, NH_3 volatilization accounted 14%

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and 10% of N applied in PS + DMPP and PS plots, respectively and c. 2% of total N applied in CAN+DMPSA and CAN plots. Since important NH_3 losses still exist even although abating strategies are implemented, structural and political initiatives are needed to face this issue.

1. Introduction

There is an increasing concern worldwide about the large nitrogen (N) losses that excessive use of fertilizers, both organic and synthetic, generate. From an environmental point of view, nitrate (NO_3^-) leaching to hydro systems, ammonia (NH_3) and nitrous oxide (N_2O) gaseous emissions are harmful N pollutants which may also contribute to lower nitrogen use efficiency (NUE), when lost from agroecosystems (Sutton et al., 2011). Surface applied manure as well as urea and ammonium (NH_4^+) based fertilizers are the main sources of NH_3 emission to the atmosphere (Misselbrook et al., 2000). Ammonia contributes to soil acidification, eutrophication and to the formation of particles of mean aerodynamic diameter smaller than 2.5 μg (PM2.5), which have been related to human respiratory problems (Misselbrook et al., 2014). Nitrous oxide is a greenhouse gas (GHG) with a global warming potential 298 times higher than carbon dioxide (CO_2) in the atmosphere, and it also contributes to destruction of stratospheric ozone (van der Weerden et al., 2016). The use of fertilizers in agriculture, both organic and synthetic, in agriculture, is considered the most important anthropogenic source of N_2O emissions (c. 70% of the total worldwide), mainly produced as a by-product or intermediate product of microbial processes (e.g. nitrification and denitrification) (Ussiri and Lal, 2013). In order to mitigate the emission of these gases, sustainable agricultural practices need to be implemented.

The use of nitrification inhibitors has been pointed out as an efficient strategy to reduce N_2O emissions without yield penalties, combined with both liquid manure, urea or ammonium-based fertilizers (Sanz-Cobena et al., 2011; Huérfano et al., 2016; Cayuela et al., 2017). These chemical compounds deactivate the enzyme responsible for the first step of nitrification (AMO) thus maintaining the NH_4^+ in soils for a longer period (Misselbrook et al., 2014; Ruser and Schulz, 2015; Gilsanz et al., 2016). As a consequence, N_2O emissions through nitrification are significantly reduced. Additionally, an indirect effect of NIs has been described, as the decline in the nitrification rates reduces the substrate availability for denitrifiers and therefore N_2O emissions from denitrification may also be lowered (Ruser and Schulz, 2015). Conversely, little is known about the effect of the new inhibitor 2 (3,4 dimethyl 1H pyrazol 1 yl) succinic acid isomeric mixture (DMPSA) (Huérfano et al., 2016; Guardia et al., 2017a). However, this extended retention of N in form of NH_4^+ after NI application in soils may increase the risk of NH_3 volatilization (Ferguson et al., 1984). To date, there is a small number of field studies quantifying the effect of NIs combined with liquid manure (Aita et al., 2014) or synthetic fertilizers (Ni et al., 2014) on NH_3 emissions.

Previous studies investigated different NIs, such as dicyandiamide (DCD) (Kim et al., 2012) or 3,4 dimethylpyrazole phosphate (DMPP) (Menéndez et al., 2008; Li et al., 2009; Zaman et al., 2009). The novel nitrification inhibitor DMPSA, differs from DMPP in the presence of the succinic group instead of phosphate. According to Pacholski et al. (2016) (CA 2933591 A1 2015/06/18 Patent), the combination with succinic acid results in (i) less volatilization of DMP; (ii) smoother and prolonged availability of DMP in the soil; (iii) possibility of combination with any mineral fertilizer (e.g. urea, calcium ammonium nitrate, diammonium phosphate) and (iv) the same inhibitory effect as established nitrification inhibitor for a lower concentration. To date there are no information about its influence over NH_3 volatilization.

Determining robust NH_3 emission factors (EF) for fertilized maize crops as well as the EFs associated with the implementation of mitigation strategies based on fertilizer application is an important challenge for NH_3 inventories of many countries where this is a highly relevant crop in terms of both surface and production. In addition, taking into account that NH_3 deposition is an indirect source of N_2O emissions (Mosier et al., 1998), quantification of NH_3 is also essential to accurately estimate the potential of agricultural management practices to mitigate both NH_3 and N_2O emissions. Ammonia measurements are influenced by several environmental and management factors, such as wind direction, wind speed, air moisture, solar radiation, and nature of fertilizers (Walker et al., 2012; Nelson et al., 2017). Utilizing an appropriate measurement method that provides an accurate quantification of NH_3 is therefore crucial and necessary to develop effective best management practices. Micrometeorological methods are considered as the most robust ones to quantify NH_3 volatilization under field conditions (Sanz-Cobena et al., 2008). Within these methods, the Integrated Horizontal Flux method (IHF) (Denmead et al., 1977) has been usually used as a reference one (Pacholski et al., 2008; Viguria et al., 2015; Yang et al., 2017). To our knowledge, there are few studies measuring NH_3 volatilization using micrometeorological methods in a maize crop, where high N fertilizers rates are normally applied (Pacholski et al., 2006, 2008; Yang et al., 2017).

In this context a field experiment was carried out aiming to quantify NH_3 volatilization and N_2O emission from a high fertilized maize crop, assessing the effect of DMPP mixed with pig slurry (PS) as basal fertilization and DMPSA mixed with calcium ammonium nitrate (CAN), as top-dressing fertilization, and used in both cases as a N_2O mitigation strategy.

Our initial hypothesis was that N_2O emission is reduced when the N fertilizer, either pig slurry or CAN, is mixed with NIs (DMPP or DMPSA), but the enlargement of the NH_4^+ pool in soil, leads in turn to an increased emission of NH_3.

2. Materials and methods

2.1. Site characteristics and experimental design

The study was conducted at "la Chimenea" field station (40°03′N, 03°31′W, 550 m a.s.l.) located in the central Tajo river basin near Aranjuez (Madrid, Central Spain). The area has a Mediterranean semiarid climate with high interannual variability. The mean annual air temperature in this area is approximately 14 °C and the mean annual precipitation is approximately 350 mm. The soil type is a Typic Calcixerept (Soil Survey Staff, 1992). Some of the physicochemical properties of the topsoil layer (0–20 cm), as measured by conventional methods, were as follows: pH_{H2O}, 8.23; total organic C, 18.51 g kg^{-1}; bulk density, 1.36 g cm^{-3}; $CaCO_3$, 198 g CO_3^{-2} kg^{-1}. Soil texture is silty clay loam (clay, 250 g kg^{-1}; silt, 490 g kg^{-1}.and sand, 260 g kg^{-1}).

The experimental area was composed of four square plots (40 m×40 m) separated by a 50 m interspace. Two fertilized treatments were randomly distributed with two replicates each (Fig. 1). The first treatment consisted in applying pig slurry (PS) as basal fertilizer at a rate of 50 kg N ha^{-1} before seeding (20th April), and calcium ammonium nitrate (CAN) at a rate of 150 kg N ha^{-1} as dressing fertilization (23rd June 2015) (PS-CAN). In this treatment, no NI was applied and represents the Control. The second treatment consisted in applying nitrification inhibitor DMPP (3,4 dimethilpyrazole phosphate, ENTEC®) diluted in pig slurry (before seeding, 50 kg N ha^{-1}) and CAN+DMPSA (ACAG®, 150 kg N ha^{-1}), which was coated onto CAN granules, as top-dressing fertilization (PS-CAN + NI). Synthetic fertilizers and inhibitors (DMPP, CAN and CAN + DMPSA) were provided by EuroChem

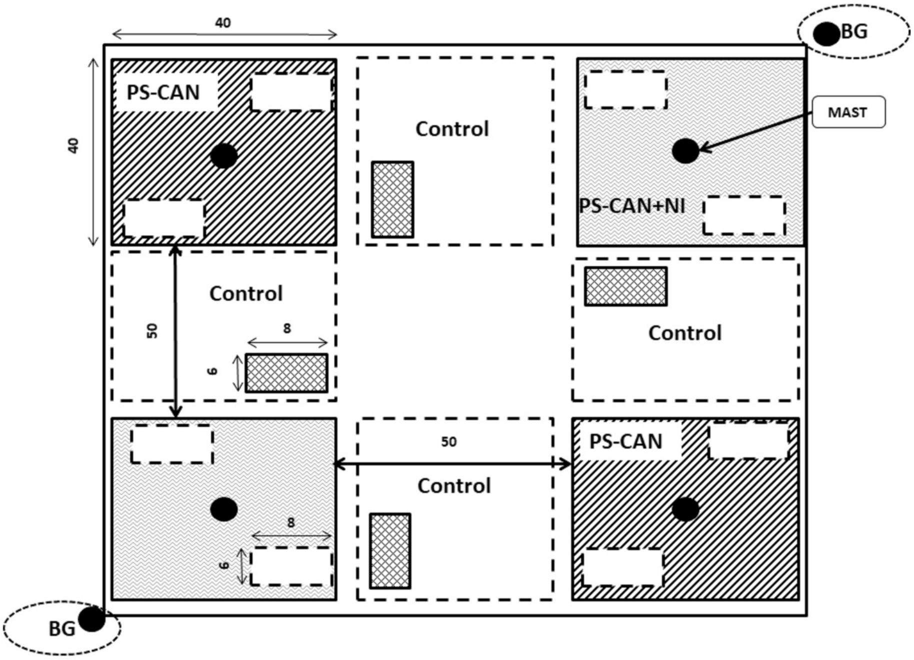

Fig. 1. Experiment design. Two plots of PS-CAN and two plots of PS-CAN + NI. Masts are represented by black circle (BG for background NH_3). Numbers near arrows as length in meters. Control plots are dashed areas between fertilized plots. Small squares inside plots indicate selected areas where N_2O and soil samples were taken. The draw is not to scale.

Agro ®. The time gap between fertilization events was enough to discard the possibility of an additive effect of DMPP in the second fertilization (Zerulla et al., 2001).

Pig slurry was collected from a pit of a pig farm nearby the experimental area being its composition (total N and NH_4^+-N content) determined prior application. Volume of slurry applied per plot was calculated previously considering the total N content (2 g N L^{-1}). Pig slurry (with or without NI) was evenly surface-applied (20th April 2015) with an immediate incorporation up to 10 cm depth with a cultivator. Combination of pig slurry as basal fertilization and mineral N as dressing is a very common fertilization practices in areas with a high density of pig farms in Mediterranean regions (Becaccia et al., 2015).

Maize (*Zea mays* L. FAO class 600) was sown on 27th April 2015 at a density of 75.000 seeds ha^{-1}. The surface between plots was also cultivated with maize but without N fertilizer. Maize was harvested at physiological maturity, on 23rd October 2015.

In each plot, several areas were selected (8 m × 6 m) in order to collect samples of N_2O, ammonium (NH_4^+) and nitrate (NO_3^-) in soil. Four additional 8 × 6 m plots in the non N fertilized area were also delimited in order to maintain a Control treatment for N_2O emission and soil NH_4^+ and NO_3^- content (Fig. 1).

Plots were irrigated using a sprinkler system (12 m × 12 m frame of sprinkler). Water application rates were estimated from the crop evapotranspiration (ETc) of the week before application (net water requirements). This was calculated daily as ETc = Kc ∗ ETo, where ETo is the reference evapotranspiration calculated by the FAO Penman– Monteith method using data from the meteorological station located in the experimental field. The crop coefficient (Kc) was obtained for the maize crop following the method of Allen and FAO (1998). The field was kept free of weeds, pests and diseases, by application of herbicides, following local practices.

Data of wind speed, wind direction, rainfall, radiation and air temperature were obtained every 30 min from the meteorological station placed at the field site. The station was equipped with anemometers at 0.8, 1.25 and 4 m height (Model 05103, R.M. Young, Traverse City, MI, USA). A temperature probe (SKTS 200, Skye Instruments Ltd., Llandrindod Wells, UK) inserted at 10 cm depth onto the soil was used to monitor soil temperature. Mean hourly data were stored on a data logger (DataHog, Skye Instruments Ltd., Llandrindod Wells, UK).

2.2. Gas measurements

2.2.1. NH_3 volatilization

The Integrated Horizontal Flux method (IHF) implemented by Leuning et al. (1985) and further modified by Sherlock et al. (1989) was used to measure NH_3 emissions. According to IHF principles, the measurements plots were surrounded by an unfertilized flat area. Therefore, in this experiment, fertilizer plots were separated by 50 m (Fig. 1). There were no wind-disturbing elements, within 100 m around plots.

As carried out previously under similar climatic conditions (Sanz-Cobena et al., 2008; Abalos et al., 2012), five Passive Flux Samplers (PFS) were mounted in a mast in the center of plots at heights of 0.25, 0.65; 1.25; 2.05 and 3.05 m above soil or canopy. This means that PFS were placed at these heights above soil (after basal fertilization event), or above canopy (after top-dressing fertilization event). Passive flux samplers were moved at different heights as the vegetation grows, in order to assess the NH_3 volatilization related to both fertilization events. Fins at the rear end kept the PFS aligned with the wind. Two additional masts with three PFS each, at height of 0.25, 1.25, 3.05 m above ground were additionally placed upwind of the treated area for determination of background NH_3 concentration (BG) (Fig. 1). The main wind directions within the last 10 years were studied prior the settlement of the experiment (i.e., SW and NE) to place background masts accordingly.

The mean horizontal flux of NH_3 (uc, μg m^{-2} s^{-1}) at each sampling height was calculated as uc = M/At, were M is the mass of NH_3-N collected (μg) in PFS during sampling period t (s), and At is the effective cross-sectional area of the sampler (m^2) as determined in wind tunnel calibrations. The net horizontal flux (F, μg m^{-2} s^{-1}) from the treated surface was then calculated according to Eq. (1):

$$F = \frac{1}{x}\left[\int_0^z (\overline{uc})_{dw} dz - \int_0^z (\overline{uc})_{bg} dz\right] \tag{1}$$

where x (m) is the mean fetch length (i.e., distance from the measurement mast to the upwind boundary of the treated area), z (m) the height of the uppermost sampler and uc the mean horizontal flux measured by each PFS at the downwind (dw) or background mast (BG). As plots were square, fetch length was calculated according the mean wind direction in one-hour periods (data not shown) (Sanz et al., 2010), Since PFS were continuously replaced during the experiment, the IHF method allowed us to calculate cumulative NH_3 emission over an entire period as the sum of NH_3 volatilized at each measurement interval. Flux rates were converted to g N ha^{-1} h^{-1} for reporting.

2.2.2. Gas sampling and analysis

Fluxes of N_2O were measured from April 2015 to late October 2015 using opaque manual circular static chambers (35.6 cm inner diameter, 19.3 cm height) (Abalos et al., 2012). Two static chambers were placed in each selected area of fertilized plots and one in each Control selected area. Each chamber was fitted into stainless steel rings, which were inserted into the soil to a depth of 10 cm before fertilization to avoid lateral diffusion of gases and influence of soil disturbance (Davidson et al., 2002). Gas samples were taken at 0, 30 and 60 min after chamber closure from the headspace of each chamber with 20 mL syringes fitted with 3-way stopcocks, and transferred to pre-evacuated vials sealed with a gas-tight neoprene septum. Thermometers were put inside three randomly selected chambers during the closure period of each measurement in order to correct the N_2O concentrations for temperature. Gas samples were taken two or three times per week during the first month after both fertilizer applications. Afterwards, the frequency of sampling was decreased progressively.

Nitrous oxide concentrations were measured by gas chromatography, using a HP-6890 gas chromatograph (GC), from Agilent Technologies (Wilmington, DE, USA), equipped with a headspace sampler (TurboMatrix 110, from Perkin Elmer). HP Plot-Q capillary columns transported the gas samples, using He as carrier gas, to a ^{63}Ni electron-capture detector (ECD) to analyze the N_2O concentrations with a limit of detection of 50 ppb.

The temperature of both injector and oven were programmed at 50 °C, while the detector's temperature was set at 350 °C. The ECD was run with Ar–CH_4 as make-up gas. The precision of the gas chromatographic data at ambient N_2O concentrations was ±1% or better. Two gas standards (2000 ± 50 and 400 ± 6 ppb N_2O) were provided by Carburos Metalicos S.A. (Barcelona, Spain). These two standards were diluted to perform a calibration curve for this gas with four different concentrations, two original standards and two diluted standards. The response of the GC was quadratic within 200–2000 ppb for N_2O. The increases in N_2O concentrations within the chamber headspace were generally linear ($R^2 > 0.90$) during the sampling period (1 h). Emission rates of N_2O fluxes were, therefore, estimated as the slope of the linear regression between concentration and time (after corrections for temperature) and from the ratio between chamber volume and soil surface area (MacKenzie et al., 1998).

Cumulative gas emissions during the experimental period were calculated as proposed by Menéndez et al. (2008) by multiplying the average flux of two successive determinations by the length of the period between sampling and adding that amount to the previous cumulative total.

2.3. Soil analyses

In order to determine the gravimetric water content and soil properties, soil samples were taken from a depth of 0–10 cm during the experimental period. Soil samples were taken one or two times per week during the first month after both fertilizer applications. Afterwards, the frequency of sampling was decreased progressively. Three soil cores were randomly sampled near to the ring in each area selected to soil and N_2O samples, and then mixed and homogenized in the laboratory. Soil NH_4^+-N and NO_3^--N concentrations were analyzed 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 Perkin Elmer) provided with a UV–V spectrophotometer detector. Water-filled pore space (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 − soil bulk density / 2.65), assuming a particle density of 2.65 g cm^{-3} (Klute and Page, 1982). The gravimetric water content was determined by oven-drying soil samples at 105 °C with a MA30 Sartorius® moisture analyzer. Samples for bulk density were obtained from four cores (2.5 cm diameter and 10 cm length) 15 days after sowing.

2.4. Calculations and statistical analyses

In this experiment, two different periods were considered for soil, GHG and NH_3 data reporting and analysis: Period I (from 20th April, after basal fertilization to 23rd June, day before top dressing fertilization); Period II (from dressing fertilization 23rd June to harvest day 23rd October).

For daily N_2O fluxes and soil NO_3^- and NH_4^+ content eight measurements per fertilizer treatment (four per plot, corresponding to two samples per selected areas within plots) and four per control treatment in each sampling date were used. For daily NH_3 flux, two measurements per treatment were done. The analysis of data was performed by using the StatgraphicsPlus 5.1 software (Statgraphics Technologies, Inc., USA).

Analyses of variance or Student-*t*-test (for NH_3 fluxes) were performed for all variables exposed above (except for climatic ones). Previously, the assumption of independence between treatments, normal distribution of samples and equal variances were checked by calculation of covariance (equal to zero), Q-Q plot and Bartlett-test, respectively ($p > 0.05$ in both cases) No transformation was necessary to assure the normality of samples. For all variables exposed above, except for NH_3 emissions, the Least Significant Difference (LSD) test was used for multiple comparisons between means. Although the IHF method is often used as reference method for its advantages of non-destructive sampling and good representativeness of environmental conditions (Denmead, 2008), most of the studies using IHF method to measure NH_3 volatilization have been carried out with one or two replications (Ni et al., 2015; Sun et al., 2016; Bai et al., 2017). This is a statistical limitation when comparing different treatments.

3. Results

3.1. Environmental condition and soil WFPS

The mean soil temperature (0–10 cm) throughout experiment was 25 °C and ranged from 13.6 to 34.2 °C (Fig. 2). The whole period of experiment, started after basal fertilization (beginning of Period I) and finished at harvest day (end of Period II). During Period II, daily soil temperature was kept at values >30 °C in the 4 weeks following fertilization.

The mean daily wind speed during the experiment was 0.91 m s^{-1} with a speed variation between the maximum and minimum of 2.37 m s^{-1} (data not shown). Higher wind speeds were observed during Period II (1.46 m s^{-1}) compared to Period I (0.64 m s^{-1}). Main wind directions within the experimental period were NE and SW, as expected.

Total rainfall was 100.7 mm from April to October. The total amount of water irrigated was c. 900 mm, starting on 28th May and ending on 27th August.

After basal fertilization, WFPS was above 40% for one week (Fig. 2). Then it decreased to c. 20% until the first irrigation event took place, one month after first fertilization. However, WFPS was generally

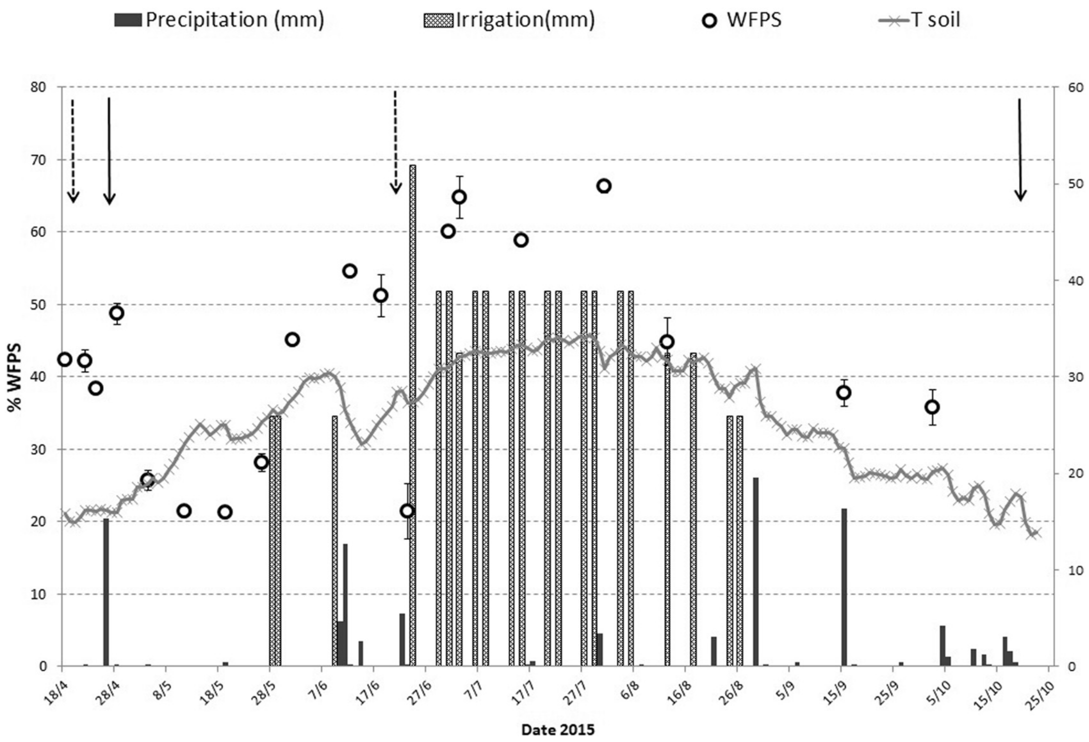

Fig. 2. Evolution of soil water-filled pore space (WFPS, %) on the left and precipitation (mm), irrigation (mm) and soil temperature (°C) on the right during the period of experiment. The dotted arrows indicate the times of N fertilization and the solid arrows indicate the sowing and the harvest day.

maintained above 60% during 40 days after the second fertilization through irrigation.

3.2. Soil mineral N

Ammonium content of the topsoil (0–10 cm) increased both in the N fertilized treatments and the control, but markedly due to N fertilizer application as shown by comparing the soil content for the 2nd and the 5th week after PS application (data not shown). The mean value of NH_4^+ for Period I was 2.32 (±0.46) and 7.03 (±1.50) mg N kg^{-1} for PS-CAN and PS-CAN + NI, respectively (Fig. 3.b). Ammonium concentration dropped below 10 mg N kg^{-1} in PS-CAN within the first week after application, whereas as PS-CAN-NI was above 10 mg N kg^{-1} for three weeks (data not shown). Mean NO_3^- concentration was significantly higher for the treatment with NI only for Period I (Fig. 3).

3.3. Ammonia fluxes

3.3.1. Ammonia fluxes following basal fertilization

Ammonia fluxes increased following application of PS (Fig. 4). In the case of PS without NI (PS-CAN treatment), fluxes of NH_3 ranged between 570 and 10 g N ha^{-1} h^{-1}, on the fertilization day (20th April) and 15 days later, respectively. The highest NH_3 volatilization was measured within the first 4 h after application. A similar pattern was observed when PS was applied with DMPP. However the emission of NH_3 peaked immediately after application reaching a maximum flux of 677 g N ha^{-1} h^{-1}. Throughout the 2 weeks following PS application, the minimum value was 4.6 g N ha^{-1} h^{-1} (Table 1).

Average cumulative NH_3 emission for Period I (Table 2) was 7.3 kg N ha^{-1} in PS-CAN, representing c. 14% of N applied. In the case of pig slurry applied with NI (DMPP) the cumulative NH_3 value was

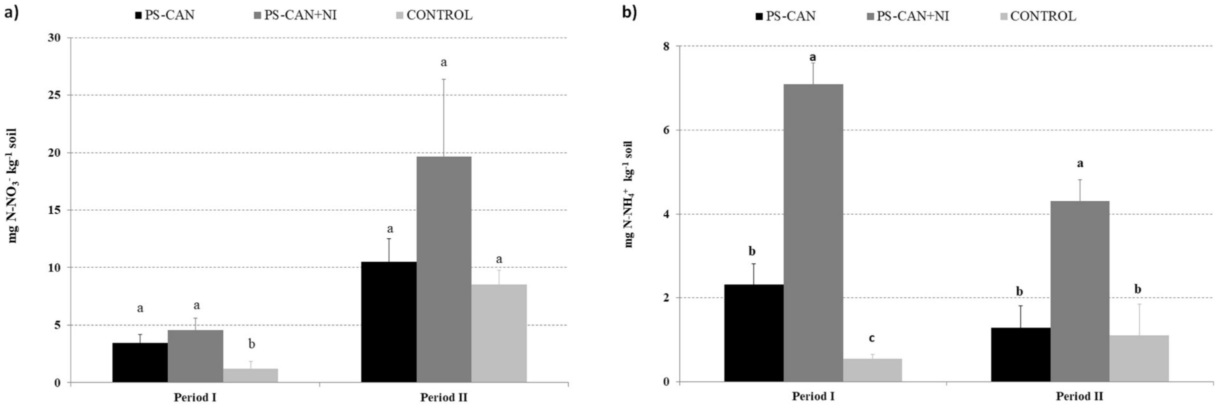

Fig. 3. a) NO_3^--N; b) NH_4^+-N; average concentrations in the 0–10 cm soil layer during the two experimental periods for the different treatments (PS-CAN, pig slurry applied at the basal fertilization and CAN applied at dressing fertilization; PS-CAN + NI, pig slurry with DMPP applied at the basal fertilization and CAN with DMPSA applied at dressing fertilization, C, Control without fertilizer applied). Different letters indicate significant differences within each period of year, by applying the LSD test at $p < 0.05$. Vertical bars indicate standard errors of the ANOVA.

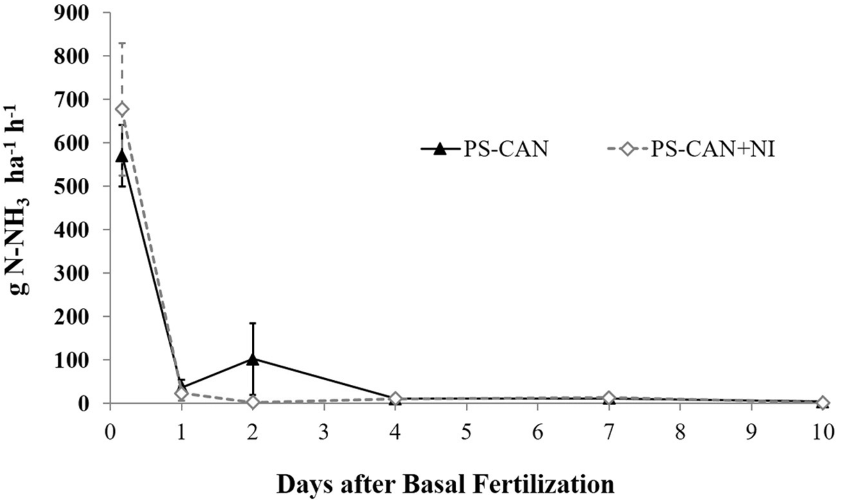

Fig. 4. Period I. Daily ammonia fluxes the following three weeks after basal fertilization (50 kg N ha^{-1}) for the different treatments (PS-CAN, PS-CAN + NI, as defined in the legend of Fig. 3). Vertical bars represent the standard errors.

5.0 kg N ha^{-1} (10% of total N applied), although the difference among these two treatments was not significant (Table 2).

A *t*-test was performed to compare the NH_3 emission rates of PS-CAN and PS-CAN + NI during these four first hours following fertilization. The peak of NH_3 in PS-CAN + NI treated soil was numerically higher than that measured in PS-CAN, but differences were not statistically different (Fig. 4).

3.3.2. Ammonia fluxes following top-dressing fertilization

Application of CAN immediately produced a detectable flux of NH_3, showing its maximum 24 h after fertilizer application, both in fertilizer with and without NI (44.3 g N ha^{-1} h^{-1} and 47.9 g N ha^{-1} h^{-1}, respectively) (Fig. 5). During the 20 days following fertilization, volatilized NH_3 ranged from 0.7 to 44.3 g N ha^{-1} h^{-1} and from 0.64 to 47.9 g N ha^{-1} h^{-1} for CAN and CAN+NI treatment, respectively (Fig. 5). without significant differences ($p < 0.05$) The mean cumulative emission of NH_3 20 days after dressing fertilization was 3.8 and 2.8 kg N ha^{-1} for treatments with and without NI, respectively (Table 2). This difference was not significant at $p < 0.05$, representing 2.5% and 1.8% of total N applied.

Considering NH_3 volatilization in the entire cropping period (fertilization with PS and CAN), N losses through this pathway were 10.9 and 7.8 kg N ha^{-1} for treatments with and without NI, respectively (Table 2). The ratio of N losses and total N applied, considering the entire crop period, were 5.5% and 4% for PS-CAN and PS-CAN + NI treatment, respectively, a difference that was not significant.

3.4. Fluxes of nitrous oxide

As expected, N_2O were influenced by inputs of fertilizers (Fig. 6). Daily mean fluxes of N_2O during Period I ranged from 0.008 to 0.56 g N ha^{-1} h^{-1} with the highest flux measured 53 days after PS fertilization for the PS-CAN treatment. Soil N_2O fluxes were lower in plots where DMPP was added. Fluxes were kept lower than 0.12 g N ha^{-1} h^{-1} during all period for this treatment.

The application of PS-CAN (top-dressing fertilization) rapidly increased N_2O fluxes, peaking 10 days after fertilization event (1.60 g N ha^{-1} h^{-1}). The incorporation of nitrification inhibitor (DMPSA) significantly ($p < 0.05$) reduced fluxes during a period of 2 weeks following application (Fig. 6). The highest flux of N_2O for the PS-CAN + NI treatment was 0.90 g N ha^{-1} h^{-1} and were then lower than 0.35 g N ha^{-1} h^{-1}, 3 weeks after fertilization, despite of frequent irrigation.

Cumulative N_2O emissions are summarized in Table 3. The use of DMPP and DMPSA significantly reduced N_2O emission respectively from PS (basal fertilization) and CAN (dressing fertilization) for the 20 or 22 days after application (Table 3). However, after 53 days no significant effect was observed for CAN application in treatment without NI than with NI treatment (0.36 vs. 0.32 kg N-N_2O ha^{-1}, Table 3). Considering the entire PS-CAN experimental period, NI reduced mean N_2O emission but this difference was not significant ($p > 0.05$). The control treatment emitted the lowest N_2O fluxes (Fig. 6).

Table 1
Description of the experiment: fertilizer and inhibitor treatments.

Treatment	Fertilizer		N rate (kg N ha^{-1})		
	First fertilization	Second fertilization	First fertilization	Second fertilization	Total
Control	–	–	0	0	0
PS-CAN	PS	CAN	50	150	200
PS-CAN + NI	PS + DMPP[a]	CAN + DMPSA[b]	50	150	200

CAN, calcium ammonium nitrate (27% total N = 13.5% NH_4^+-N + 13.5% NO_3^--N).
ACAG® = CAN + DMPSA (27% total N = 7% NH_4^+-N + 5% NO_3^--N).
PS = PIG SLURRY (2 g-N·L^{-1}).

[a] DMPP, solution of 3,4 dimethylpyrazole phosphate.

[b] DMPSA: 3,4 dimethylpyrazole succinic acid.

Table 2
Mean cumulative NH_3 fluxes for the different treatments (PS-CAN, pig slurry applied at the basal fertilization and CAN applied at dressing fertilization, PS-CAN + NI, pig slurry with DMPP applied at the basal fertilization and CAN with DMPSA applied at dressing fertilization). N.S. indicates non-significant differences applying a *t*-test at $p < 0.05$. Standard deviations are given into brackets.

Treatment	Mean NH_3 cumulative emissions (kg-N ha^{-1})		
	Period I (22 DABF[a])	Period II (22 DADF[b])	Total
PS-CAN	7.28 (1.73)	3.77 (1.35)	10.9 (2.91)
PS-CAN + NI	4.98 (0.54)	2.81 (0.32)	7.8 (0.86)
t-Student	N.S.	N.S.	N.S.

[a] DABF (days after basal fertilization).

[b] DADF (days after dressing fertilization).

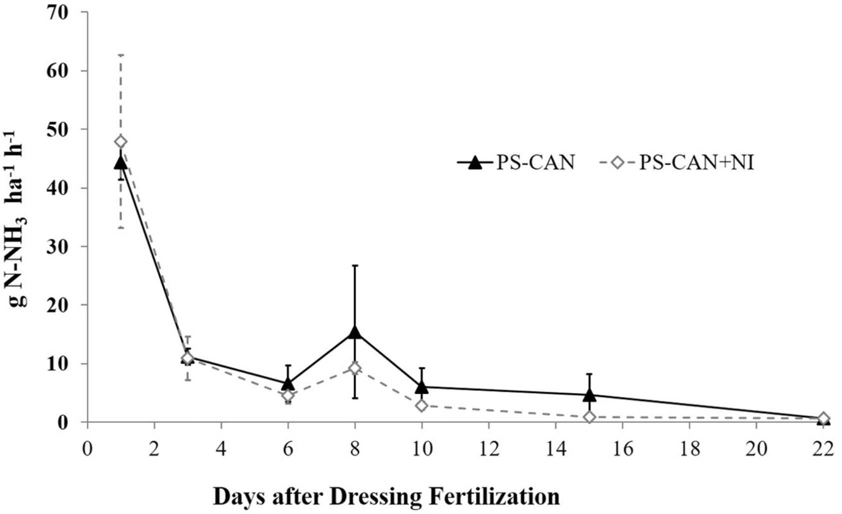

Fig. 5. Period II. Daily ammonia fluxes the following three weeks after top-dressing fertilization (150 kg N ha^{-1}) for the different treatments (PS-CAN; PS-CAN+NI as defined in the legend of Fig. 3). Vertical bars represent the standard errors.

4. Discussion

4.1. Effect of nitrification inhibitors on nitrous oxide emissions

This study showed that the use of DMPP could be considered an effective strategy to reduce direct N_2O emission from PS (reduction of c. 70% of N_2O emission), mainly because, as reported by Chadwick et al. (2011), under these conditions an important fraction of emitted N_2O after its application was produced through nitrification. Our results also confirmed those of Guardia et al. (2017b) who observed a 49% inhibitory effect of DMPP on N_2O emission when 120 kg N ha^{-1} of liquid PS fraction was applied to a maize crop. Additionally, DMPSA mitigated 40% of total N_2O fluxes within the first three weeks after fertilizer application at dressing, with N_2O losses in DMPSA plots similar to the unfertilized treatment (Table 3). Guardia et al. (2017b) found a significant inhibitory effect of 57% when applying CAN and DMPSA (180 kg N ha^{-1}) also in a maize crop in a clay soil, suggesting that nitrification was the dominant N_2O production process at the peaking time. The nitrification inhibitory effect of DMPSA is not well known yet, but probably its effect was based on the presence of dimethylpyrazole (DMP), which is released through the degradation of succinic acid in soil. A technical advantage of DMPSA, in comparison with DMPP (also a precursor of DMP), is the possibility of its combination with any mineral N fertilizer such as CAN. Three weeks after NI application the effectivity of DMPSA was low and consequently most of NH_4^+ was nitrified (NH_4^+ < 10 mg N kg^{-1}, similar to the treatment without NI). Due to the frequent irrigation events in this period (i.e. twice per week), moisture conditions were maintained above 60% WFPS most of the time and, consequently, a small amount of NO_3^- may have been lost through denitrification, thus producing similar N_2O emission in all treatments, even in Control plots. Therefore, the percentage of N_2O reduction using the new NI was lower (30%) and differences were not statistically significant. Menéndez et al. (2012) described that the effectiveness of the NI DMPP in an incubation experiment was conditioned by the magnitude of the losses from the fertilizer without NI, being lower

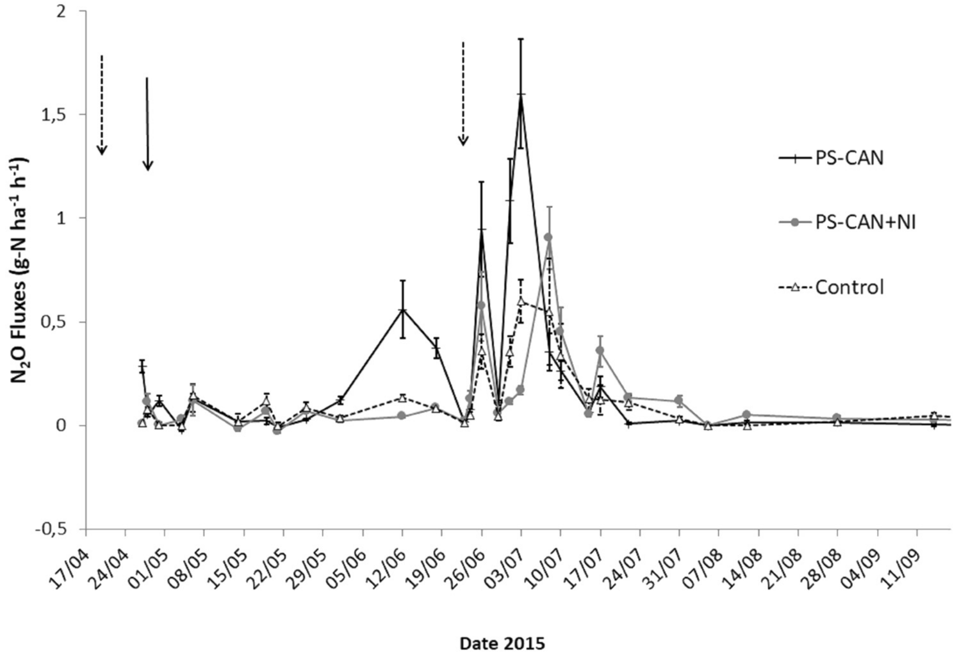

Fig. 6. Daily N_2O emissions during the whole period of the experiment for the different treatments (PS-CAN, control, PS-CAN + NI, as defined in the legend of Fig. 3). Dotted arrows indicate the time of N fertilization and solid arrow the sowing date. Vertical bars indicate standard errors.

Table 3
Mean cumulative N_2O fluxes for the different treatments (PS-CAN, pig slurry applied at the basal fertilization and CAN applied at dressing fertilization, PS-CAN + NI, pig slurry with DMPP applied at the basal fertilization and CAN with DMPSA applied at dressing fertilization, C, Control without fertilizer applied). Different letters within columns indicate significant differences applying Fischer's Least Significant Difference (LSD) test at $p < 0.05$. N.S. indicate no significant differences applying a *t*-test at $p < 0.05$ for the treatment with and without NI. Standard deviation are given into brackets.

	Mean N_2O Cumulative Emissions (kg-N ha^{-1})			
	Period I	Period II		Total
Treatment	20 DABF	22 DADF	53 DADF	Harvest day
PS-CAN	0.18 (0.15) a	0.30 (0.11) a	0.36 (0.22)	0.57 (0.37).
PS-CAN + NI	0.05 (0.03) b	0.18 (0.07) b	0.32 (0.18).	0.40 (0.17)
Control	0.01 (0.005) b	0.17 (0.11) b	0.27 (0.14).	0.29 (0.14).

for low emission rates. This would have been the case in our experiment, where N_2O emission from CAN was very low (0.36 kg N ha^{-1}).

A more complete assessment of the effect of NI over total N_2O emission needs to also incorporate indirect N_2O emission associated to NH_3 volatilization as well as nitrate leaching. Our experiments focused on direct N_2O emission but NH_3 volatilization was also quantified, allowing the calculation of indirect N_2O emissions following NH_3 deposition. According to IPCC guidelines (IPCC emission factor EF_4) 1% of NH_3 emitted is converted to N_2O after deposition (Lam et al., 2017), meaning that only 0.11 (PS-CAN) and 0.08 kg N_2O ha^{-1} (PS-CAN + NI) would have been produced indirectly in our experiment (see Table 2), which is a small amount in comparison to the direct N_2O emission. Therefore, based on the results shown here, the use of the NI would favor the reduction of both direct and indirect N_2O emissions. Moreover, a recent review suggested that, as observed with the direct N_2O EF (Cayuela et al., 2017), the emission factor for Mediterranean areas associated to deposition of NH_3 could be lower than 1% mainly due to climate conditions.

The higher concentration of NO_3^- in soil for period I when NI was used could also be considered a beneficial effect of the DMPP. As in this period the necessity of N by plant was not high, we can speculate that higher NO_3^- losses could also be produced when NI was not used, contributing to indirect emission of N_2O.

4.2. Effect of nitrification inhibitors on ammonia volatilization

Ammonia emissions were not increased by the use of NIs (DMPP or DMPSA), neither synthetic nor organic, even despite both inhibitors enlarged the pool of NH_4^+ in soil within the period of six to 30 days after fertilization (Fig. 4b). As a whole, compared with PS alone, DMPP reduced NH_3 average cumulative emissions by 2.3 kg N ha^{-1}, yet this difference was not significant ($p > 0.05$) and mainly occurred within the first 24 h after application. The rapid mechanical incorporation of pig slurry into the soil and the subsequent adsorption of NH_4^+ to soil colloid reduced the risk of NH_3 volatilization in such a way that presence and effect of NI over the pool of NH_4^+, the main precursor of NH_3, did not affect these gaseous losses. Additionally, the necessary mechanical agitation of PS for mixing it with DMPP prior application may have facilitated the homogenization of slurry composition in relation to NH_4^+ distribution over soil, thus probably favoring a faster adsorption of NH_4^+ to soil. Our results were consistent with the meta-analysis performed by Pan et al. (2016) which did not find significant impact of DMPP on NH_3 emissions, although in the review of these authors, slurry with DMPP was not used under field conditions.

The NI DMPSA did not increase NH_3 losses, in contrary to what has been shown by Qiao et al. (2015), for other NIs. In the review of these authors, 78 experimental observations were analyzed, but none applying PS or DMPSA. In the case of CAN + DMPSA, despite the fertilizer was applied over the soil surface, the addition of water the day after application might have facilitated the dissolution of CAN and its distribution in a wider soil volume. This practice also improved the absorption of NH_4^+ by clay and humus present within the soil colloid, thus limiting desorption of NH_3 to the soil atmosphere and solution. We may assume that if irrigation was high, and NH_4^+ was introduced several cm below the upper soil, NH_3 released in the soil atmosphere could be re-adsorbed in other locations before escaping to the atmosphere by gaseous diffusion. This assumption is in agreement with Holcomb et al. (2011) who reported significant reduction in cumulative NH_3 losses in winter wheat as the amount of irrigation water increased. Sanz-Cobena et al. (2008) also proposed 10 mm irrigation immediately after urea application as a possible explanation of low NH_3 fluxes measured with IHF under field conditions in Central Spain.

4.3. Effect of N management on ammonia volatilization in an irrigated maize crop

The selection of the adequate source of N fertilizer must be a priority to prevent reactive N losses from crops with high N demand (Aguilera et al., 2013). Combination of pig manure, used at sowing, and synthetic fertilizer as top-dressing is the most common fertilization strategy in irrigated crops of areas with high density of pigs. Application of 50 kg N ha^{-1} of liquid manure before seeding led to direct NH_3 losses of c. 11.5% of total N applied. The majority of NH_3 emissions occurred during the first day of PS application with a peak 4 h after fertilizing. This is a common pattern of emission already observed after surface application of slurry in semiarid cropping soils (Gericke et al., 2011). As said, the application of DMPP did not change the pattern and the amount of this emission. Nevertheless, this amount was considerably lower than that measured by Nicholson et al. (2017) (i.e. 20–40% of N applied), possibly due to specific management practices and more unfavorable weather conditions than in our case (i.e., application over stubble in autumn; higher soil moisture in spring and low wind speed at surface level, respectively), where slurry was immediately incorporated into soil using a cultivator, a recommended NH_3-abating application method (Bittman et al., 2014). Although not considered as a treatment in our study, an immediate mechanical incorporation of pig slurry into the soil facilitates the quick adsorption of NH_4^+ to soil colloid thus enhancing the potential of NH_3 abatement (Bittman et al., 2014). Similarly than the findings made by Tiwary et al. (2015), although incorporation of PS enhances the contact of NH_4^+ within the soil, it was difficult to fully prevent N volatilization in the following hours after incorporation. This could be explained by the high NH_3 (g)/NH_4^+ ratio found under the pH conditions of the liquid manure and the soil solution (c. 8.2), which may have promoted desorption of NH_3 from the soil solution, thus rapidly diffusing to the atmosphere of the upper soil. In the case of N synthetic fertilizers, their use as top-dressing seems preferable than liquid manure since this facilitates N application at the moment of maximum N demand by crops. The substitution of urea by CAN, or non-urea fertilizers, is a recommended strategy to mitigate NH_3 emission (Pan et al., 2016). Furthermore, the incorporation of fertilizer with a cultivator or by mean of irrigation is highly recommended. In our experiment, c. 50 mm of water was applied immediately following CAN fertilization thus facilitating its dilution and incorporation onto the soil. The pattern of NH_3 emission after CAN application (with or without DMPSA) was different than that from PS. There was a minor peak of NH_3 emission (370 g N ha^{-1} day^{-1}) 7 days after the irrigation event. Although these have been the first results using DMPSA, other studies using only CAN gave similar level of losses, i.e. Bussink (1994) observed N losses amounting 1.5% of total N applied (250 kg N ha^{-1} applied) in grassland.

4.4. Structural implications of this research

Our results, in line with previous related research, raise an important challenge for the use of manures as fertilizers, a pillar of circular economy in agro-food systems at the regional scale. (Sanz-Cobena et al., 2014a) estimated a 57% reduction by manure incorporation without yield penalties at the Spanish national scale (i.e., 113 Gg NH_3 yr^{-1}).

Therefore, in highly fertilized areas, incorporation cannot be enough for ensuring the achievement of environmental targets of fertilizing practices. Our results indeed show that, even with the implementation of abatement application practices such as slurry incorporation (Bittman et al., 2014), emissions could remain as high as c. 14% of applied N. Based on this, other reactive N abating initiatives, beyond technical approaches, need to be explored. Most livestock producing macroregions of the world are net importers of feed and net exporters of animal products (Lassaletta et al., 2014). This disconnection hampers circular economy since nutrients in manure are hardly recirculated under sustainable conditions within the local cropping systems. Relocation of livestock systems close to cropping systems may facilitate the recycling of manures in an optimal way thus avoiding over application of these materials, and hence reducing losses (Garnier et al., 2016). Again at a larger scale, reduction of the share of animal protein in the human diet might also help finding a better equilibrium between manure production and crop capacity to absorb it, thus reducing N losses to the environment (Westhoek et al., 2013; Billen et al., 2014).

According to Sanz-Cobena et al. (2014b), incorporation of synthetic fertilizer may mitigate 84%, but still contributing to 42 Gg NH_3 y^{-1} at the Spanish level. Therefore, similar to the case of manure fertilizers, the potential of any mitigation strategy addressed to synthetic fertilizers' management must be assessed focusing not only on technical solutions but also including potential structural initiatives at regional basis (Sanz-Cobena et al., 2017).

5. Conclusions

We assessed the use of NI as an agronomic strategy to reduce the effect of fertilization on both N_2O and NH_3 emissions. A reduction of N_2O emission owing to the use of NI was found with PS fertilization, and for CAN for the about three weeks following the application at least. Rapid losses of NH_3 occurred in the following hours after PS application, and remain an important challenge for the use of these manures as fertilizers, even if effective abating practices are implemented.

Regarding NH_3 volatilization, the use of NIs did not increase its fluxes, contrarily to expected, probably because the benefit of incorporating PS into the soil as well as the irrigation applied immediately after CAN fertilization. The significantly higher NH_4^+ concentration in soils observed as a consequence of NIs for several weeks, did not result in higher NH_3 fluxes than those measured from the soil without NI in the same period.

For direct N_2O emissions, the visible reduction in their fluxes was not significant using DMPSA applied with CAN after about 6 weeks, probably because high WFPS of soil, driven by irrigation, which favored denitrification. However it remains that the positive and significant abating effect on direct N_2O emission, especially when PS was applied with DMPP, could lead to recommendation of use of these compounds as a N_2O abating strategy even if indirect emissions from NH_3 deposition are considered.

Whereas complete reduction of NH_3 emissions from manure application to cropping soils would require structural measures to be fulfilled, for N_2O reduction, especially from NH_4^+ based-inorganic fertilizers, possibilities of agronomic mitigation are higher through e.g., split applications, incorporation with irrigation, etc., thus decreasing the GHG budget of agricultural systems.

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