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1	Fertilization scenarios in sprinkler irrigated corn under Mediterranean
2	conditions: effects on greenhouse gas emissions
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#### 27 ABSTRACT

Agricultural soils emit greenhouse gases (GHG). Excessive application of N fertilizer may lead to the accumulation of mineral N in the soil, which is susceptible to loss to the environment. The objective of this study was to quantify the effect of two levels of available mineral N before planting (L, low; H, high) and two rates of ammonium nitrate fertilizer (0 and 300 kg N ha<sup>-1</sup>) on soil methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O) emissions in a sprinkler irrigated corn field located in NE Spain during two growing seasons (2011 and 2012). For both soil N levels at planting, several sampling dates showed higher N<sub>2</sub>O emissions in the 300 kg N ha<sup>-1</sup> treatment compared with the 0 kg N ha<sup>-1</sup> treatment. Applications of N fertilizer resulted in a short-lived increase of N2O emitted. Differences among fertilization treatments were found for soil CO<sub>2</sub> emissions in 2011 and for soil N<sub>2</sub>O emissions in 2011 and 2012. No differences were found between treatments for CH<sub>4</sub>. In the 2012 season, the application of 300 kg N ha<sup>-1</sup> in the L scenario reduced N<sub>2</sub>O yield-scaled emissions (g N-N<sub>2</sub>O kg above-ground N uptake) by 30% due to a significant increase in corn yield (7.6 Mg grain ha<sup>-1</sup>) when compared to the treatment without N. Conversely, under the H scenario, N application doubled yield-scaled N<sub>2</sub>O emissions. Results of this study demonstrate fertilization strategies need to take into account mineral N levels in soil before sowing to reduce GHG emissions during the growing season.

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**Abbreviations**: GHG, greenhouse gas; L, low soil mineral nitrogen at planting; H, high soil mineral nitrogen at planting; CH<sub>4</sub>, methane; CO<sub>2</sub>, carbon dioxide; N<sub>2</sub>O, nitrous oxide; DOY, day of the year; WFPS, water-filled pore space; GWP, global warming potential; GHGI, greenhouse gas intensity; SOC, soil organic carbon; EF, emission factor; EF<sub>GS</sub>, emission factor during the growing season.

# 52 INTRODUCTION

In irrigated corn (Zea mays L.) production systems of NE Spain, high yield
levels require large amounts of soil N available for crop uptake. In this area, fertilization
rates applied to corn are on the order of 300-450 kg N ha <sup>-1</sup> (Sisquella et al., 2004;
Isidoro et al., 2006). Prior studies have concluded that N rates in those systems could be
significantly reduced without compromising maximum grain yields (Berenguer et al.,
2009; Yagüe and Quílez, 2010), especially under high efficiency irrigation systems.
Similarly, in other areas of the world, overfertilization is a common feature in intensive
corn production systems (Cui et al., 2013).
Excessive N applications over the last decade have resulted in serious
environmental problems. A major problem associated with irrigated agroecosystems in
NE Spain is groundwater pollution by nitrate leaching (Daudén et al., 2004; Berenguer
et al., 2008) leading to some areas being declared nitrate vulnerable zones according to
the European Directive 91/676/EEC (European Commission, 1991). However, in
Mediterranean irrigated corn systems, other environmental impacts of N fertilization
such as greenhouse gas (GHG) emissions have only recently been investigated.
Agricultural activity can result in significant GHG emissions to the atmosphere.
In 2010 non-CO <sub>2</sub> emissions in the agricultural sector were estimated to be 10-12% of
global anthropogenic GHG emissions (IPCC, 2013a). According to the latest National
GHG Inventory, the contribution in Spain was estimated to be within this range (about
10.6% in 2011) and agricultural soils were the principal source responsible for the total
agricultural sector emissions (MAGRAMA, 2013).
Soils emit nitrous oxide (N2O) resulting from nitrification and denitrification
processes (Beauchamp, 1997; Venterea et al., 2012). The main agricultural management
practice promoting N <sub>2</sub> O emissions is N fertilization, which enriches soils with

ammonium and/or nitrate ions subject to microbial transformation. Consequently, positive relationships between N rates and N<sub>2</sub>O emissions are commonly found in the literature (e.g., Chantigny et al., 1998; Bouwman et al., 2002; McSwiney and Robertson, 2005; Mosier et al., 2006). In addition, yield-scaled N<sub>2</sub>O emissions (N<sub>2</sub>O-N emitted per kg above-ground biomass N uptake) have been found to sharply increase when N exceeds crops requirements (Van Groenigen et al., 2010). There is not a clear relationship between mineral N fertilization and soil CO<sub>2</sub> fluxes (Alluvione et al., 2009; Morell et al., 2011). Nitrogen addition can increase crop growth and C inputs into the soil. Consequently, N fertilization can result in greater CO<sub>2</sub> fluxes due to changes on soil C turnover and stimulated rhizosphere respiration (Xu and Wang, 2008; Álvaro-Fuentes et al., 2012). Finally, agricultural soils can act as either CH<sub>4</sub> source or sink depending on the oxygen availability for microbial activity (Hütsch, 2001) and while aerobic conditions result in CH<sub>4</sub> oxidation, this process can be inhibited by N fertilization (Plaza-Bonilla et al., 2014a).

Sprinkler irrigation systems are increasingly used in many irrigated areas of Spain and around the world in field crop production systems due to their inherent higher efficiency and the possibility to automate the irrigation process. In those irrigated systems, high corn yields together with high N fertilization rates and soil water levels can result in favorable conditions for the production and emission of soil GHG (Aguilera et al., 2013). In this study, we evaluated the impact of different N fertilization scenarios based on the application of N under different soil N levels at planting on soil GHG emissions, corn yields and yield-scaled GHG emissions under Mediterranean conditions. We hypothesized that yield-scaled N<sub>2</sub>O emissions would be positively associated with residual N levels in sprinkler irrigated corn systems.

#### MATERIAL AND METHODS

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### **Experimental site and crop management**

The study was conducted in Almudévar (42°01'47''N, 0°35'21''W), an important irrigated agricultural area in NE Spain equipped with modern sprinkler systems. Climate is characterised by average maximum and minimum air temperatures of 19.8 and 7.9 °C, respectively, and a mean annual precipitation of 451 mm. Particular climate characteristics for the two corn seasons studied are presented in Fig. 1. Mean annual evapotranspiration is 1284 mm. The study was performed in a 6 ha field with the soil classified as Typic Xerofluvent (Soil Survey Staff, 1994). The field had been cropped with corn during the four years previous to this study. Soil properties at the initiation of the experiment are presented in Table 1. The selected field presented a gradient in soil texture in which clay and sand contents greatly differed between areas. Accordingly, we selected two different areas of about 1 ha within the field with contrasting soil texture (Table 1). In 2011, we set up one experiment in which four fertilization scenarios were compared in the area with lower clay content (Experiment 1). In 2012, the same fertilization scenarios and experimental design was set up in the area with higher clay content (Experiment 2). Since soil texture and initial soil N levels were different between areas (Table 1), we analyzed Experiment 1 and Experiment 2 independently. In each experiment, the same four fertilization scenarios were compared. The scenarios resulted from the combination of two soil mineral N levels at planting, low (L) and high (H), and two N fertilizer rates, unfertilized (0) and fertilized with 300 kg N ha<sup>-1</sup> (300). The previous season of each experimental year (i.e., 2010 and 2011) the corn field was fertilized with two contrasting N rates (0 and 300 kg N ha<sup>-1</sup>) to create two areas with different soil mineral N available for the following season (Table 1).

Fertilization management during the previous season was similar to the management performed in the fertilized scenarios during the two experiments. This management consist of the application of 300 kg N ha<sup>-1</sup> as ammonium nitrate (33.5% N) split into three equal rates of 100 kg N ha<sup>-1</sup>: one at pre-planting (April 12<sup>th</sup> 2011, DOY 102, and April 11<sup>th</sup> 2012, DOY 102) and two sidedress applications at the V5-V6 stage (June 9<sup>th</sup> 2011, DOY 160, and June 6<sup>th</sup> 2012, DOY 158) and V14-V15 stage (July 12<sup>th</sup> 2011, DOY 193, and July 16<sup>th</sup> 2012, DOY 198). Both experiments were set as a split-plot design with N level at planting as main-plot and N rate as sub-plots. Each scenario was replicated four times with plot size of 12.5 m x 3.75 m.

Corn ('Pioneer var. PR34N43') was planted on April 19<sup>th</sup> 2011 (DOY 109) and April 26<sup>th</sup> 2012 (DOY 117) at a density of 73,000 plants ha<sup>-1</sup> with 75 cm row spacing. In both seasons, soil tillage was performed one month before planting and consisted of chisel ploughing just after a pass with a shredder to chop corn residues from the previous season. Grain corn harvest occurred on October 3<sup>rd</sup> 2011 (DOY 276) and October 1<sup>st</sup> 2012 (DOY 275). Plots were sprinkler-irrigated (solid set system) with a total amount of applied water similar in both growing seasons (8100 m<sup>-3</sup> ha<sup>-1</sup> per season) (Fig. 2), distributed in 59 and 66 irrigation events in Experiment 1 and Experiment 2, respectively. Weed and pest control in the field were made according to the standard practices in the area.

#### **GHG** measurements

On June  $2^{nd}$  2011 (DOY 153) and May  $10^{th}$  2012 (DOY 123) a 315-mm diameter PVC collar was inserted 5 cm into the soil in each of the 16 experimental plots. Soil CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O emissions were measured every two weeks during the 2011 season (Experiment 1) and every 10 days during the 2012 season (Experiment 2)

using 20-cm tall vented closed chambers attached to the collars and similar to those described in Holland et al. (1999). The time elapsed between the insertion of the collars and the first sampling was at least one week in order to avoid any alteration in soil gas emission. At each sampling date, 17 mL of gas was removed from inside each chamber using a polypropylene syringe at 0, 20 and 40 minutes after closing the chamber and injected in 12 mL Exetainer borosilicate glass vials (model 038W, Labco, High Wycombe, UK). In order to avoid internal increases of temperature, the chambers were covered with a reflective insulation film. Every sampling started at 9:30 am and lasted for about one hour and a half. A total of 48 gas samples were collected on every sampling date (16 plots x 3 sampling times per plot). Emission rates were calculated taking into account the linear increase in gas concentration in the chamber over time and correcting for air temperature. Gas samples were analyzed with an Agilent 7890A gas chromatography system equipped with an electron-capture (ECD) and a flameionization (FID) + methanizer detectors and three valves in order to obtain the three gases of interest (i.e., CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) for every gas injection. A HP-Plot Q column (30 m x 0.32 mm x 20 µm) was used with a pre-column of the same characteristics but 15 m long. The injector and the oven temperature were set to 50°C. The temperature of the FID and the ECD detectors was set to 250 and 300°C, respectively. The methanizer temperature was set to 375°C. For the FID detector, H<sub>2</sub> was used as a carrier gas and N<sub>2</sub> as a make-up gas at 35 and 25 mL min<sup>-1</sup>, respectively. In the case of the ECD detector, 5% methane in argon was used as a make-up gas at 30 mL min<sup>-1</sup>.

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## **Crop and soil measurements**

At harvest, all corn plants were collected from the two central rows of each experimental plot (12 m<sup>2</sup>). The ears were separated from the rest of the plant, and both

dried at 65 °C, weighed, ground and analyzed for total N content by dry combustion (TruSpec CN, LECO, St. Joseph, MI, USA). Grain yield was reported on a 14% moisture content basis.

Within one meter distance from each chamber about 50 g of soil was taken from the 0-5 cm soil layer with a flat spade for soil moisture determination (gravimetric water content). In addition, soil temperature at 5 cm depth was measured with a hand-held temperature probe. Both measurements were taken at every sampling point 20 minutes after the closing of the chamber. Water-filled pore space (WFPS) was obtained as the quotient between the volumetric soil water content and total soil porosity (Linn and Doran, 1984). Soil porosity was calculated assuming a particle density of 2.65 Mg m<sup>-3</sup>. Soil bulk density was determined by the cylinder method (Grossman and Reinsch, 2002) at the end of each growing season. In the Experiment 1, soil water content and soil temperature were only measured in the two scenarios with high initial soil N level. However, in the Experiment 2, both soil variables were measured in all four scenarios. Soil temperature and WFPS values presented in Fig. 2 are average values for the different treatments. An automated weather station 2 km from the experimental site registered daily air temperature and precipitation.

#### Calculations and statistical analyses

For each experiment and GHG gas (i.e., CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O), cumulative emissions were calculated with the trapezoid rule (Plaza-Bonilla et al., 2014b). For each scenario, the net global warming potential (GWP, kg CO<sub>2</sub> eq ha<sup>-1</sup>) was calculated considering soil CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions during the growing season and the CO<sub>2</sub> emissions associated with the management inputs and farm operations. Each net GWP value was divided by the corn grain yield of each scenario to calculate the greenhouse

gas intensity (GHGI) based on growing season GHG emissions (Mosier et al., 2005). Likewise, yield-scaled  $N_2O$  emissions were calculated as the cumulative growing season  $N_2O$ -N emitted in each scenario and experiment per unit of above-ground biomass N uptake (Van Groenigen et al., 2010). For each experiment, an  $N_2O$ -emission factor for corn during the growing season (EF<sub>GS</sub>) was calculated as the cumulative growing season  $N_2O$  emission in the fertilized treatment minus the emission in the control, divided by the amount of fertilizer applied (i.e. 300 kg N ha<sup>-1</sup>).

Gas emissions were analysed with the *MIXED* procedure of the SAS software (SAS Institute, 1999) considering sampling effect within the same plot as repeated measures over time. When significant, differences among means were identified at P = 0.05 using an LSD test. A first-order autoregressive model was used to model the covariance structure of the data.

#### **RESULTS AND DISCUSSION**

#### Soil CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O emissions

Air temperature and precipitation over the two growing seasons are presented in Fig. 1. Mean air temperature over the growing season was 21.1 and 22.0 °C for Experiment 1 and 2, respectively. Total growing season precipitation for both growing seasons (Experiment 1 and 2) was 123 and 99 mm, respectively (Fig. 1).

Soil temperature, WFPS and water applied during the irrigation events are presented in Fig. 2. Mean soil temperature at 5 cm soil depth was 18.9 °C for Experiment 1 and 18.1 °C for Experiment 2. Mean WFPS (0-5 cm soil depth) for Experiment 1 and 2 were 49.7 and 49.5%, respectively (Fig. 2).

As explained previously, GHG emissions were measured during one corn season for each experiment, similar to other studies where GHG emissions were measured during a single growing season (e.g., Meijide et al., 2007; López-Fernández et al., 2009). In Experiment 1, soil CO<sub>2</sub> emissions averaged over the entire growing season were similar among the four fertilization scenarios. In contrast, mean soil CO<sub>2</sub> emissions in Experiment 2 were greater in the unfertilized scenario with low N level at planting compared to the fertilized scenario with high N level at planting (Table 2). In both experiments, the seasonal CO<sub>2</sub> emissions from corn production were in the range of values reported in the literature (e.g., Omonode et al., 2007; Alluvione et al., 2009).

The two Experiments showed a different temporal soil CO<sub>2</sub> emission pattern (Fig. 3). In Experiment 1, variation in soil CO<sub>2</sub> emissions between sampling dates were lower than in Experiment 2. In Experiment 1 daily values ranged from 1369 to 4472 mg CO<sub>2</sub>-C m<sup>-2</sup> d<sup>-1</sup>, but in Experiment 2 the values ranged between 283 to 5905 mg CO<sub>2</sub>-C m<sup>-2</sup> d<sup>-1</sup> (Fig. 3). Differences in soil texture between sites may have contributed to variation in CO<sub>2</sub> emissions. This finding could be explained by different soil physical processes. First, the higher clay content in Experiment 1 (Table 1) could result in a greater proportion of soil organic carbon (SOC) protected from microbial decomposition (Six et al., 2002; Plaza-Bonilla et al., 2013). According to the model developed by Parton et al. (1987) the decay rate of active soil organic carbon diminishes at increasing silt plus clay soil contents due to C-physical protection. Li et al. (2015) tested the sensitivity of CO<sub>2</sub> flux to soil temperature and WFPS depending on soil texture using a hierarchical Bayesian model. They observed a lower sensitivity of CO<sub>2</sub> emissions to soil temperature and WFPS in soils with a finer texture (i.e. greater proportion of clay). Van Gestel (1993) pointed out that, among other factors, the flush of C mineralization by drying/rewetting processes depends on the amount of soil

organic matter protected by clay adsorption. In our experiment, the application of irrigation water would have led to successive soil drying and rewetting cycles, leading to CO<sub>2</sub> fluxes which could have been buffered by the greater adsorption of active soil organic carbon in Experiment 1. Moreover, the greater heat capacity in soils of finer textures, which reduces soil temperature fluctuations (Abu-Hamdeh, 2003), could also explain the different dynamics of CO<sub>2</sub> emissions in Experiments 1 and 2.

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In Experiment 2, the four scenarios showed an increase in soil CO<sub>2</sub> emissions during the first 50 days after the first sampling date and afterwards emissions kept steady (Fig. 3). This would be the expected trend since soil CO<sub>2</sub> emissions reported in this study are the sum of the CO<sub>2</sub> resulting from microbial activity plus that from root tissue respiration. Plant growth has a significant impact on microbial activity through root exudates, which are easily decomposed by soil microorganisms (Kuzyakov and Domanski, 2000). In corn, the contribution of rhizosphere respiration (i.e., root respiraton plus decomposition of root exudates) to the total soil respiration can be significant with values close to 50% around the period of maximum crop activity (Rochette et al., 1999). This may explain the increase in soil CO<sub>2</sub> emissions observed over Experiment 2 until 190-200 DOY from which the soil CO<sub>2</sub> emissions decreased (Fig. 3). The 190-200 DOY period corresponded to the second and third weeks of July with the crop showing the highest growth rates (i.e., V14-VT) and when the emissions were expected to be the highest. In Experiment 1, soil CO<sub>2</sub> emissions achieved two peak values in the third and tenth sampling dates (i.e., 165 and 240 DOY, respectively) (Fig. 3). After the peak during 240 DOY, soil CO<sub>2</sub> emissions dropped precipitously. We did not find any anomaly in the crop development in Experiment 1 as reflected by the similar average grain yield between both experiments (Table 4). Furthermore, soil

temperature and soil water content values of both experiments were within the same range (Fig. 2).

In both experiments, similar CH<sub>4</sub> emissions were measured among fertilization scenarios (Table 2; Fig. 4). In Experiment 2, all four compared scenarios showed negative CH<sub>4</sub> fluxes indicating greater proportion of methanotrophic activity within the soil matrix. However, in Experiment 1, the unfertilized scenario with low initial N level at planting and the scenario fertilized with high initial N level showed mean positive emission values indicating greater proportion of methanoghenic processes (Table 2). High variability in CH<sub>4</sub> flux values made it difficult to find a possible explanation to this different behaviour in emissions between experiments. As it can be observed in Table 2, despite the large disparity between CH<sub>4</sub> values, no statistical difference was found between treatments.

In the two experiments, fertilization scenarios showed differences in mean soil N<sub>2</sub>O emissions. In Experiment 1, soil N<sub>2</sub>O emissions ranged between -0.48 and 3.17 mg N<sub>2</sub>O-N m<sup>-2</sup> d<sup>-1</sup> and between -0.20 and 3.00 mg N<sub>2</sub>O-N m<sup>-2</sup> d<sup>-1</sup> in the Experiment 2 (Fig. 5). These values are within the range found in other similar corn studies (Venterea et al., 2005; Halvorson et al., 2010; Omonode et al., 2011). However, compared with other irrigated corn experiments performed in Central Spain (López-Fernández et al., 2007; Meijide et al., 2007), our N<sub>2</sub>O emission values are lower. This difference could be explained by the fact that previous studies compared different organic fertilizer types, which usually enhance N<sub>2</sub>O emission due to the increase in the availability of labile carbon that act as a source of energy for heterotrophic bacteria. It has been established that the availability of labile forms of soil organic carbon (SOC) stimulates NO<sub>3</sub><sup>-1</sup> reduction and thus N<sub>2</sub>O production since heterotrophic denitrifying bacteria use carbon as an electron donor (Tiedje et al., 1982; Firestone and Davidson, 1989).

In both experiments, the greatest mean seasonal values were found in the fertilized scenarios (Table 2). Likewise, in both experiments, the fertilized scenarios (i.e., 300L and 300H) showed increases of N<sub>2</sub>O emissions after N fertilizer applications (Fig. 5). The direct supply of NO<sub>3</sub> and NH<sub>4</sub> through the application of ammonium nitrate as fertilizer increased their availability for soil aerobic nitrification and anaerobic denitrification processes. It has been well documented that these two processes are the main sources of N<sub>2</sub>O in soils (Firestone and Davidson, 1989; Bremner, 1997). Depending on the availability of O<sub>2</sub> in the soil atmosphere during the days following N applications, the proportion of N<sub>2</sub>O produced from nitrification and denitrification could vary (Ma et al., 2010). In both experiments, the N<sub>2</sub>O peak after the first sidedress application (DOY 160-170) was measured with WFPS values near 30%. However, the N<sub>2</sub>O peak after the second sidedress application (DOY 200-210) was measured with WFPS values above 60% (Fig. 2). Differences in WFPS suggest different microbial mechanisms affected N<sub>2</sub>O emission peaks after each sidedress application. According to Linn and Doran (1984), nitrification is reduced above 60% WFPS due to oxygen limitation in soil matrix while N<sub>2</sub>O is produced mainly from denitrification, whereas at WFPS < 60% N<sub>2</sub>O is produced by nitrification (Hernandez-Ramirez et al., 2009). Negative N<sub>2</sub>O emission values were found in six sampling dates (DOY 165, 243

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Negative N<sub>2</sub>O emission values were found in six sampling dates (DOY 165, 243 and 264 in Experiment 1 and DOY 139, 165 and 202 in Experiment 2) ranging from - 0.02 to -0.48 mg N<sub>2</sub>O-N m<sup>-2</sup> d<sup>-1</sup> (Fig. 5). Except for one sampling date (DOY 139), all the negative N<sub>2</sub>O values were observed in scenarios with low initial N level at planting (Fig. 5). Although none of the negative values found were statistical different from zero, our results are in line with other experiments in which values below zero were also observed (Chapuis-Lardy et al. 2007) where N<sub>2</sub>O consumption was favored by certain factors such as low soil mineral N content and elevated soil moisture content for which

high denitrification rates had been observed. On the contrary, other authors have observed  $N_2O$  consumption values under low soil moisture contents (Flechard et al., 2005; Plaza-Bonilla et al., 2014b). Accordingly, in our experiment, the higher number of dates with  $N_2O$  consumption values in the plots with low initial N level at planting may be explained by differences in mineral N since WFPS values were similar between plots (data not shown). Moreover, this inference is also supported by the fact that most sampling dates with  $N_2O$  consumption were found in unfertilized scenarios (Fig. 5). Still, such speculation is tenuous as all  $N_2O$  consumption values were not different from zero.

## Cumulative growing season emissions, net GWP and yield-scaled emissions

Differences in cumulative growing season emissions among fertilization scenarios were only found for N<sub>2</sub>O (Table 3). In Experiment 1, cumulative N<sub>2</sub>O emissions ranged from 548 to 2539 g N<sub>2</sub>O–N ha<sup>-1</sup> with the highest values found in the two fertilized scenarios. In Experiment 2, cumulative emissions ranged from 124 to 1920 g N<sub>2</sub>O–N ha<sup>-1</sup> and the highest values were observed in the scenario fertilized with initial high soil N at planting (Table 3). The addition of N fertilizer increases soil mineral N losses as N<sub>2</sub>O through higher nitrification and denitrification rates (Chantigny et al., 1998; Bouwman et al., 2002). The cumulative N<sub>2</sub>O-N values obtained in our study are comparable to the values reported in the meta-analysis performed by Aguilera et al. (2013) for Mediterranean systems. In this analysis, the authors estimated a mean cumulative N<sub>2</sub>O emission of 4.0±2.6 kg N<sub>2</sub>O-N ha<sup>-1</sup> for irrigated areas (with high water additions) and mean cumulative emission during the growing season of 4.5±3.2 kg N<sub>2</sub>O-N ha<sup>-1</sup> when corn was cropped. Thus, our values are in the low range of values reported by Aguilera et al. (2013). Soil N<sub>2</sub>O emissions are highly variable in both

space and time and this variability is caused by a large number of soil, climate and management factors (Leip et al., 2011; Venterea et al., 2012).

In both experiments, net GWP was calculated considering emissions from soil, farm operations and N fertilizer production, transportation and storage (Table 4). No significant differences were found among treatments for net GWP. When net GWP was analysed as a function of crop yield (i.e., GHGI), similar values among treatments were also found. Net GWP and GHGI values from this study should be interpreted with caution since the values relied on emission measurements only during the growing season. In the literature, some studies present net GWP for the entire year (Mosier et al., 2005, 2006). However, since the objective of our study was to evaluate the effects of different fertilization scenarios with different initial soil N levels at planting on GHG emissions during the growing season, no attempt was made to measure soil GHG emissions over the non-growing period. To solve this lack of data one possibility would be to estimate GHG emissions during the non-growing season through linear interpolation (Aguilera et al., 2013) or process-based modeling. However, in order to avoid large uncertainties in the GHG estimation, net GWP was only calculated for the growing season.

Yield-scaled N<sub>2</sub>O emissions were calculated considering the accumulated soil N<sub>2</sub>O emitted by each scenario and the total above-ground biomass N uptake by the crop (Van Groenigen et al., 2010). Only the fertilization scenarios of Experiment 2 showed significant differences in yield-scaled N<sub>2</sub>O (Table 5). The fertilized scenario with the greatest initial soil N content had greater yield-scaled N<sub>2</sub>O emissions compared to the same unfertilized scenario (Table 5). Consequently, in Experiment 2, the initial hypothesis (i.e., yield-scaled N<sub>2</sub>O emissions would be positively associated with residual N levels ) was not rejected. In Experiment 1, the fertilized scenario with high N

level at planting showed 25% higher yield-scaled N<sub>2</sub>O emissions compared to the unfertilized scenario, despite not being significantly different. Van Groenigen et al. (2010) observed a significant increase in yield-scaled N<sub>2</sub>O emissions when N rates exceeded 200 kg N ha<sup>-1</sup>. In contrast, scenarios with low initial N content at planting showed slightly higher but not significantly different yield-scaled N<sub>2</sub>O emissions in the unfertilized compared to the fertilized treatments (Table 5). Such results may be explained by the significant response of the corn grain yields to N fertilizer application in scenarios with the low level of mineral N before planting, with a 52% and 97% increase in corn yield when applying 300 kg N ha<sup>-1</sup> when compared to the control without N for Experiments 1 and 2, respectively (Table 4). High N levels before planting showed grain yield increases of 5% and 6% with 300 kg N ha<sup>-1</sup>. Berenguer et al. (2008) reported a lack of response of corn grain yield to the addition of N fertilizer when high levels of N were present in the soil before planting. Those results highlight the importance of a N fertilization management plan that accounts for the available soil mineral N at planting in order to reduce yield-scaled N<sub>2</sub>O emissions. Similarly, the Emission Factor (EF) calculated in both experiments for the growing season of corn showed that EF was not constant but actually changed according to the residual nitrogen available prior to planting (Table 6).

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#### **CONCLUSIONS**

In irrigated corn systems of NE Spain a rational fertilization strategy based on the amount of N in the soil before planting is key to maintain high yields. In this study, we have found that in those agroecosystems N fertilization affects growing season N<sub>2</sub>O emission but not CO<sub>2</sub> or CH<sub>4</sub> emission. Applications of N fertilizer resulted in short-lived increases of N<sub>2</sub>O emissions within the week following application. However,

different soil mineral N levels at planting also have an impact on the N<sub>2</sub>O emitted over the growing season, but to a lesser extent than variation in N fertilizer rate. In our study, when low levels of mineral N were available before planting, the application of N fertilizer led to a significant response of corn yields but without affecting yield-scaled N<sub>2</sub>O emissions. Conversely, under the scenario of high levels of N, the application of fertilizer did not lead to greater corn productivity, which increased yield-scaled N<sub>2</sub>O emissions. These results suggest efficient N fertilizer management considering soil N levels at planting is needed to minimize soil N<sub>2</sub>O emitted per unit of N uptake in high-yield irrigated corn systems.

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595	Figure captions
596	
597	Fig. 1. Daily air temperature and precipitation during the growing season in Experiment
598	1 (2011) and Experiment 2 (2012).
599	
600	Fig. 2. Average soil temperature at 5 cm depth and water-filled pore space (WFPS) for
601	the 0-5 cm soil layer in Experiment 1 (A) and Experiment 2 (B) and irrigation water
602	applied in Experiment 1 (C) and Experiment 2 (D). Soil temperature and WFPS values
603	represent means for different treatments.
604	
605	Fig. 3. Temporal soil CO <sub>2</sub> emissions in Experiment 1 (A) and Experiment 2 (B) during
606	the growing season under four fertilization scenarios: 0L, unfertilized and initial low
607	soil N content at planting; 0H, unfertilized and initial high soil N content at planting;
808	300L, fertilized (300 kg N ha <sup>-1</sup> ) and initial low soil N content at planting; and 300H,
609	fertilized (300 kg N ha <sup>-1</sup> ) and initial high soil N content at planting. Bars indicate
610	standard error. For the same sampling date, significant differences between fertilization
611	scenarios are indicated with an asterisk (P<0.05). Vertical arrows indicate fertilizer
612	applications.
613	
614	
615	Fig. 4. Temporal soil CH <sub>4</sub> emissions in Experiment 1 (A) and Experiment 2 (B) during
616	the growing season under four fertilization scenarios: 0L, unfertilized and initial low
617	soil N content at planting; 0H, unfertilized and initial high soil N content at planting;
618	300L, fertilized (300 kg N ha <sup>-1</sup> ) and initial low soil N content at planting; and 300H,
619	fertilized (300 kg N ha-1) and initial high soil N content at planting. Bars indicate

scenarios are indicated with an asterisk (P<0.05). Vertical arrows indicate fertilizer applications. Fig. 5. Temporal soil N<sub>2</sub>O emissions in Experiment 1 (A) and Experiment 2 (B) during the growing season under four fertilization scenarios: 0L, unfertilized and initial low soil N content at planting; 0H, unfertilized and initial high soil N content at planting; 300L, fertilized (300 kg N ha<sup>-1</sup>) and initial low soil N content at planting; and 300H, fertilized (300 kg N ha<sup>-1</sup>) and initial high soil N content at planting. Bars indicate standard error. For the same sampling date, significant differences between fertilization scenarios are indicated with an asterisk (P<0.05). Vertical arrows indicate fertilizer applications. 

standard error. For the same sampling date, significant differences between fertilization

Table 1. Selected soil properties for both experiments.

Soil properties	Soil depth	Experiment 1	Experiment 2
Soil nitrate content at planting (mg NO <sub>3</sub> -N kg <sup>-1</sup> )	0-60 cm		
Low (L)		7.9	3.2
High (H)		24.7	25.9
pH (H <sub>2</sub> O; 1:2.5)	0-25 cm	8.4	8.1
Electrical conductivity (1:5) (dS m <sup>-1</sup> )	0-25 cm	0.2	0.3
Electrical conductivity (1:5) (dS m <sup>-1</sup> ) Particle size distribution (g kg <sup>-1</sup> )	0-25 cm		
Sand		120	320
Silt		560	580
Clay		320	100

Table 2. Mean growing season CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O emissions for different N levels at planting and N fertilization rates in both experiments.

	N level at planting	N fertilization rate (kg N ha <sup>-1</sup> )	CO <sub>2</sub> (mg CO <sub>2</sub> -C m <sup>-2</sup> d <sup>-1</sup> )	CH <sub>4</sub> (mg CH <sub>4</sub> -C m <sup>-2</sup> d <sup>-1</sup> )	N <sub>2</sub> O (mg N <sub>2</sub> O-N m <sup>-2</sup> d <sup>-1</sup> )
Experiment 1			<del></del>		
•	Low	0	2935 (142)	-0.31 (0.25)	0.46 (0.19)c
		300	2913 (221)	0.03 (0.23)	1.14 (0.20)ab
	High	0	2951 (232)	0.14 (0.21)	0.65 (0.13)bc
		300	2772 (168)	-0.32 (0.16)	1.24 (0.18)a
Experiment 2					
•	Low	0	3875 (230)a†	-0.13 (0.36)	0.35 (0.09)b
		300	3349 (254)ab	-0.44 (0.30)	0.81 (0.16)a
	High	0	3300 (269)ab	-0.28 (0.26)	0.36 (0.09)b
		300	2760 (209)b	-0.12 (0.32)	1.04 (0.20)a

 $<sup>\</sup>dagger$  Within each experiment and column, different letters indicate significant differences between treatments at P < 0.05. Values in parenthesis represent standard error.

Table 3. Cumulative growing season  $\mathrm{CO}_2$ ,  $\mathrm{CH}_4$  and  $\mathrm{N}_2\mathrm{O}$  emissions for different N levels at planting and N fertilization rates in both experiments.

	N level at	N fertilization	$CO_2$	CH <sub>4</sub>	N <sub>2</sub> O
	planting	rate (kg N ha <sup>-1</sup> )	$(kgCO_2-C ha^{-1})$	$(gCH_4-C ha^{-1})$	$(gN_2O-N ha^{-1})$
Experiment 1					_
	Low	0	4869 (301)	-402 (488)	1121 (116)b†
		300	5345 (807)	60 (396)	1849 (237)a
	High	0	5630 (1144)	249 (175)	1027 (235)b
		300	4822 (360)	-564 (157)	2041 (195)a
Experiment 2					
-	Low	0	5643 (440)	-22 (481)	499 (163)b
		300	4907 (525)	-709 (722)	890 (138)b
	High	0	4776 (634)	-539 (291)	523 (31)b
	-	300	4335 (308)	-309 (631)	1439 (258)a

<sup>†</sup> Within each experiment and column, different letters indicate significant differences between treatments at P < 0.05. Values in parenthesis represent standard error.

Table 4. Net global warming potential (GWP) and greenhouse gas intensity (GHGI) during the corn growing season for different N levels at planting and N fertilization rates in both experiments.

	N level at planting	N fertilization rate (kg N ha <sup>-1</sup> )	Farm operations (kg CO <sub>2</sub> eq ha <sup>-1</sup> )¶	N fertilizer (kg CO <sub>2</sub> eq ha <sup>-1</sup> )#	N <sub>2</sub> O (kg CO <sub>2</sub> eq ha <sup>-1</sup> ) ††	CH <sub>4</sub> (kg CO <sub>2</sub> eq ha <sup>-1</sup> ) ††	Soil respiration (kg CO <sub>2</sub> ha <sup>-1</sup> )	Crop residue (kg CO <sub>2</sub> ha <sup>-1</sup> ) ¶¶	Net GWP (kg CO <sub>2</sub> eq ha <sup>-1</sup> ) ##	Grain yield (kg ha <sup>-1</sup> )	GHGI (kg CO <sub>2</sub> eq kg grain <sup>-1</sup> )
Experiment 1								, " "			
	Low	0	215	0	467b†	-15	17852	20022	-1503	9928c	-0.17
		300	215	402	770a	2	19600	20022	967	15121a	0.08
	High	0	215	0	428b	9	20643	21202	93	13246b	-0.03
		300	215	402	850a	-21	17679	21202	-2077	13952ab	-0.15
Experiment 2											
•	Low	0	196	0	208b	-1	20691	20022	1072	7900b	0.16
		300	196	402	371b	-26	17994	20022	-1086	15534a	-0.07
	High	0	196	0	218b	-20	17511	21202	-3297	13395a	-0.28
		300	196	402	599a	-12	15897	21202	-4120	14260a	-0.30

<sup>†</sup> Within each experiment and column, different letters indicate significant differences between treatments at P < 0.05

<sup>¶</sup> Farm operations represented shredding corn stalks, chiseling, rototilling (twice), herbicide application (twice), planting and harvesting. In Experiment 2, a pass of rototiller was replaced by a pass of disk cultivator. Emission factors were obtained from IDAE (2005).

<sup>#</sup> Carbon emission of 1.3 kg CO<sub>2</sub> eq/kg N for production, transportation and storage of the N fertilizer (Lal, 2004).

<sup>†† 1</sup> kg N<sub>2</sub>O ha<sup>-1</sup> = 265 kg CO<sub>2</sub> ha<sup>-1</sup>; 1 kg CH<sub>4</sub> ha<sup>-1</sup> = 28 kg CO<sub>2</sub> ha<sup>-1</sup> (IPCC, 2013b)

<sup>¶¶</sup>Values estimated considering the mean corn yield of the H300 and H0 treatments, a harvest index of 0.48 (Berenguer et al., 2009) and a C content for residue of 0.44 kg C kg<sup>-1</sup> of dry residue (Jantalia and Halvorson, 2011).

<sup>##</sup> Negative values imply net greenhouse gas removal from the atmosphere, whereas positive values imply net greenhouse gas emission to the atmosphere.

Table 5. Above-ground biomass N uptake and yield-scaled  $N_2O$  emissions for different N levels at planting and N fertilization rates in both experiments.

	N level at planting	N fertilization rate (kg N ha <sup>-1</sup> )	Above-ground biomass N uptake (kg N ha <sup>-1</sup> )	Yield-scaled N <sub>2</sub> O emissions (g N-N <sub>2</sub> O kg above- ground N uptake)¶
Experiment 1				
	Low	0	116 (14)c†	10.1 (1.6)
		300	243 (6)a	7.7 (1.2)
	High	0	178 (24)b	6.2 (2.0)
	_	300	251 (19)a	8.1 (0.4)
Experiment 2				
•	Low	0	124 (13)b	4.3 (1.3)ab
		300	290 (8)a	3.1 (0.5)ab
	High	0	240 (30)a	2.3 (0.2)b
	Č	300	282 (13)a	5.1 (0.9)a

 $<sup>\</sup>dagger$  Within each experiment and column, different letters indicate significant differences between treatments at P < 0.05. Values in parenthesis represent standard error.

<sup>¶</sup> Yield-scaled N<sub>2</sub>O emissions reflect growing season emissions only.

Table 6.  $N_2O$  emission factor for different N levels at planting during the growing season of corn (EF<sub>GS</sub>) in both experiments

	N level at planting	$\mathrm{EF}_{\mathrm{GS}}$
Experiment 1		
	Low	0.0024†
	High	0.0034
Experiment 2		
	Low	0.0013
	High	0.0031

<sup>†</sup> EF was calculated using both pre-plant and in-season N applications.

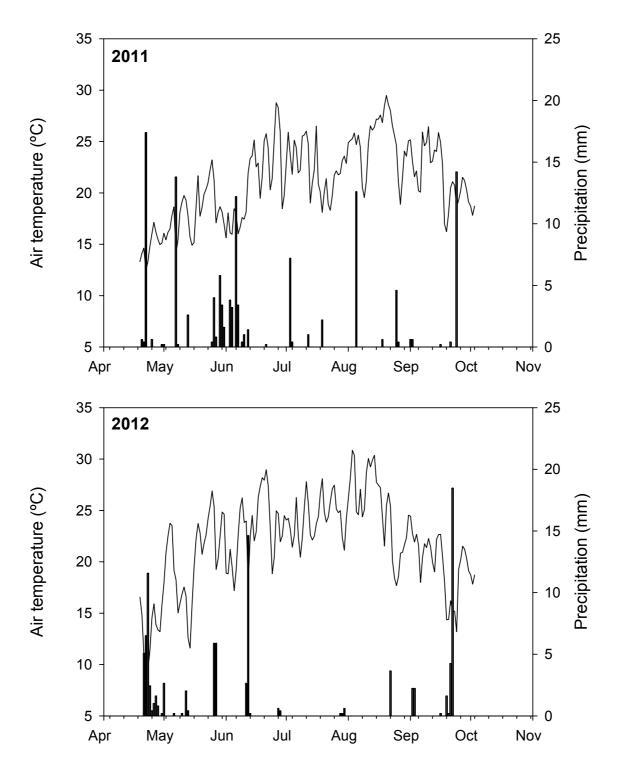


FIG 1

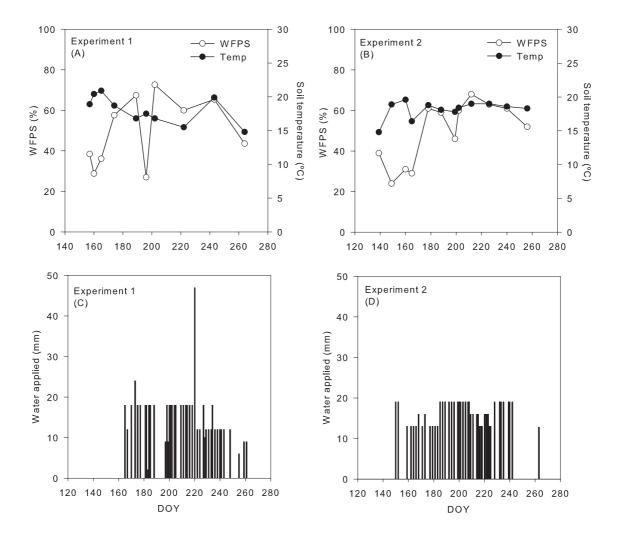


FIG 2

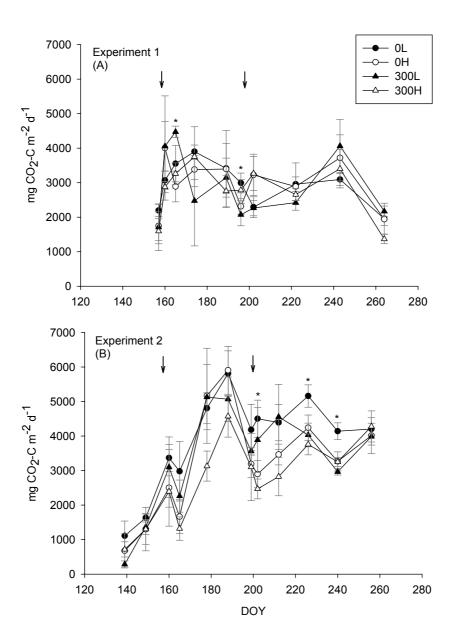
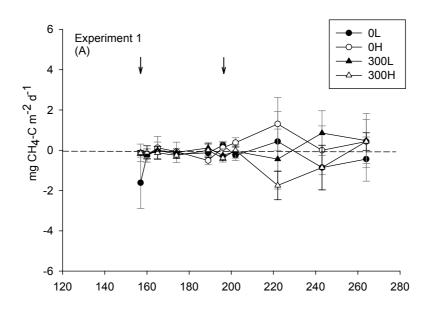


FIG 3



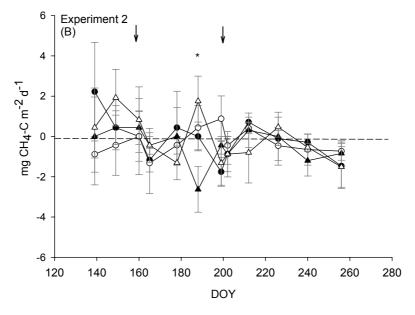


FIG 4

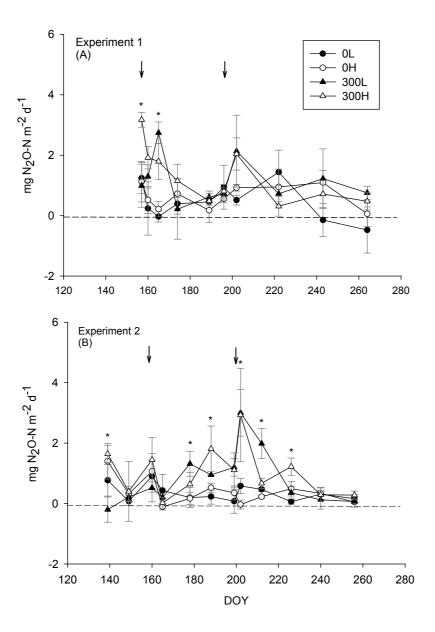


FIG 5