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# Effect of N dose, fertilisation duration and application of a nitrification inhibitor on GHG emissions from a peach orchard

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## Abstract

Despite only occupying 5% of the worldwide arable area, fruit tree crops are of vital economic importance in many regions. Intensive cropping practices can lead to greenhouse gas (GHG) emissions. In order to reduce these emissions, numerous studies have been made on lowering N inputs or applying nitrification inhibitors (NIs) which tend to maintain or even increase yield while reducing N leaching and nitrogenous emissions to the atmosphere. However, very few studies have been conducted on potential GHG emissions from the peach crop. In this work, a three-year study was carried out in a commercial peach orchard with a split-plot design with three replicates, in which the main factor was N dose (25, 50 and 100 kg N ha$^{-1}$ year$^{-1}$, and 50 kg N ha$^{-1}$

year$^{-1}$ applied during a shorter period of time in 2015 and 2016; and only 70 kg N ha$^{-1}$ year$^{-1}$ in 2017). Subplots in the study were used to analyse the effect of the application of a NI (3,4-dimethylpyrazole phosphate; DMPP). The aim was to qualitatively compare the effect of these factors on $N_2O$, $N_2O+N_2$, $CH_4$ and $CO_2$ emissions from a peach orchard soil in order to recommend agricultural practices that minimise emissions without concurrent yield reductions. We show that $N_2O$ and $N_2O+N_2$ emissions were linked to fertilisation and increased with N dose. The $N_2O$ emissions were mitigated (up to 49%) by DMPP up to the 50 kg N ha$^{-1}$ dose (not significantly). It seems that between 70 and 100 kg N ha$^{-1}$ the application of DMPP loses effectiveness. Methane oxidation increased with N dose and decreased with DMPP application; $CO_2$ emissions increased with DMPP and were unaffected by N dose. The intermediate N dose (50 kg N ha$^{-1}$) applied during a shorter period of time increased yield (not significantly) and NUE without increasing GHG emissions.

*Keywords:* fertigation, DMPP, $N_2O$, $CO_2$, $CH_4$ oxidation, NUE

## HIGHLIGHTS

- DMPP reduced $N_2O$ (losing efficacy at 70-100 kg N ha$^{-1}$) and tended to increase yield
- Methane oxidation increased with N dose but decreased with DMPP application
- The 100 kg N ha$^{-1}$ dose is the highest $N_2O$ emitter per canopy area unit
- $CO_2$ emissions increased with DMPP application, and were not affected by N dose
- 50 kg N ha$^{-1}$ applied until the start of pit hardening increased yield, not emissions

## 1. Introduction

Mineral and organic fertilisers maintain high crop productivity. However, fertiliser application to crops, in rainfed and irrigated regions with a Mediterranean climate which experience high temperatures, may result in noticeable greenhouse gas (GHG) emissions (Florio et al., 2016). These emissions cause radiative forcing and, in the case of nitrous oxide ($N_2O$), also deplete the ozone layer (Ravishankara et al., 2009). Greenhouse gas emissions are being quantified and reported by several authors (Smith et al., 2014; Oertel et al., 2016; EUROSTAT, 2017).

Soils can be both sources and sinks of $N_2O$ and methane ($CH_4$). Nitrous oxide mainly comes from nitrification and denitrification processes in soils. However, new pathways of $N_2O$ emission have been described in recent years (van Groenigen et al., 2015). According to Chapuis-Lardy et al. (2007) the soil can act as a $N_2O$ sink, at least temporarily. Methane is principally produced when organic matter is degraded under anaerobic conditions (Rime and Niklaus, 2017), although, according to Jugold et al. (2012) and Wang et al. (2013) aerobic $CH_4$ production has also been validated from non-microbial processes. The soil $CH_4$ oxidation is driven by methanotrophic bacteria (Rime and Niklaus, 2017). As for $CO_2$, the soil acts a source primarily due to soil respiration, and can also be a sink by carbon sequestration in the soil (Rastogi et al., 2002).

It is known that higher N doses lead to higher GHG emissions. According to Xie et al. (2017) cumulative emissions of $N_2O$ increase with N fertiliser dose. A recent review of $N_2O$ emissions from fruit orchards (Gu et al., 2019) showed that they were much higher than those from cropland. Fruit orchard soil $N_2O$ emissions have been found to range between 0.23 and 8.64 kg $N_2O$-N ha$^{-1}$year$^{-1}$ (Liu et al., 2008; Pang et al., 2009; Lin et al., 2010; Lin et al., 2012; Alsina et al., 2013; Fentabil et al., 2016; Swarts et al., 2016; Decock et al., 2017; Pang et al., 2019). Overall, the N doses of these studies were high, between 200 and 300 kg N ha$^{-1}$ year$^{-1}$. In tree orchards, the soil acts mainly as a sink of $CH_4$ (Schellenberg et al., 2012; Iqbal et al., 2013). Sitaula et al. (2000) reported that $NH_4^+$ fertilisers may inhibit $CH_4$ oxidation in agricultural soils at least in the early stage of N input. The same was observed by Schellenberg et al. (2012) in an almond orchard, although the authors did not find any significant correlation with soil $NH_4^+$. Aronson and Helliker (2010) reported that $CH_4$ oxidation may increase at low N content, whereas at higher N content, with 100 kg N ha$^{-1}$ year$^{-1}$ as the turning point, tends to inhibit $CH_4$ oxidation. Plaza-Bonilla et al. (2014) observed no significant differences in cumulative $CO_2$ emissions when increasing the mineral N applied to barley. In a study by Morell et al. (2011) also in a barley crop, the soil mineral N application seemed to enhance $CO_2$ emissions in the wettest season. In summary, increasing our knowledge about GHG emissions from orchard crops will enable the development of measures to better mitigate them.

In tree crops, higher N inputs are not always associated with higher crop productivity, and applying excessive N has several disadvantages, including excessive canopy growth, negative effects on peach quality, a delay of fruit maturation and N leaching below the rooting zone (Domingo, 2010). It is probably for these reasons that, in recent years, many growers have cut back substantially on the amount of N applied to peach orchards. At one time, doses above 200 kg N ha$^{-1}$ and even more were common (Daane et al., 1995). Current recommendations are 100 kg N ha$^{-1}$ for peach (Tagliavini and

Marangoni, 2002). Although lower N doses than the current recommendation one have been tested in few studies (Dolinski et al., 2005; Brunetto et al., 2007), there are also some papers where remarkable doses of mineral N are applied (Guo et al., 2018).

Management agricultural practices that synchronise N supply with crop uptake or keep the N in a form that is less prone to losses are required to meet food security goals and protect the environment (Vilas et al., 2019). This could be achieved following the 4R approach - right time (timing of N application), right amount (dose), right placement (e.g. use of drip-fertigation), and right source- to N fertiliser management (Venterea et al., 2016). The use of nitrification inhibitors (NIs), which are a type of enhanced-efficiency fertilisers, allow to better synchronize fertiliser N release with crop uptake, offering the potential for enhanced N use efficiency (NUE) and reduced losses to the environment (Li et al., 2018). Nitrification inhibitors have been shown to reduce the risk of N leaching and GHG emissions without reducing either crop yields or N inputs (Florio et al., 2016) because of their potential to delay bacterial $NH_4^+$ oxidation to $NO_2^-$ for a certain time span (Zerulla et al., 2001). In fact, the Intergovernmental Panel on Climate Change (IPCC) recognises their use as an option with promising potential for reducing agricultural $N_2O$ emissions (Smith et al., 2014). Along with dicyandiamide (DCD), 3,4-dimethylpyrazole phosphate (DMPP) is one of the most commonly used commercial NIs in Europe (Gilsanz et al., 2016). The effectiveness of DMPP in reducing N losses depends to a large extent on the longevity of the inhibitory effect, but it is also been affected by complex interactions between crop, soil, climate, and management factors (Vilas et al., 2019).

To date, it has been demonstrated the effectiveness of DMPP in reducing $N_2O$ emissions in both field (De Antoni Migliorati et al., 2014; Scheer et al., 2016; Recio et al., 2018) and laboratory conditions (Di and Cameron, 2011; Menéndez et al., 2012; Huang et al., 2014) when added to mineral and organic fertilisers. However, its effectiveness can be limited at high environmental temperatures (Chen et al., 2010; Mahmood et al., 2011) and is highly dependent on soil moisture content (Menéndez et al., 2012).

Some studies have shown neither a reduction in methanotrophic activity nor a positive effect on soil $CH_4$ oxidation after DMPP application (Zerulla et al., 2001; Menéndez et al., 2012; Rime and Niklaus, 2017). Menéndez et al. (2012) found that DMPP application did not reduce $CO_2$ emissions in a laboratory experiment, while Maienza et al. (2014), in a microcosm study, observed almost a 10% reduction in soil respiration after DMPP addition. However, Weiske et al. (2001) found up to 28% lower $CO_2$ fluxes during a certain period of time after the application of DMPP in the fertilised plots. Nevertheless, more information is needed about the effect of DMPP application on the emission of both gases.

Likewise, there is little consensus on the agronomic benefits of DMPP (Vilas et al., 2019). Several studies have shown a positive effect of DMPP application on yield, for instance, Guillaumes et al. (2007) observed an increase in ryegrass yield from pots, while Casar et al. (2007) reported a higher yield in pear and apple orchards located in northeast Spain in comparison with conventional fertilisation. However, other authors found no yield improvement with DMPP use (Scheer et al., 2016; Li et al., 2017).

Different field studies with NIs conducted under semiarid Mediterranean conditions have been carried out on irrigated crops (Villar and Guillaumes, 2010; Guardia et al., 2017; Recio et al., 2018). However, none of them analysed their effect on GHG emissions from a peach orchard.

Tagliavini and Marangoni (2002) suggested that the timing of N applications could has an effect on peach yield. Villar et al. (2018), in the same study as the current, have shown a positive effect when N fertiliser is applied until pit hardening. However, themselves recommend further research in order to confirm these findings. Different timings of N fertiliser application have been tested in other tree crops (Braun et al., 2009 (hazelnut); Rowlings et al., 2013 (lychee)). Nevertheless, there is little information about the effect of timing on peach fertilisation. To our knowledge, no studies have been conducted to evaluate the effect on GHG emissions of applying the same dose of nitrogen during a shorter period of time.

Agricultural lands cultivated with fruit crops have expanded across the globe in the last decade. Globally, in 2016, the orchard area was 65 Mha, accounting for approximately 5% of crop fields (Gu et al., 2019). They are of great economic importance in many regions as well as in world trade (Carranca et al., 2018). In 2017, total fruit production in Europe (excluding nuts and berries) amounted to 32.6 million tonnes. Of that, 2.9 million tonnes corresponded to peach. With 37.2% of production, Spain is the leading peach producer in Europe (EUROSTAT, 2018).

The agriculture sector needs to reduce GHG emissions while at the same time delivering food to a growing society, and climate friendly farming can provide practices for intensive cropping systems that can contribute to solving climate challenges (European Commission, n.d.).

The hypothesis considered in the current study is that the agricultural practices of decreasing N dose, applying a NI, and applying N during a shorter time span can help to minimise GHG emissions without compromising yield. Therefore, the objective of this study was to qualitatively assess the effect on GHG emissions and yield from a peach orchard of different N doses combined with and without DMPP application and considering the duration of fertilisation application.

## 2. Materials and Methods

### 2.1. Experimental site

The study was carried out at a commercial peach orchard (*Prunus persica* (L.) Batsch var. platycarpa (Decne.) L. H. Bailey 'Planet Top') grafted onto GF-677 rootstock in the Ebro Valley in the municipality of Aitona (Lleida, NE Spain, 41º 31' 23" N; 0º 26' 03" E; 131 a.s.l.) during 2015, 2016 and 2017.

The climate is continental semi-arid Mediterranean with an average annual rainfall of 362 mm and an average annual air temperature of 14.7ºC (Meteorological Service of Catalonia, n.d.).

Annual total rainfall was 240 mm in 2015, 420 mm in 2016 and 219 mm in 2017. However, during the sampling period the total rainfall was only 97 mm in 2015, 56 mm in 2016, and 58 mm in 2017. The average daily air temperature during the sampling period was 24 ºC in 2015 and 2016, and 22 ºC in 2017 (Fig. 1, see Supplementary material). Meteorological data were obtained from the closest meteorological station located at Aitona.

Soil temperature was recorded in the field every sampling day using a digital thermometer (SA880SSX, Oregon Scientific, Tualatin, Oregon, US) inserted into the soil at a depth of 10 cm.

The soil is classified as a Typic Calcixerepts (SSS, 2014), with a moderate depth and a silty loam texture. Some of the relevant soil properties are presented in Table 1 (see Supplementary material). The study site is on both claystone and calcareous rock with intercalations of marls and claystone units. These geological materials have low permeability.

## 2.2. Experimental design

The peach trees, spaced 4.5 x 2.5 m (889 trees ha$^{-1}$), were planted in April 2009 in a ridge system. The ridge was formed using the soil already present in the field. The irrigation water quality was very good: without nitrates and with low electrical conductivity ($EC_{1:5}$< 0.5 dS m$^{-1}$). The crop irrigation needs were calculated using the FAO methodology described in Allen et al. (1998). All treatments received the same amount of water per year, 682 mm in 2015; 589 mm in 2016 and 478 mm in 2017.

There were two different experimental designs at the same site: one during 2015 and 2016, and a different one in 2017. The experimental design in 2015 and 2016 was a split-plot with three replicates. The main factor was nitrogen (N) dose and the fertilisation duration for one of the N doses. There were subplots with the application or not of a nitrification inhibitor (NI). The NI added to the fertiliser solution was the 3,4-dimethylpyrazole phosphate (DMPP; indicated with "+" when added) at 1% w/w. Four nitrogen (N) doses were tested using a NPK (5-2.2-6) fertiliser solution with N as 50% ammonium and 50% nitrate (pH<2): (1) N25: 25 kg of N ha$^{-1}$ as a control treatment to guarantee a minimum crop productivity; (2) N50: 50 kg N ha$^{-1}$; (3) N100: 100 kg N ha$^{-1}$; (4) N50s: 50 kg N ha$^{-1}$ applied only until the start of pit hardening. The first three doses were applied until the end of pit hardening as traditionally done in the area. Therefore, the N dose was the same for N50s and N100 only until the start of pit hardening (Table 2). A very low N dose has been tested (25 kg N ha$^{-1}$), but there is no zero control with which compare the effect of N application. It was considered that in a commercial field the absence of N supply could severely compromise the yield.

Fertilisation was applied daily through drip-fertigation for a different number of hours depending of the treatment. The total amount of water (with and without fertiliser) was the same for all treatments. Each elementary plot consisted of six trees and the GHG emissions were studied from the central two ones.

The different fertilisation time span was applied only with the medium N dose (50 kg N ha$^{-1}$), which was considered the most appropriate one according to the soil organic matter content and its expected mineralisation, and due to previous experience with peach crop physiology and nutrient needs in the conditions of the present study.

As the ‘Planet Top’ peach variety turned out to be less profitable than expected, the owner decided to change it. In the winter of 2016-17, the trees were re-grafted with the ‘Samantha’ variety. In light of the 2015 and 2016 results and to facilitate crown growth, in 2017 only a 70 kg N ha$^{-1}$ dose (with and without DMPP) was applied to further determine the effect of N and DMPP on $N_2O$ emissions.

In 2017, the experimental design was a split-plot with 9 replicates. As in 2015 and 2016, each elementary plot consisted of six trees, of which the central two were sampled. The fertiliser used was an NPK (1.5-0.5-2.5) solution with pH=2.3. The N was 100% ammonium. Fertilisation was applied daily through drip-fertigation.

## 2.3. Greenhouse gases determination

### *2.3.1. Nitrous oxide, methane and carbon dioxide determination*

The GHG sampling, during fertigation, lasted from mid-May in 2015 and 2016 until peach harvesting (August). In 2017, the sampling lasted from June to October and only the $N_2O$ emissions were analysed. Although irrigation continued until October in 2015 and 2016, the GHG sampling was halted beforehand due to the low recorded emissions after the cessation of fertigation.

The GHG emissions were sampled on a weekly basis using the static closed chamber method (Rolston, 1986). This method is widely used for determining GHG emissions from soils (Alves et al., 2012). Cylindrical PVC static chambers (23 cm long and 19.5 cm in diameter) coated internally with an epoxy resin were used to study the $N_2O$, $CH_4$

and $CO_2$ emissions. They were inserted 5 cm into the wet soil area generated by fertigation. Chambers were closed with a vented screwed lid with a three-way key (Maris et al., 2016). Air samples from inside the chambers were taken immediately after closing the chamber (0 min), and 20 and 40 min later. Air inside the chamber was mixed by filling and emptying the syringe five times before withdrawing the sample through a Teflon® tube connected to a three-way key and into 100 ml plastic syringes, adapted with a tight valve (Maris et al., 2016).

After 40 min from closing the chamber, when the last air sample was taken, the three-way keys were left open and the chambers were removed from the soil. Syringes were transported to the laboratory (25 min drive) and the concentrations of three GHGs in the sampled air were immediately determined using a photoacoustic analyser (Innova 1412 Photoacoustic Multigas Monitor).

### *2.3.2. Nitrous oxide plus dinitrogen gas determination*

Dinitrogen gas ($N_2$) is a major product of denitrification in soils, but it is produced in insufficient quantities to be measured against atmospheric $N_2$ (Teira-Esmatges, 1998). Therefore, the analysis of nitrous oxide plus dinitrogen ($N_2O$+$N_2$) was made using the acetylene ($C_2H_2$) inhibition method (Yoshinari and Knowles, 1976) in 2015 and 2016.

Undisturbed soil cores were taken from the surface wet soil generated by fertigation using PVC tubes (16.5 cm long and 7 cm in diameter), placed in an insulated box and taken to the laboratory. The soil cores were taken at the same time as the air samples.

Once in the laboratory, the soil cores were placed in a glass jar (1.5 L) equipped with an airtight glass lid. A hole in the lid contained an airtight three-way key which was directly connected via a Teflon® tube to the photoacoustic analyser (Innova 1412 Photoacoustic Multigas Monitor). A total of 10% (v/v) of the gas enclosed in the glass jars was replaced by $C_2H_2$ using a 100 mL syringe, and allowed to diffuse into the soil sample for 20 minutes. This process inhibited the last step of denitrification, the reduction of $N_2O$ to molecular nitrogen ($N_2$).

The evolution of the gas inside the glass jar caused a gradual rise in concentration which was measured at regular intervals (0, 20 and 40 minutes) after closing the lid. The semi-static closed chamber technique (Burford and Hall, 1977) was used to obtain the $N_2O+N_2$ daily fluxes.

### *2.3.3. Daily fluxes and cumulative GHG emissions calculations*

Daily fluxes of GHG were calculated from the linear increase or decrease of the gas concentration as the difference between the gas concentration at time 0 and at time 40 minutes.

To calculate the cumulative emissions of all the GHGs studied, the daily fluxes were integrated throughout the study period. The cumulative emissions are expressed as mass of each GHG per hectare during the whole sampling period, and the fluxes as mass of GHG per hectare and day. Daily fluxes and cumulative emissions are reported only for the wet zone created by fertigation, which represents 1/3 of the field surface.

## 2.4. Water-filled pore space and nitrate content determination

After the gas analysis, the soil samples were dried at 105 °C to a constant weight in order to gravimetrically determine moisture content. The water-filled pore space (WFPS) was then calculated (Eq.(1)) by dividing gravimetric water content (expressed as a volume using the water density) by total soil porosity:

$$\text{WFPS} = \text{VWC}/(1-\text{BD}/\text{PD}) \times 100 \qquad (1)$$

where VWC (volumetric water content) is soil moisture content, BD is soil bulk density and PD is particle density, which for this soil was assumed to be 2.65 g $\text{cm}^{-3}$.

During fertigation, a soil sample (20 cm depth) was taken monthly from each elementary plot to determine the soil nitrate ($NO_3^-$-N) content using a Nitracheck$^{\text{TM}}$ 404 reflectometer (Table 3, see Supplementary material). The data from 2017 has not shown.

The soil ammonium ($NH_4^+$-N) content was determined by colorimetry at the start and the end of the sampling period. In 2015 and 2017, the $NH_4^+$-N contents were negligible (data not shown). In 2016, only the N50 and N50s treatments were analysed (data not shown).

## 2.5. Peach harvest and canopy area determination

In 2015 and 2016 (there was no harvest in 2017), the fruits were collected manually and gradually when the diameter reached at least 70 mm. Both the total number of fruits and the total yield per tree were determined (Villar et al., 2018).

The orthoimage technique was used to evaluate canopy area following the method described by Lordan et al. (2015a). This parameter was analysed in July of 2015 and 2016.

## 2.6. Emission and nitrogen use efficiency calculations

The $N_2O$ emission factor (EF) was calculated according to the IPCC (2006), as the difference between the $N_2O$ emitted from the fertilised soil and that from the control and divided by the total amount of N applied as fertiliser. Since there was no zero N dose, the emissions measured before initiation of fertigation (0.34 kg $N_2O$ ha$^{-1}$) were used as the control emissions. The EF was not calculated for the treatments with negative cumulative GHG emissions. The ratio between $N_2O$ and $N_2O$+$N_2$ was also calculated.

The $N_2O$ emissions, $CH_4$ oxidation and $CO_2$ emissions were converted to global warming potential (GWP) values. The GWP is expressed in units of carbon dioxide equivalent ($CO_2$-eq) over a 100-year time horizon and is obtained by multiplying the GHG emissions by a radiative forcing potential of 265 for $N_2O$, 28 for $CH_4$ and 1 for $CO_2$ (Myhre et al., 2013). The greenhouse gas intensity (GHGI) was calculated as GWP divided by yield in kilograms per hectare.

The nitrogen use efficiency (NUE; kg $kg^{-1}$) was calculated as the ratio of crop yield to N supply, where N supply includes the mineralised soil N, the soil inorganic N before fertilisation, and the total amount of N applied as mineral fertiliser (Maris et al., 2018).

## 2.7. Statistical analysis

The data distribution normality of the fluxes ($N_2O$, $N_2O+N_2$, $CH_4$, and $CO_2$) was examined by means of the Shapiro-Wilk's test and normalised when needed. The effect of the main factors on cumulative emissions of $N_2O$, $N_2O+N_2$, $CH_4$ and $CO_2$, and NUE was examined by ANOVA, and the Tukey's test and the Student's t-test, at a significance level of $p< 0.05$, were used for separation of means between treatments. The differences between treatment factors in cumulative GHG emissions were performed using orthogonal contrasts ($p< 0.05$).

Linear and parabolic regression analyses were carried out to define the relationship between cumulative GHG emissions and N dose (with and without DMPP application). The two 50 kg N $ha^{-1}$ doses (only until the start of pit hardening and during the rest of fertigation) were studied together. Non-parametric Spearman rank coefficient (at a $p< 0.05$ significant level) was carried out to analyse the relationship between GHG emissions and the driving factors (WFPS and soil temperature). JMP was used for data analysis (JMP® version 13; SAS Institute Inc., Cary, NC, 2015).

# 3. Results

## 3.1. Water-filled pore space (WFPS) during sampling period

In 2015 and 2016, the WFPS remained mainly between 50 and 70%. In 2015, there was a noticeable WFPS decrease on day 30 of sampling due to an accidental cessation of fertigation (Fig. 2, see Supplementary material). In 2016, the WFPS decreased drastically after day 84 of sampling with the cessation of drip-irrigation for harvesting. In 2017, the WFPS was lower than the previous two years of the study and ranged between 39% and 59%.

## 3.2. Nitrogenous emissions

In 2015, the daily $N_2O$ fluxes were positive from all treatments, except N25 until day 42 (fertilisation was finished; Fig. 3a). The N50s, N100 and N100+ treatments had higher daily $N_2O$ fluxes than the other treatments. In 2015, daily $N_2O$ emissions were positively correlated with soil temperature (-0.41; $p< 0.05$). In 2016, the N25+ and N25 treatments presented negative $N_2O$ fluxes until fertilisation was concluded on day 54 of sampling (Fig. 3b). After fertilisation concluded, the $N_2O$ daily fluxes remained close to zero. As in 2015, the N100+ treatment presented the highest daily flux. In 2017, the daily $N_2O$ fluxes were positive during the fertigation period from the N70 treatment but mainly negative from the N70+ treatment (Fig. 3c).

In 2015, the pattern of the daily fluxes of $N_2O+N_2$ was the same as that of $N_2O$ (Fig. 4a). In 2016, the $N_2O+N_2$ daily fluxes were positive from all treatments, except N25+ and N25 until day 24 of sampling (Fig. 4b). For the rest, the pattern of emissions was similar to that of $N_2O$. No correlation was observed between daily $N_2O+N_2$ fluxes and WFPS (-0.06; $p > 0.05$).

The cumulative $N_2O$ emissions from N100+ treatment were significantly ($p < 0.05$) different from the ones of N25+, N25 and N50+ treatments in both years (Table 4). This was also the case for the N100 treatment, except in 2015 (not different from the N25+ treatment) and in 2016 (not different from the N50+ treatment). In 2017, significant differences ($p < 0.05$) in cumulative $N_2O$ emissions were found between the N70+ treatment (-1 ± 0.7 kg $N_2O$-N $ha^{-1}$) and the N70 treatment (5 ± 3 kg $N_2O$-N $ha^{-1}$).

The EFs increased with increasing N dose (Table 4). The addition of DMPP led to lower EFs at the same N dose, except at the highest dose.

In both 2015 and 2016, cumulative $N_2O+N_2$ emissions were significantly higher from the N100+ (not in 2015) and N100 treatments than from the N25+ and N25 ones (Table 4). These emissions tended to increase with N dose, but significantly so only for the highest dose (not between N100+ and N50).

The $N_2O/N_2O+N_2$ ratio was higher in 2016 than in 2015, and also from the treatments with N application only until pit hardening (N50s+ and N50s; Table 4).

The shorter period of N fertilisation in the 50 kg N $ha^{-1}$ dose did not have a significant effect on cumulative nitrogenous emissions, nor in comparison with the same N dose with larger period of fertirrigation, as observed in the contrast analysis (Table 4). There was also no significant effect on cumulative GHG emissions due to the duration of fertigation application in 2015 and 2016, analysed together (Table 5).

### *3.2.1. Effect of DMPP application and N dose on cumulative $N_2O$ and $N_2O$+$N_2$ emissions*

In both 2015 and 2016, the application of DMPP reduced $N_2O$ emissions by 41% at the 50 kg N ha$^{-1}$ dose, though not significantly (Table 4). Figs. 5a and 5b show a slope change in the linear relationship between treatments with DMPP and cumulative $N_2O$ emissions at the 50 kg ha$^{-1}$ N dose in both years, showing an interaction between N dose and DMPP. The effect of DMPP on $N_2O$+$N_2$ emissions was the same as on $N_2O$ emissions (Figs. 5c and 5d).

### *3.2.2. Effect of N fertilisation period (duration of N application) on $N_2O$ and $N_2O$+$N_2$ emissions*

Only until the start of pit hardening (short “s” period), during which the N50s+, N50s, N100+ and N100 treatments received the same amount of N, were there no differences in cumulative $N_2O$ emissions in 2015 or 2016 between these treatments (Fig. 6), as expected.

The shorter fertigation period treatments (N50s+ and N50s) led to higher $N_2O$ emissions than the N50+ and N50 ones, though the differences were not significant ($p > 0.05$) during the “s” time span (Fig. 6) or during the whole sampling period (Table 4).

## 3.3. Methane and carbon dioxide emissions

In both 2015 and 2016, the soil of the crop acted as a sink of methane ($CH_4$). In 2015, $CH_4$ oxidation was observed until day 30 of sampling (Fig. 7a) in all treatments. Methane oxidation exhibited a positive correlation with soil temperature (0.59; $p < 0.05$). In 2016, $CH_4$ oxidation was observed throughout most of the sampling period (Fig. 7b). In the same year, daily $CH_4$ oxidation fluxes were slightly correlated with WFPS (0.13; $p < 0.05$).

Cumulative $CH_4$ oxidation tended to increase with N dose (Table 6). Although in both years all treatments presented $CH_4$ oxidation, the treatments with DMPP tended to oxidise less than the treatments without DMPP. In 2016, the N100 treatment was significantly ($p < 0.05$) the most oxidising one (except for the N100+ and the N50 treatments; Table 6). The DMPP application had a significant effect on cumulative $CH_4$ oxidation both in 2015 and in 2016 (Table 6).

As observed for $N_2O$ and $N_2O+N_2$ emissions, in 2015, the dose of 50 kg N $ha^{-1}$ was a turning point in the polynomial relationship between cumulative $CH_4$ oxidation and N dose (Fig. 5e). In 2016, there was a linear relationship between cumulative $CH_4$ oxidation and N dose (Fig. 5f). In this case, however, the treatments with DMPP application showed a similar trend to the ones without DMPP.

Regarding the $CO_2$ emissions, both in 2015 and in 2016, the soil of the peach orchard acted as a source of this gas (Fig. 8). The $CO_2$ daily fluxes were mainly positive during the fertigation period. After the cessation of fertilisation, the $CO_2$ daily fluxes remained close to zero (Fig. 8). In 2015, daily $CO_2$ fluxes were negatively correlate with soil temperature (-0.77; $p < 0.05$).

There were no significant differences between treatments in either 2015 or 2016 (Table 6). However, the treatments with DMPP tended to produce higher $CO_2$ emissions than the treatments without DMPP (significantly in 2015; $p < 0.05$). There was no effect of N dose on cumulative $CO_2$ emissions (Table 6).

### 3.4. Global warming potential, relative emissions and nitrogen use efficiency

The global warming potential (GWP) was mainly negative in both 2015 and 2016 due to $CH_4$ oxidation (Table 7). Overall, the treatments without DMPP presented more negative GWP than with it. In 2015, there were no statistical differences between treatments. This was not the case in 2016 for which all treatments were significantly different from N100, except the N50 and N100+ treatments.

The most productive treatments were the N50s+ (16% higher harvest than the N50+) and N50s (21% higher than the N50), though not significantly different in either 2015 or 2016 from the N100+ and N100 treatments (Table 7). In 2015, the N50s+, N50s, N100+ and the N100 treatments had the highest production, significantly higher than the N25. In 2016, the N50s+ and the N50s treatments had the highest production, significantly higher also than the N25.

All treatments presented mainly negative GHGI values (Table 7). In 2015, there were no significant differences between treatments, but in 2016 significant differences were found between the N25+, N50 +, N50s +, N50s treatments and the N100.

Another tree growth development parameter that can be observed is the canopy area (Fig. 9, see Supplementary material). The highest N dose devoted more N to the production of leaf biomass than the other doses, though not significantly ($p > 0.05$).

The treatments with DMPP presented a larger canopy area than the treatments without it, except for the N100+ and N100 treatments. The ratio between cumulative $N_2O$ emissions and canopy area shows that the highest N dose (100 kg N $ha^{-1}$) was the highest emitter per canopy area unit (Fig. 10).

The NUE values (Table 8) showed that the N25+, N50s+ and N50s treatments were significantly more efficient than the N50, N100+ and N100 treatments (in 2015). In 2016, the N50s+ and N50s were more efficient than the other treatments except the N25+ and N50+ treatments. The effect of N dose on the NUE was significant, with 50s kg N $ha^{-1}$ the most efficient dose in both 2015 and 2016. In 2015, the 25 kg N $ha^{-1}$ dose was as efficient as the 50s one, but less productive. The DMPP application tended to increase NUE, but significantly so only in 2015.

## 4. Discussion

### 4.1. Nitrous oxide and molecular nitrogen emissions

The $N_2O$ and $N_2O+N_2$ emissions were related to N fertiliser use. In the period when the soil was irrigated but not fertilised the daily $N_2O$ and $N_2O+N_2$ emissions stayed low or slightly negative, showing that mineral N availability limited emissions. Maris et al. (2015) also report this last finding in an olive orchard. Overall, there were significantly lower fluxes from the lowest N dose (N25+ and N25 treatments) than from the highest N dose (100 kg N $ha^{-1}$).

In 2017, the $N_2O$ emission pattern was different, probably because fertilisation lasted longer and the N dose applied per day was lower than in 2015 and 2016 (Fig. 3c).

The daily $N_2O$ fluxes were higher than those reported by Schellenberg et al. (2012) from an almond orchard and by Aguilera et al. (2015) from fruit trees in Spain. And the daily $N_2O+N_2$ fluxes were higher than those published by Maris et al. (2015).

The highest N dose resulted in significantly higher cumulative nitrogenous emissions than the lowest one (Table 4). The higher $NO_3^-$-N content (Table 3, see Supplementary material) in the topsoil, especially in the first month of fertigation, might explain the difference between the lowest and the highest N doses. As Rime and Niklaus (2017) reported, the application of synthetic fertilisers or manure to soils accelerates N cycling and the associated $N_2O$ emissions.

The EF values ranged from −0.14 to 4.15% of applied N (Table 4). In 2015, the EFs from the 25 and 50 kg N $ha^{-1}$ doses (except for the N50s treatment; Table 4) were lower than the 1% proposed by the IPCC (2006). These EFs were higher than those reported by Cheng et al. (2017) in a peach orchard, and than those published by Cayuela et al.

(2017) in a Mediterranean perennial crops (0.54%, including vineyards, almonds and olive orchards). The EF value increased with N dose, and at the same dose with different fertilisation period. In a review of fruit orchards carried out by Gu et al. (2019), EFs ranging from -0.44 to 2.7% were reported. Similar EF values to those found in the current study were reported by Huérfano et al. (2019) in a grassland crop.

The $N_2O/N_2O+N_2$ ratio increased with N dose and ranged from 0.21 to 0.96 for all treatments (Table 4), indicating that denitrification was the predominant process responsible for nitrogenous emissions. Similar $N_2O/N_2O+N_2$ ratios were reported by Ciarlo et al. (2008) from undisturbed soil cores. No references were found for peach.

Higher $N_2O/N_2O+N_2$ ratios have been observed at higher N inputs (Table 4), which is in accordance with Wang et al. (2018), who found that N fertilisation significantly increases soil denitrification. The distribution of nitrogen in the wet bulb generated through drip-fertigation could explain higher $N_2O$ production from denitrification. Neilsen et al. (1997) observed higher root densities in the wetter zone under drippers and higher N concentration during fertigation.

In addition, when the soil water content increases during irrigation, it results in poor soil air permeability, which provides anaerobic conditions favourable for denitrification (Wang, 2018). Although denitrification activity is reported to be heightened when WFPS exceeds 60-65% (Smart et al., 2011) or when reaching 70% (Bateman and Baggs, 2005) and anaerobic conditions prevail, Smart et al. (2011) found that under fertigation in field conditions, the breakpoint between WFPS and $N_2O$ emission is somewhat lower. In the present study, higher WFPS values (up to 70%) were reached most frequently during fertigation period in 2016, and also higher $N_2O+N_2$ emissions were reached than in 2015 (Table 4).

The canopy area of the 100 kg N ha$^{-1}$ treatments was larger than that of the lower doses (Fig. 9, see Supplementary material). This dose was the highest $N_2O$ emitter per canopy area unit (Fig. 10), suggesting that at this dose N was not efficiently taken up by the trees. The NUE was lower at the 100 kg N ha$^{-1}$ dose than at the other doses (Table 8) because the 100 kg N ha$^{-1}$ dose uses more N to produce biomass. The NUE values in the present study were slightly higher than those reported by Qin et al. (2016) -between150 and 350 kg kg$^{-1}$- in a citrus crop.

### 4.2. Effect of DMPP on nitrogenous emissions

The application of the DMPP nitrification inhibitor (NI) reduced $N_2O$ emissions by 49% in 2015 and by more than 30% in 2016 at the 50 kg N ha$^{-1}$ dose, though not significantly (Table 4). Similar reductions in cumulative $N_2O$ emissions were obtained by Pfab et al. (2012) in lettuce and cauliflower crops, and a higher one (> 60%) by De Antoni Migliorati et al. (2014) in a wheat-maize rotation. Macadam et al. (2003), in a permanent pasture, also found that DMPP reduced $N_2O$ emissions by 58% (mineral fertiliser).

There is little information available about the effect of NI on $N_2O+N_2$ emissions from tree orchards. In this study, on average, there was a 36% reduction of $N_2O+N_2$ induced by DMPP in 2015 from all N doses (except the 25 kg N ha$^{-1}$; Table 4). It was lower (17%) in 2016 for the 50 kg N ha$^{-1}$ dose, though not significant in either year. Maris et al. (2015), in an olive orchard, observed a 35% reduction of $N_2O$+$N_2$ emissions from the treatment with DMPP application.

The mitigation effect of DMPP was not observed at the highest N dose (100 kg N $ha^{-1}$; Figs. 5a, b, c and d). It may be possible that DMPP loses effectiveness beyond a certain N dose (more or less high depending on the crop). Since nitrogen has a priming effect, it might be speculated that if microbial activity increases enough, a threshold of surplus N is reached above which the application of DMPP application loses effectiveness.

The results of 2017 indicate that the dose at which the change in the effect of DMPP occurs is probably somewhere between 70 and 100 kg N $ha^{-1}$ since the effect of DMPP on $N_2O$ emissions was significant.

Except for the 100 kg N $ha^{-1}$ treatment, a higher canopy area was obtained in all treatments with DMPP than in those without DMPP (Fig. 9, see Supplementary material). Martínez-Alcántara et al. (2013) also observed a higher biomass with DMPP than without it in a citrus crop. Also Martínez-Alcántara et al. (2013) reported an increase on NUE with DMPP application.

### 4.3. Effect of the different duration of N fertilisation on nitrogenous emissions

The lack of 100 kg N $ha^{-1}$ dose that should have been applied only until pit hardening (would has called N100s) makes the experimental design asymmetric. Nonetheless, it was considered that applying this higher N dose in such a short time period could have harmful effects to the environment.

Applying 50 kg N ha$^{-1}$ only until pit hardening (contrary to the general practice) did not significantly increase nitrogenous emissions (Table 4 and Fig. 6) and increased yield, though not significantly.

### 4.4. Effect of N dose and DMPP application on $CH_4$ and $CO_2$ emissions

Cumulative $CH_4$ oxidation tended to increase with N dose (Table 6). This is in accordance with Aronson and Helliker (2010), who found that up to 100 kg N ha$^{-1}$ year$^{-1}$ the soil acted as a sink of $CH_4$ in maize. In the present study, the dose of 100 kg N ha$^{-1}$ would not be high enough to produce the inhibition of methanotrophic activity described by Steudler et al. (1989) and Reay and Nedwell (2004), who reported that $CH_4$ oxidation in soils is reduced by N application. The relationship between N dose and cumulative $CH_4$ emissions was polynomial in 2015 (Fig. 5e) and linear in 2016 (Fig. 5f), as for cumulative $N_2O$ and $N_2O+N_2$ emissions.

The application of DMPP tended to reduce $CH_4$ oxidation with respect to the treatments without DMPP (Table 6). Several authors including Menéndez et al. (2012) and Rime and Niklaus (2017) reported no effect of DMPP on $CH_4$ oxidation, while other authors as Maris et al. (2015) reported significantly increase on $CH_4$ oxidation due to DMPP addition. The results of the present study may be due to that the DMPP could inhibits ammonium monooxygenase (Menéndez et al., 2012), which is structurally very similar to the methane monooxygenase enzyme of methanotrophs, and that both enzymes share -although with different affinity- a range of substrates (Rime and Niklaus, 2017).

The soil of the peach orchard acted as a source of $CO_2$ in 2015 and 2016 (Table 6). The daily $CO_2$ fluxes were within the ranges reported by Kallenbach et al. (2010), which were between <48 and >120 kg $CO_2$ $ha^{-1}$ $d^{-1}$ in a sub-surface drip-fertigated tomato crop in a semi-arid Mediterranean climate. Carbon dioxide emissions were not significantly affected by N dose (Tables 5 and 6). Until now, N fertilisation has exhibited contradictory effects with respect to soil $CO_2$ emissions: increase, decrease (Kong et al., 2013) or no effect (Plaza-Bonilla et al., 2014; in a long-term experiment).

The application of DMPP tended to increase cumulative $CO_2$ emissions (Table 6), though significantly so only in 2015. Some authors have reported a reduction of $CO_2$ emissions after DMPP application in different crops (Weiske et al., 2001). However, others have found no effect of DMPP application on $CO_2$ emissions (Müller et al., 2002; Menéndez et al., 2006).

## 4.5. Global warming potential, yield and greenhouse gas intensity

The global warming potential (GWP) was mainly negative in both 2015 and 2016 (Table 7). Overall, Sainju (2016) reported a less negative GWP in a poplar plantation (-105 kg $CO_2$-eq $ha^{-1}$).

Average peach yield of all treatments in 2015 and 2016 was about 40 t $ha^{-1}$. As for average yield per tree, the present study obtained higher values than those reported by Lordan et al. (2015b) in another peach orchard located in the Ebro Valley.

A negative GHGI (consequence of a negative GWP) indicates sinks of GHG emissions to the soil (Mosier et al., 2006). The values obtained in this study are within the range reported by Sainju (2016) for different agricultural crops.

## 5. Conclusions

The $N_2O$ and $N_2O+N_2$ emissions were linked to fertilisation and increased with N dose. Denitrification was the main process. The nitrogenous fluxes peaked between 43 and 69% of WFPS, but only when fertilising at the same time. The 100 kg N ha$^{-1}$ dose was the highest $N_2O$ emitter per canopy area unit. The $N_2O$ emissions were mitigated (by up to an average of 41%) with the DMPP application up to the 50 kg N ha$^{-1}$ dose, though without significant differences from the treatments without DMPP. The mitigation effect of DMPP was not observed at the 100 kg N ha$^{-1}$ dose. It seems that the dose at which the application of DMPP loses effectiveness lies between 70 and 100 kg N ha$^{-1}$.

Only the low and intermediate tested doses presented EF values below the IPCC default value (1%) in either of the two years for which these values were calculated (2015-2016).

Methane oxidation increased with N dose and decreased with DMPP application, while $CO_2$ emissions increased with DMPP application and were unaffected by N dose.
The intermediate N dose (50 kg N ha$^{-1}$), applied only until the start of pit hardening, increased yield (not significantly) and NUE without increasing GHG emissions. Emissions were further reduced by the use of DMPP, which also tended to increase yield.

Further research in the topic of the study is needed, specifically working with $^{15}N$ labelled fertilisers and the study of N budgets would allow improving the understanding of the N cycle in a tree orchard. These studies should lead to improved N use efficiency and concurrently reducing N losses to the environment.

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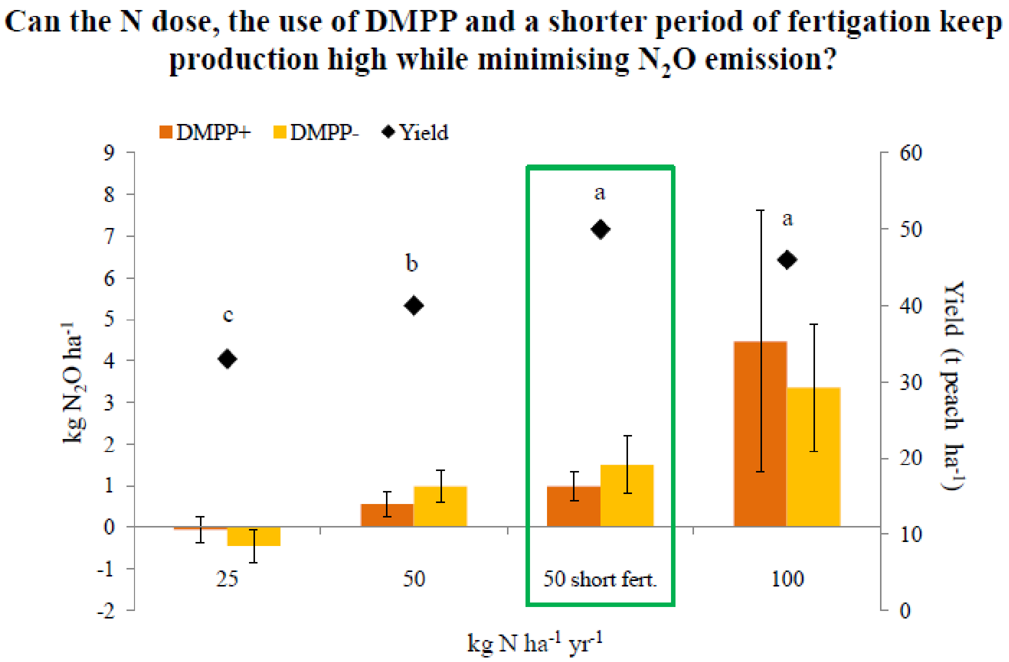
## Graphical abstract



## Tables

Table 2. Dose of applied N until the start of pit hardening and thereafter (rest of fertigation -until the end of pit hardening-) per treatment in 2015 and 2016.

| Treatment | | Only until the start of pit hardening (kg N ha$^{-1}$) | Rest of fertigation (kg N ha$^{-1}$) |
|---|---|---|---|
| N25+ | N25 | 12.5 | 12.5 |
| N50+ | N50 | 25 | 25 |
| N50s+ | N50s | 50 | 0 |
| N100+ | N100 | 50 | 50 |

Table 4. Cumulative $N_2O$-N, emission factor (%), cumulative ($N_2O$+$N_2$)-N emissions and their ratio per treatment and year plus/minus the standard deviation; as well as the contrast analysis to assess the effect of DMPP application (with (+) or without (-)), the effect of the N dose and the effect of fertilisation duration.

| Treatment | Cumulative kg $N_2O$-N $ha^{-1}$ | | EF (%) | | Cumulative kg ($N_2O$+$N_2$)-N $ha^{-1}$ | | $N_2O$-N/($N_2O$+$N_2$)-N (%) | |
|---|---|---|---|---|---|---|---|---|
| | 2015 | 2016 | 2015 | 2016 | 2015 | 2016 | 2015 | 2016 |
| N25+ | 0.49 ± 0.48bc | -0.59 ± 0.14c | 0.60 | - | -0.39 ± 0.28b | -0.36 ± 0.20b | - | - |
| N25 | -0.22 ± 0.15c | -0.67 ± 0.27c | - | - | -0.11 ± 0.10b | -0.48 ± 0.16b | - | - |
| N50+ | 0.27 ± 0.23c | 0.82 ± 0.37bc | -0.14 | 0.96 | 0.59 ± 0.26ab | 1.52 ± 0.95ab | 0.46 | 0.54 |
| N50 | 0.54 ±0.10bc | 1.43 ± 0.68abc | 0.40 | 2.18 | 2.55 ±1.95ab | 1.94 ± 0.71ab | 0.21 | 0.74 |
| N50s+ | 0.67 ± 0.29bc | 1.31 ± 0.41abc | 0.66 | 1.92 | 1.31 ± 0.63ab | 1.55 ± 1.02ab | 0.51 | 0.84 |
| N50s | 1.31 ± 0.90bc | 1.69 ± 0.47abc | 1.94 | 2.70 | 1.61 ± 1.09ab | 1.76 ± 0.50ab | 0.81 | 0.96 |
| N100+ | 4.45 ± 3.50a | 4.49 ± 2.78a | 4.11 | 4.15 | 4.93 ± 4.04ab | 5.00 ± 2.80a | 0.90 | 0.90 |
| N100 | 3.04 ± 1.46ab | 3.67 ± 1.60ab | 2.70 | 3.33 | 5.55 ± 1.94a | 4.74 ± 2.63a | 0.55 | 0.77 |
| *DMPP effect* | | | | | | | | |
| DMPP+ vs | ns | ns | | | ns | ns | | |
| *N dose effect* | | | | | | | | |
| 25 vs 50 | ns | * | | | ns | * | | |
| 25 vs 100 | * | * | | | * | * | | |
| 50 vs 100 | * | * | | | * | * | | |
| 50s vs 100 | * | * | | | * | * | | |
| *Fertilisation period effect* | | | | | | | | |
| 50 vs 50s | ns | ns | | | ns | ns | | |

Different letters per column indicate significant differences among treatments ($p < 0.05$, Tukey's test).
*: significant ($p < 0.05$); ns: not significant ($p > 0.05$).

Table 5. Analysis of variance of the studied factors (N dose, DMPP application and fertilisation duration), and the cumulative $N_2O$-N, ($N_2O$+$N_2$)-N, $CH_4$ and $CO_2$ emissions in 2015 and 2016 together.

| Factor effect | $N_2O$-N | ($N_2O$+$N_2$)-N | $CH_4$ | $CO_2$ |
|---|---|---|---|---|
| N dose | * | * | * | ns |
| DMPP | ns | ns | * | * |
| N dose x [DMPP] | * | ns | ns | ns |
| Fertilisation period | ns | ns | ns | ns |

*: significant ($p < 0.05$); ns: not significant ($p > 0.05$).

Table 6. Cumulative $CH_4$ and $CO_2$ emissions per treatment and year plus/minus the standard deviation; as well as the contrast analysis to assess the effect of DMPP application (with (+) or without (-)) and the effect of the N dose.

| Treatment | Cumulative kg $CH_4$ $ha^{-1}$ | | Cumulative kg $CO_2$ $ha^{-1}$ | |
|---|---|---|---|---|
| | 2015 | 2016 | 2015 | 2016 |
| N25+ | -44 ± 13a | -86 ± 11a | 1622 ± 943 | 1362 ± 237 |
| N25 | -127 ± 118a | -89 ± 22a | 1202 ± 514 | 1342 ± 292 |
| N50+ | -19 ± 10a | -119 ± 31a | 2058 ± 659 | 2292 ± 414 |
| N50 | -115 ± 62ab | -204 ± 97ab | 1462 ± 286 | 1536 ± 575 |
| N50s+ | -81 ± 58a | -128 ± 20a | 2036 ± 535 | 1449 ± 390 |
| N50s | -20 ± 60a | -123 ± 13a | 1670 ± 494 | 1366 ± 728 |
| N100+ | -97 ± 76a | -194 ± 66ab | 1926 ± 443 | 2171 ± 476 |
| N100 | -283 ± 240a | -320 ± 108b | 1289 ± 145 | 1386 ± 531 |
| *DMPP effect* | | | | |
| DMPP+ vs DMPP- | * | * | * | ns |
| *N dose effect* | | | | |
| 25 vs 50 | ns | * | ns | ns |
| 25 vs 100 | ns | * | ns | ns |
| 50 vs 100 | ns | * | ns | ns |
| 50s vs 100 | * | * | ns | ns |

Different letters per column indicate significant differences among treatments ($p < 0.05$, Tukey's test).

*: significant ($p < 0.05$); ns: not significant ($p > 0.05$).

Table 7. Global warming potential (GWP), yield and greenhouse gas intensity (GHGI) per treatment and year.

| Treatment | GWP (kg $CO_2$-eq $ha^{-1}$) | | Yield (kg $tree^{-1}$) | | GHGI (kg $CO_2$-eq $kg^{-1}$ yield) | |
|---|---|---|---|---|---|---|
| | 2015 | 2016 | 2015 | 2016 | 2015 | 2016 |
| N25+ | 10 | -1212a | 48ab | 34bc | 0.00 | -0.04a |
| N25 | -2233 | -1614a | 37b | 29c | -0.06 | -0.07ab |
| N50+ | 1829 | -1299a | 48ab | 45abc | 0.04 | -0.03a |
| N50 | -1553 | -4437ab | 49ab | 40abc | -0.04 | -0.13ab |
| N50s+ | -46 | -1797a | 62a | 50ab | -0.01 | -0.04a |
| N50s | 1455 | -1621a | 60a | 52a | 0.03 | -0.03a |
| N100+ | 633 | -3213ab | 61a | 42abc | 0.01 | -0.08ab |
| N100 | -5728 | -6787b | 60a | 45abc | -0.12 | -0.17b |

Averages followed by different letters per column are significantly different ($p < 0.05$, Tukey's test).

Table 8. Nitrogen use efficiency per treatment and year, and the effect of N dose and the use of the nitrification inhibitor (NI). DMPP+: DMPP application; DMPP-: no DMPP application.

| Treatment | NUE (kg yield $kg^{-1}$ N) | |
|---|---|---|
| | 2015 | 2016 |
| N25+ | 458a | 333ab |
| N25 | 357ab | 294bc |
| N50+ | 358ab | 345ab |
| N50 | 312b | 271c |
| N50s+ | 453a | 375a |
| N50s | 446a | 394a |
| N100+ | 316b | 243c |
| N100 | 313b | 223c |
| *Effect of:* | | |
| N dose | * | * |
| 25 | 407a | 314b |
| 50 | 335b | 308b |
| 50s | 450a | 385a |
| 100 | 315b | 233c |
| NI | * | ns |
| DMPP+ | 396a | 319a |
| DMPP- | 357b | 300a |

Averages followed by different letters per column are significantly different ($p < 0.05$, Tukey's test and Student's t-test). *: significant ($p < 0.05$); ns: not significant ($p > 0.05$).

# Figures

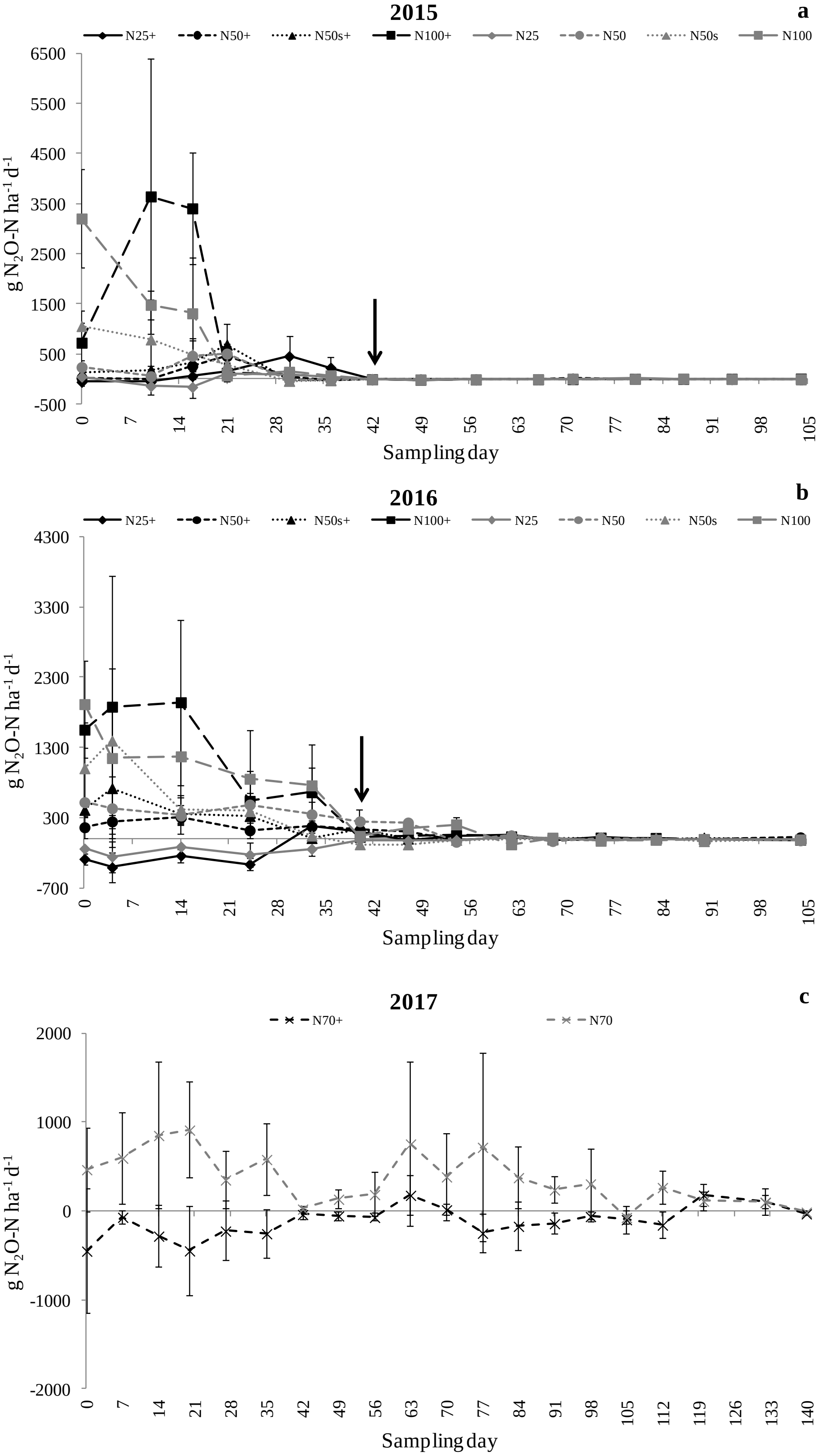


Figure 3. Average daily nitrous oxide ($N_2O$-N) fluxes during the sampling period in 2015 (a), in 2016 (b), and 2017 (c) per treatment. The error bars correspond to the standard deviation. The arrow indicates the cessation of fertilisation.

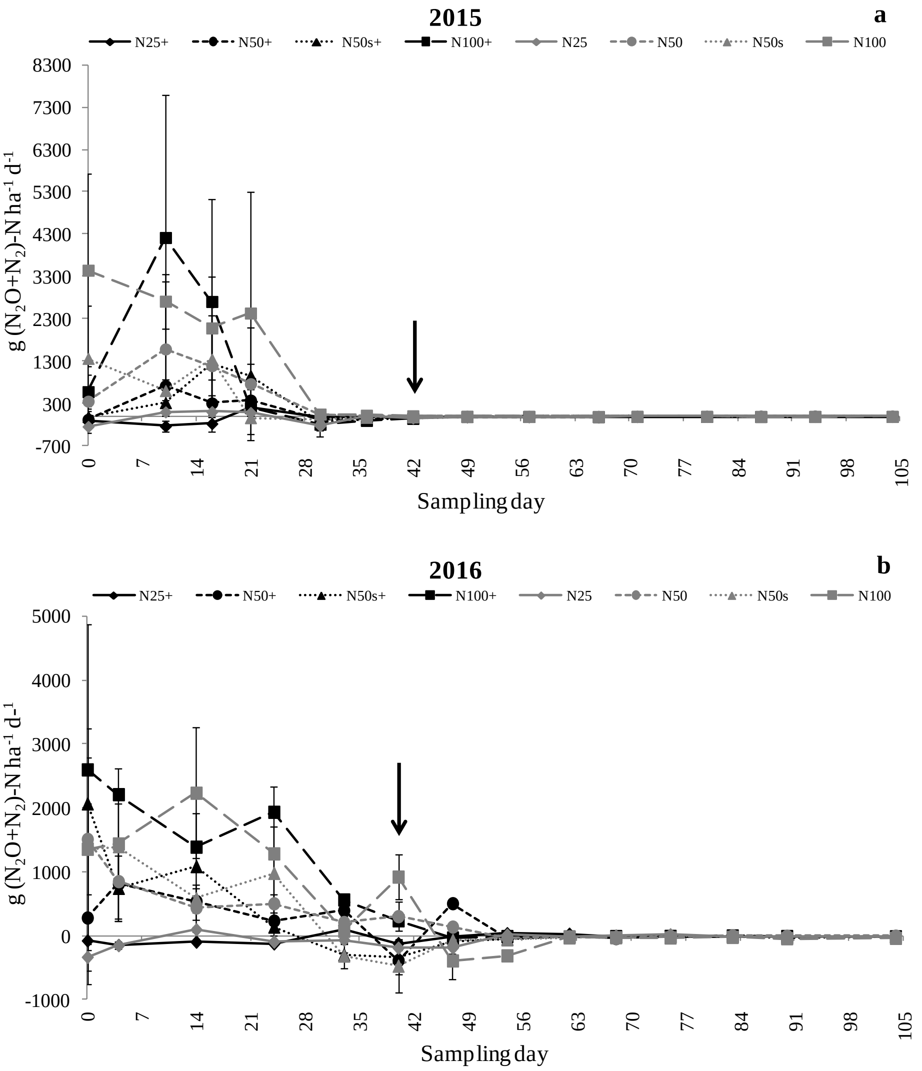


Figure 4. Average daily nitrous oxide plus dinitrogen (($N_2O+N_2$)-N) fluxes during the sampling period in 2015 (a) and 2016 (b) per treatment. The error bars correspond to the standard deviation. The arrow indicates the cessation of fertilisation.

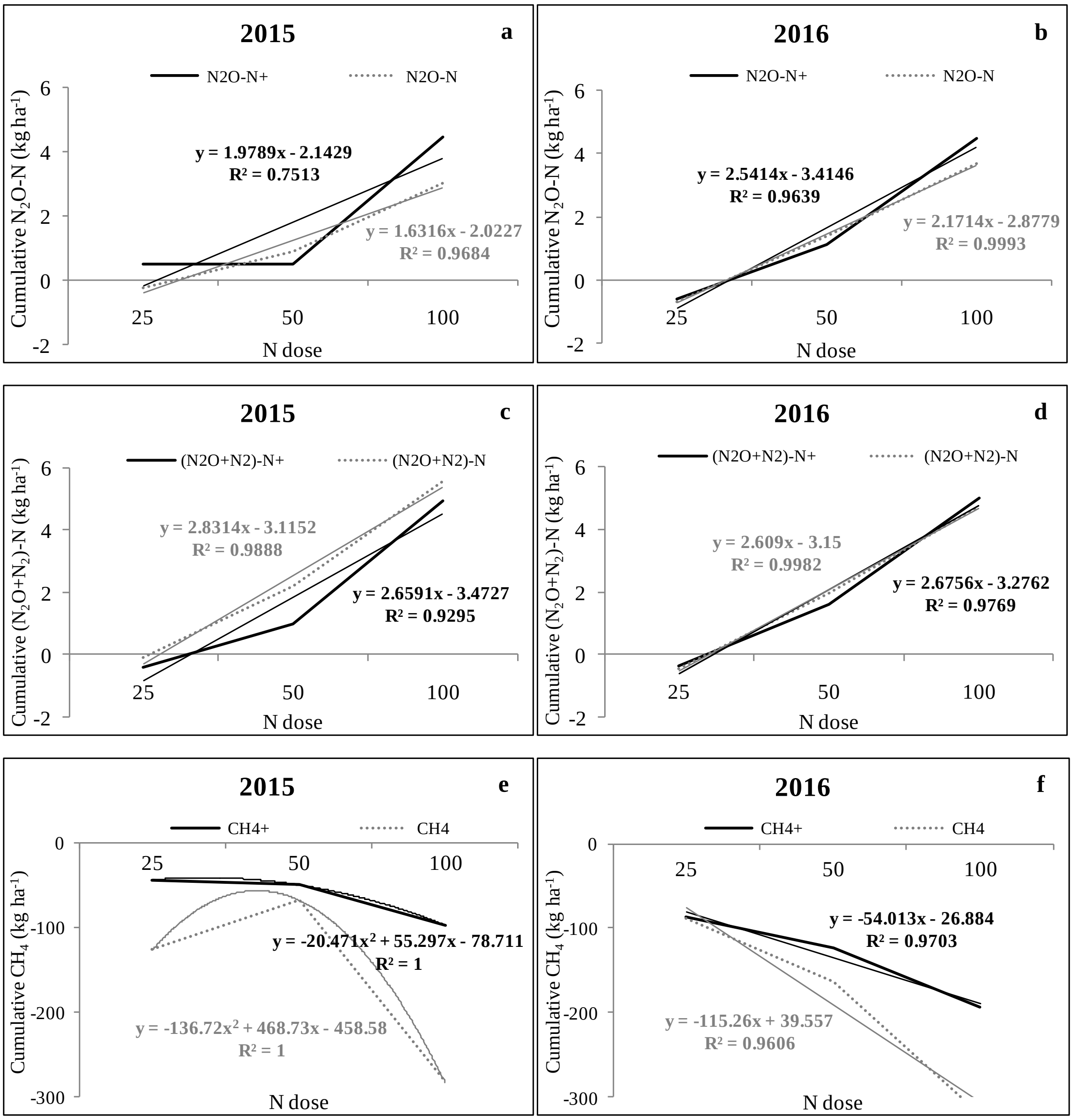


Figure 5. Relationship between cumulative $N_2O$-N (a, b), ($N_2O$+$N_2$)-N (c, d) and $CH_4$ (e, f) emissions and N dose in 2015 and in 2016.

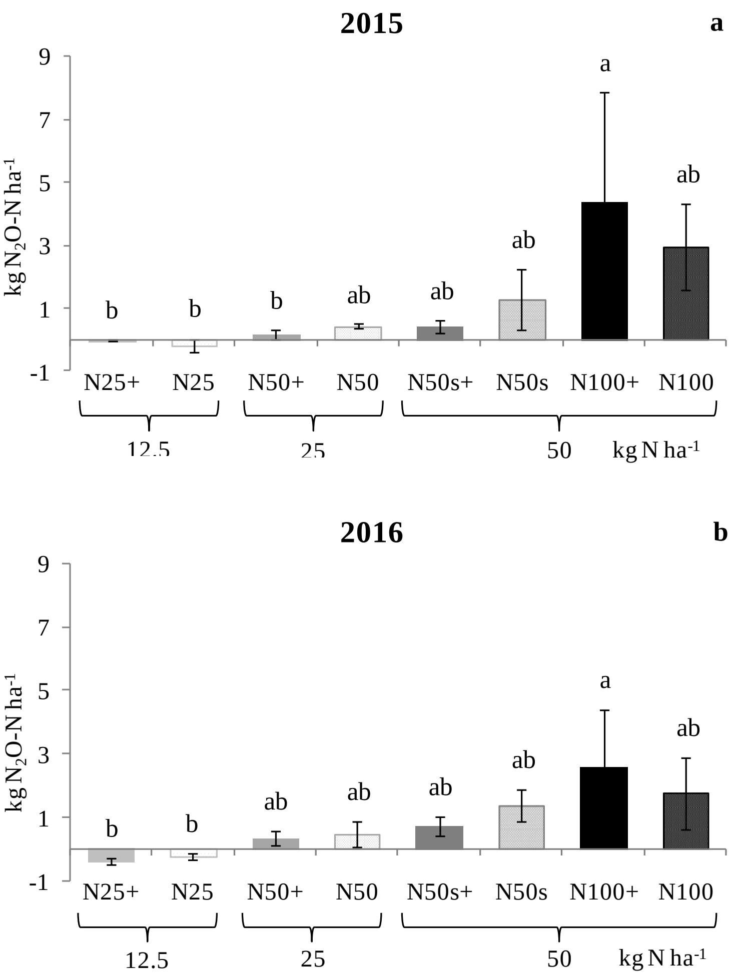
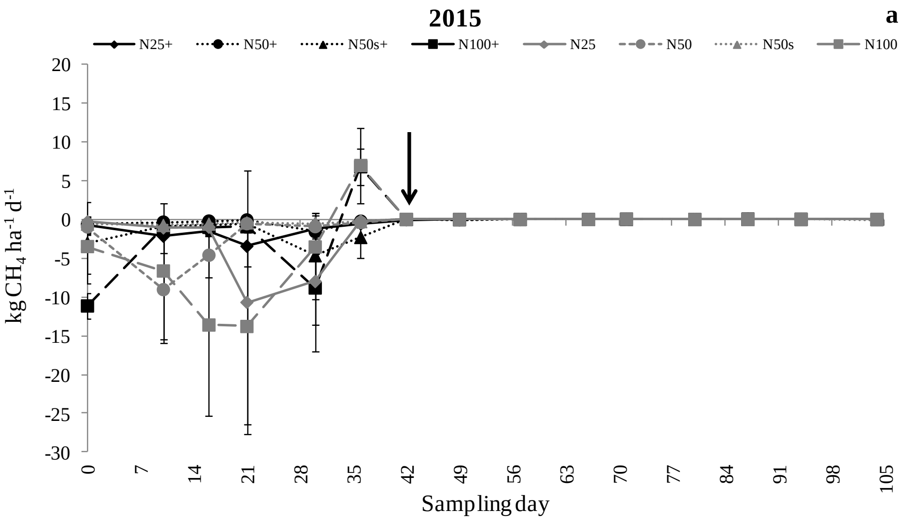


Figure 6. Average cumulative $N_2O$-N emissions during the “s” time from all the treatments and effective N dose during that period in 2015 (a) and in 2016 (b). The error bars correspond to the standard deviation.



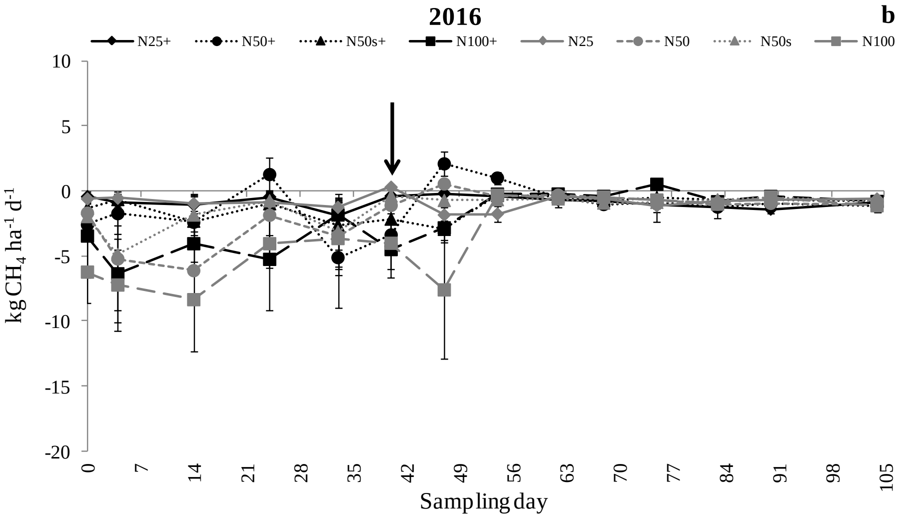


Figure 7. Average daily $CH_4$ fluxes during the sampling period in 2015 (a) and 2016 (b) per treatment. The error bars correspond to the standard deviation. The arrow indicates the cessation of fertilisation.

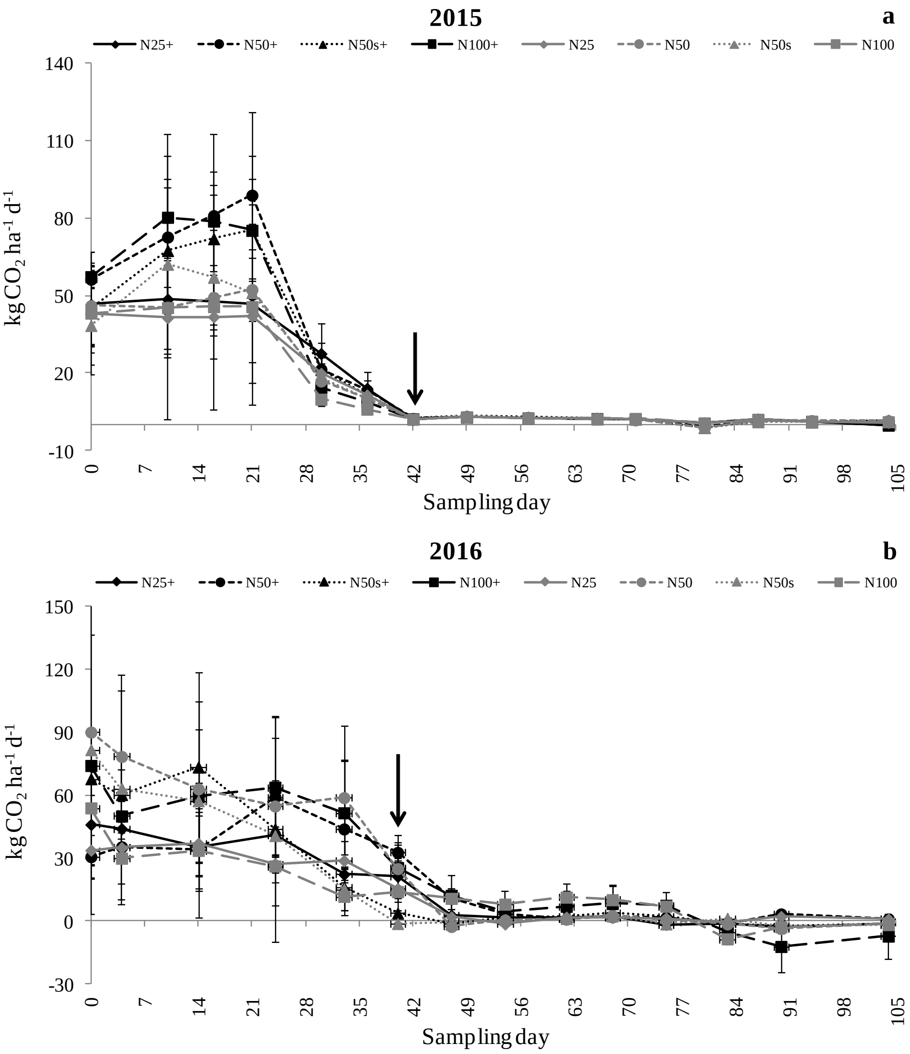


Figure 8. Average daily $CO_2$ fluxes during the sampling period in 2015 (a) and in 2016 (b) per treatment. The error bars correspond to the standard deviation. The arrow indicates the cessation of fertilisation.

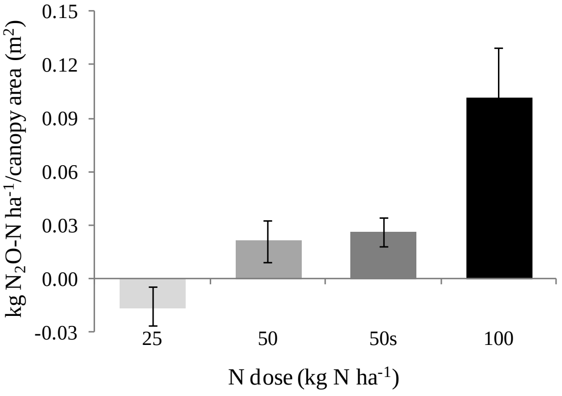


Figure 10. Cumulative $N_2O$-N emissions per estimated canopy area. The error bars correspond to the standard deviation.

# SUPPLEMENTARY MATERIAL

## Tables

Table 1. Chemical soil properties and granulometric analysis of the study soil.

| | Depth<br>0-40 cm |
|---|---|
| Organic matter (Walkley-Black; %) | 2.2 |
| pH (1:2.5 saturated paste extract) | 8.0 |
| EC (1:5 saturated paste extract; dS m$^{-1}$) | 7.1 |
| Clay (%) | 21 |
| Silt (%) | 55 |
| Sand (%) | 23 |

Table 3. Soil $NO_3^-$-N content in 2015 and 2016.

| | $NO_3^-$-N (mg kg dry soil$^{-1}$) | | | | |
|---|---|---|---|---|---|
| Treatment | 2015 | | 2016 | | |
| | May | June | May | June | July |
| N25+ | 58 | 11 | - | - | - |
| N25 | 43 | 12 | 13 | 12 | - |
| N50+ | 36 | 10 | 88 | 20 | - |
| N50 | 65 | 11 | 31 | 23 | 22 |
| N50s+ | 71 | 15 | 78 | 18 | 15 |
| N50s | 27 | 14 | 25 | 15 | 13 |
| N100+ | 75 | 13 | 62 | 19 | - |
| N100 | 82 | 19 | 53 | 15 | - |

# Figures

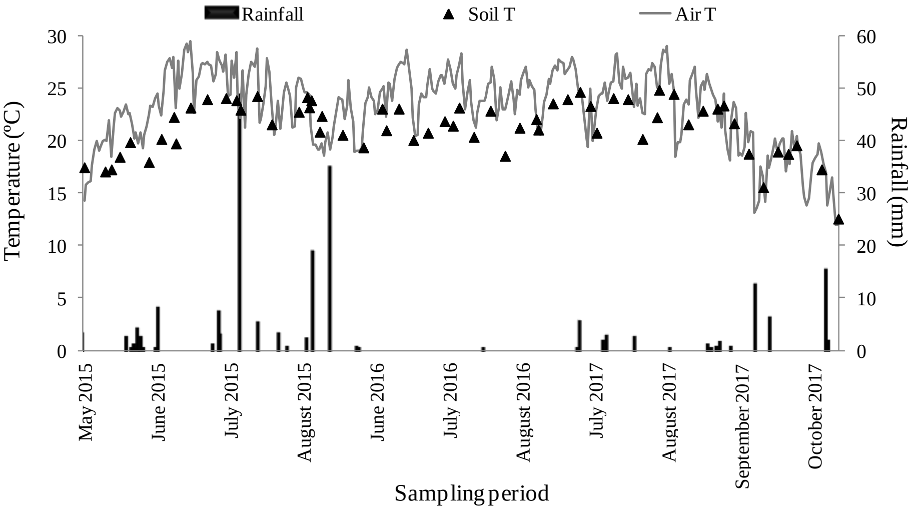


Figure 1. Average soil and air temperatures (T) and daily rainfall during the sampling period in 2015, 2016 and 2017.

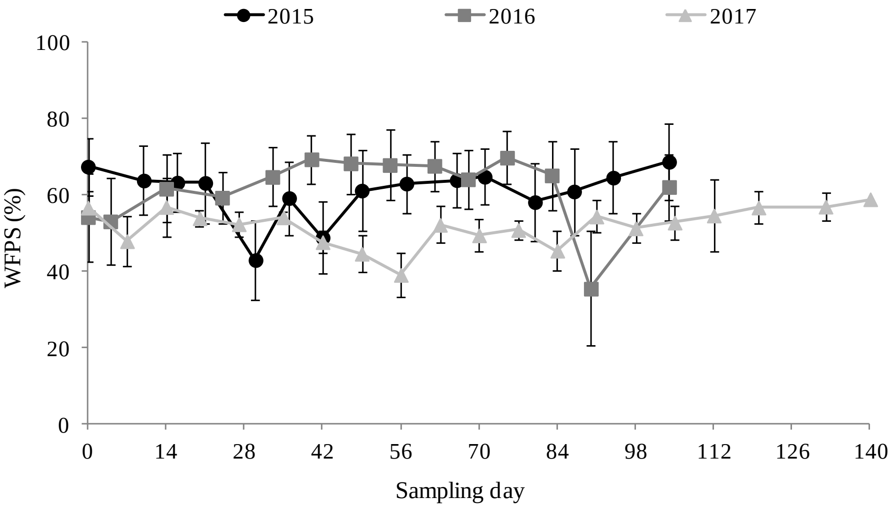


Figure 2. Evolution of average water-filled pore space (WFPS) in 2015, 2016 and 2017 during the sampling period.

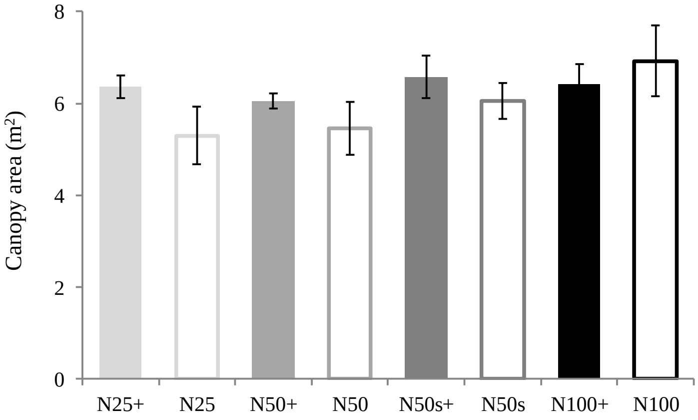


Figure 9. Average canopy area per treatment. The error bars correspond to the standard deviation.