Feasibility of stabilised nitrogen fertilisers decreasing greenhouse gas emissions under optimal management in sprinkler irrigated conditions

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Highlights

- A single application of urea with DMPP abated direct N_2O emissions.
- Urease inhibitors were not able to abate N_2O emissions.
- Yield-scaled N_2O emissions were reduced by N-stabilised fertilisers in deep soils.
- Indirect N_2O emissions were low (<13% of direct) and not affected by treatments.

Abstract

Stabilised nitrogen (N) fertilisers with nitrification and urease inhibitors have been proposed to abate greenhouse gas (GHG) emissions in agrosystems. Nevertheless, differences in their application and in the management of water and nitrogen rates make it difficult to evaluate their actual utility. The aim of this study was to analyse the possibility for GHG emissions reduction in a 3-year rotation (maize-maize-wheat) by substituting the traditional split-urea application to maize by a single side-dress application of stabilised urea fertiliser. The experiment was performed in 24 drainage lysimeters in two contrasting soil types (Shallow and Deep) under efficient irrigation practices and adjusted N rates under Mediterranean conditions. Nitrous oxide (N_2O) and methane (CH_4) were measured using static closed unvented chambers, and the soil mineral N was monitored through periodic soil samplings. CH_4 emissions were generally negligible with occasional tendency the soil acting as a sink more than as a net source Direct N_2O emissions during the whole rotation showed lower values when a nitrification inhibitor (3,4-dimethylpyrazole phosphate) was added than with conventional urea (Deep soil: 73% lower, $p<0.05$; Shallow soil: 60% lower, ns). Urease inhibitors (N-(n-butyl) thiophosphoric triamide and monocarbamide dihydrogen sulphate) could not abate direct N_2O emissions, and their effect depended on the soil type. However, all stabilised fertilisers mitigated N_2O emissions in Deep soil when scaled by grain yield (average 54%). Indirect N_2O emissions associated with nitrate leaching were not affected by the treatments but contributed more to total N_2O emissions in Shallow soil (12%) than in Deep soil (6%). These results suggest that adequate use of nitrification inhibitors could have environmental benefits without lessening agronomic production.

Keywords

Nitrification inhibitor, urease inhibitor, nitrous oxide, methane.

1. Introduction

Agriculture produces direct and indirect greenhouse gas (GHG) emissions: nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2) mainly (FAO, 2015). According to the Intergovernmental Panel on Climate Change (IPCC, 2014), agricultural factors that contribute to GHG release from soils are manure applied to soils, crop residues, synthetic fertilisers, and tillage, among others. Crop nitrogen fertilisation stands out from the rest of the management factors since fertilisation is considered to be responsible for 70% of the worldwide N_2O anthropogenic emissions (Ussiri and Lal, 2013). Nitrous oxide, in addition to standing as the most significant ozone-depleting emissions type, is the third most important GHG (UNEP, 2013) in terms of global warming potential (GWP) due to its long atmospheric lifetime (121 years; Myhre et al., 2013) and its radiative properties (the GWP of 1 kg N_2O is equivalent to 265 kg of CO_2 when summed over a 100-year period; Myhre et al., 2013).

The large amounts of water and nitrogen applied in irrigated conditions creates favourable soil conditions for N_2O production (Sanz-Cobena et al., 2017) either by nitrification and denitrification processes (Hénault et al., 2012), the two dominant processes of soil N_2O production. In this context of irrigated agriculture, there is a group of irrigation and fertilisation practices with high GHG mitigation potential. In relation to irrigation, adjusting irrigation rates to crop needs and the use of pressure irrigation systems (drip and sprinkler), in comparison to flood or furrow irrigation systems, can decrease N_2O fluxes (Sanz-Cobena et al., 2017). Franco-Luesma et al. (2019) found no effect of sprinkler irrigation frequency on soil N_2O emissions in maize although night irrigation tended to increase emissions compared to daily irrigation. In relation to fertilisation practices, adjustments to N rates to crop needs, N splitting, fertigation, substitution of synthetic fertilisers by manures, injection or immediate incorporation of fertilisers and manure (or slurries) after its application, and use of nitrification and urease inhibitors have been proposed as strategies to reduce N_2O fluxes (Sanz-Cobena et al., 2017).

Nitrification inhibitors (NIs) and urease inhibitors (UIs) as additives to N fertilisers were developed to synchronize the N supply to the N crop demand, avoiding N losses, and thus increasing nitrogen use efficiency (NUE) (Ussiri and Lal, 2013). These fertilisers with inhibitors, frequently called stabilised fertilisers, maintain N in less susceptible to loss forms. The increase in the duration of N in soils (Huérfano et al., 2015) and the improvement of the NUE (Abalos et al., 2014) could allow a reduction in the N rates or a lessening of the number of fertiliser applications.

NIs depress the activity of *Nitrosomonas* bacteria in the soil, delaying the first step of the nitrification, which is the oxidation of NH_4^+ to NO_2^- (Zerulla et al., 2001a, 2001b). NIs contribute to the reduction in N_2O emissions (Cayuela et al., 2017; Recio et al., 2018; Sanz-Cobena et al., 2017) and nitrate leaching losses (Díez-López et al., 2008; Díez et al., 2010; Quemada et al., 2013) but can increase the risk for NH_3 volatilisation (Ferguson et al., 1984).

UIs delay the conversion of urea to ammonium (enzymatic hydrolysis of urea) by inactivation of the urease enzyme (Ussiri and Lal, 2013). According to several studies, UIs can potentially reduce losses of N by ammonia (NH_3) volatilisation (Abalos et al., 2012; Cantarella et al., 2018; Sigurdarson et al., 2018), N_2O emissions (Sanz-Cobena et al., 2014, 2012) and nitrate leaching losses (Abalos et al., 2014; Cameron et al., 2013).

The most commonly used NIs around the world are dicyandiamide (DCD), 2-chloro-6-(trichloromethyl) pyridine (nitrapyrin), and 3,4-dimethylpyrazole phosphate (DMPP) (Trenkel, 2010). Regarding the UIs, the most extensively used is N-(n-butyl) thiophosphoric triamide (NBPT). Another UI, non-‘EU fertilising product’, monocarbamide dihydrogen sulphate (MCDHS), has been considered by the Spanish Government since 2011 (Orden PRE/630/2011; international patent WO 2007/132032 A1), but no information is available in the scientific literature confirming its potential to stabilise ureic N.

Most of the studies performed using NIs and UIs to compare their effect to that of conventional fertilisers on yield and N_2O losses do not consider the possibility of reducing the number of N side-dress applications as a strategy and incentive for farmers to use stabilised N fertilisers. Another important factor to elucidate the real impact of stabilised fertilisers on GHG emissions is to assess their effectiveness under limiting N rates (Rose et al., 2018) and efficient irrigation management practices. Therefore, the objective of this study is to evaluate the effect of three different inhibitors in urea (urea with DMPP, NBPT, and MCDHS) applied in a single application in comparison with the traditional urea application on GHG emissions under a 3-year rotation (maize-maize-wheat) and under two soil types in Mediterranean irrigated conditions. The hypothesis is that in comparison to the conventional strategy (split urea in maize), a single application of urea stabilised with inhibitors can reduce N_2O emissions, maintaining crop productivity.

2. Materials and methods

2.1. Site and experimental design

The trial was conducted in the experimental field ‘Soto Lezcano’, located in the middle Ebro Valley (Zaragoza, Spain), from 2015 to 2017. The area is characterised by a semiarid Mediterranean-continental climate (mean annual maximum and minimum daily air temperatures of 21.4 and 8.3 ºC, respectively; yearly average precipitation of 319 mm and yearly average reference evapotranspiration of 1,239 mm; period 2004-2018).

The experiment was carried out in twenty-four drainage lysimeters of 5 m^2 (2.0 x 2.5 m), which had been filled by layers in 2012 with disturbed soil from two different contrasting soil types from the region according to soil depth and stoniness (Supplementary material - Figure S1). The battery of the 24 lysimeters was located in a 660-m^2 plot (30 x 22 m). The main physical-chemical characteristics of the two soils are shown in Table 1. Thus, 12 lysimeters were characterised by deep soil depth and the absence of stones (Deep soil), and 12 lysimeters were characterised by shallow soil depth and frequent stoniness (Shallow soil). Therefore, Deep soil presented a meaningfully higher soil water holding capacity (223 mm) than that of Shallow soil (63 mm).

The experimental design was a completely randomised block with three replicates for each type of soil. The fertiliser treatments consisted of a) conventional urea (Urea), b) urea with the nitrification inhibitor 3,4-dimethyl pyrazole phosphate at 0.8% (w:w, relative to inhibited N) (DMPP), c) urea with the urease inhibitor N-(n-butyl) thiophosphoric triamide at 0.13% (w:w) (NBPT), and d) urea with the urease inhibitor monocarbamide dihydrogen sulphate at 1.5% (w:w) (MCDHS). These stabilised fertilisers were provided by the fertiliser companies allowed to commercialise the inhibitors in Spain. The stabilised fertilisers were solid and were applied by manual broadcast to the soil surface. A rotation of maize-maize-wheat (*Zea mays* L. hybrid 'Pioneer P1758' and soft wheat *Triticum aestivum* L. cv. 'Rimbaud') was cropped following the management practices described in Table 2. For the maize crop and in the Urea treatment, the N fertiliser was split into two applications (two-thirds at V6 and one-third at V13 stage), whereas treatments with stabilised fertilisers were applied as a single application at V6. The rate of N fertiliser of maize was calculated assuming a total crop uptake of 250 kg N ha^{-1} and discounting the available soil mineral nitrogen (0-50 cm) at pre-planting for each soil type and year (Table 2). In the wheat crop, all treatments received a single N application at the same time (cereal tillering) at a rate of 150 kg N ha^{-1}. The other macronutrients were also managed to avoid limitations. Thus, conventional fertilisers were applied at pre-planting to maize (50-100-150 kg N-P_2O_5-K_2O ha^{-1}) and wheat (229-154 kg P_2O_5-K_2O ha^{-1}) to avoid P and K limitations.

Weekly irrigation rates were calculated from the reference evapotranspiration (Penman-Monteith equation). Crop coefficients of maize and wheat were estimated according to Martínez-Cob (2008) and FAO procedures (Allen et al., 1998), respectively. The lysimeter area was irrigated using a sprinkler irrigation system, but a drip irrigation network (pluviometry of 5 mm h^{-1}) was installed in each lysimeter to compensate for small wind-caused differences in pluviometry among lysimeters. In addition, a 15-20% leaching fraction was included in the calculations to maintain a good soil salt balance due to the moderate salinity of the irrigation water (electrical conductivity average = 1.53 dS m^{-1}).

Weeds and pests were controlled using the standard practices of the region, yet no special problems were detected during the rotation.

2.2. Measurements

Greenhouse gaseous emissions

Static closed unvented chambers (similar to those of Holland et al., 1999) were used to measure N_2O and CH_4 fluxes. One polyvinyl chloride (PVC) collar was inserted 10 cm into the soil in each lysimeter several days before the first sampling. Collars were located between two rows of maize with no plants inside, while in wheat, the collars included plants. Nitrogen fertiliser was applied individually inside each collar to ensure the target rate. PVC chambers coated with a reflective bubble wrap material were fitted into the collars (19.7 cm height, 30.0 cm inner diameter, and 13.9 L volume) at the time of sampling. Fifteen mL of air from inside each chamber was taken 0, 30, and 60 min after chamber closure using a polypropylene syringe and injected into 12-mL Exetainer® borosilicate glass vials (Labco Ltd., Lampeter, UK). Air samplings were mostly performed between 10:00 and 11:30 a.m. (Greenwich mean time) considering that soil temperature was the main factor driving diurnal changes in N_2O fluxes (Alves et al., 2012) and that soil temperature at that time was close to the daily average of soil temperature. The frequency of the GHG samplings was higher (every 1-3 days) after fertilisation to capture the expected peak fluxes of N_2O. There were a total of 37, 25 and 28 sampling dates in each season (maize 1, maize 2 and wheat, respectively), of which 29, 22 and 21 were performed for the period from seeding to harvest.

Air samples were analysed by gas chromatography using an Agilent 7890B chromatograph with an electron-capture (ECD) and flame-ionisation detector (FID). An HP-Plot Q column (15 m long, 0.32 mm section and 0.02 mm thick) was used with helium as a carrier gas at 25 mL min^{-1}, and a 5% methane in argon gas mixture at 30 mL min^{-1} was used as a make-up gas for the ECD. The FID, the ECD and the methaniser were set to 250, 280, and 375 ºC, respectively. The injector was set to 50 ºC, whereas the oven was set to 35 ºC. The obtained detection limits of CH_4 and N_2O were 0.2 and 0.05 ppm (v:v), respectively.

Soil was sampled from 0 to 10 cm to monitor the mineral N concentration in the upper part of the soil profile, one in every two GHG samplings. In these samples, soil water content was obtained by gravimetry (drying at 105 ºC until constant weight), and nitrate (NO_3^-) and ammonium (NH_4^+) concentrations were determined in soil extracts (10 g wet soil + 30 ml of KCl 2N, shaken for 30 min and filtered through cellulose filter) by colourimetry using a segmented flow analyser (AutoAnalyser3, Bran+Luebbe, Germany).

Topsoil moisture and temperature (at the 5-cm depth) were also monitored continuously (15’ interval) in two lysimeters from each soil type using Hydraprobe sensors (Stevens Water Monitoring Systems Inc., USA). Soil water-filled pore space (WFPS) was estimated according to Linn and Doran (1984) as the quotient between volumetric soil water content and total soil porosity. Soil calibration curves (R^2=0.72-0.75) were obtained separately for both soil types to convert sensor readings to volumetric soil water content and WFPS values. Total soil porosity (0-5 cm) was calculated considering a particle density of 2.65 Mg m^{-3}, and the soil bulk density was measured ‘in situ’ using the cylinder method (Grossman and Reinsch, 2002) as 1.47 and 1.43 Mg m^{-3} for Deep and Shallow soil, respectively. Daily air temperature and precipitation were registered through an automated weather station located 350 m from the experimental site.

Nitrate leaching

Weekly drainage from each lysimeter was collected in 50-L graduated tanks set in an underground gallery, and the volume was measured. A 30-mL subsample was collected from each tank to analyse NO_3^- concentrations using a segmented flow analyser (AutoAnalyser3, Bran+Luebbe, Germany). The mass of NO_3^- leached was calculated for each sampling date as the product of the drainage volume by the NO_3^- concentration.

Grain yield

The crops were harvested at maturity (October 2nd, 2015; September 13th, 2016; and July 3rd, 2017) to determine grain yield. The results are reported on the basis of 140 g kg^{-1} moisture content for maize and 120 g kg^{-1} moisture content for wheat.

2.3. Data calculations

Fluxes of GHG were calculated fitting a linear regression to gas concentration in the chamber (corrected for air temperature) versus time. Cumulative emissions were estimated for different periods by multiplying the averaged fluxes by the length of the period of two consecutive gas samplings. Fluxes obtained from the static chambers are named as ‘direct’ emissions.

‘Indirect’ N_2O emissions are those associated with nitrate leaching which were estimated according to the method established in the 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC, 2019). For each lysimeter, the cumulative mass of N lost as nitrate leaching was multiplied by the emission factor EF_5 of 0.011.

Total N_2O emissions were calculated as the sum of direct and indirect N_2O emissions associated with nitrate leaching.

Yield-scaled N_2O emissions were calculated as the ratio between the cumulative N_2O emissions and the grain yield.

Basal N_2O fluxes were estimated for each lysimeter by removing N_2O peaks to obtain the hypothetical cumulative emissions of a control treatment without N fertilisation. A unique treatment-averaged basal N_2O flux was obtained for each soil type and season. Estimated N_2O emission factors (EF, %) were calculated for each lysimeter as the difference between the cumulative N_2O emissions (kg N ha^{-1}) measured in each treatment and the estimated basal cumulative N_2O emissions, and this sum was divided by the amount of N applied (kg N ha^{-1}) and multiplied by 100.

2.4. Statistical analysis

Different time periods were considered for the statistical analysis; they were referred to as ‘seasons’ from sowing to the following sowing, ‘crop period’ from sowing to harvest, ‘intercrop period’ from harvest to sowing next year, and ‘fertilisation period’ from the first side-dress fertiliser application to one month after the second side-dress application.

Variables were transformed (natural logarithm and Box-Cox transformation) when necessary to normalise their distribution and to homogenise the variances, subjected to two-way (treatment and soil type) analysis of variance. Comparisons among treatments, with Tukey’s test, were established within each soil type since soils are not an eligible variable by the farmer.

A paired t-test was used to evaluate differences in daily WFPS and soil temperature between soil types. A one-sample z-test was used to check whether cumulative CH_4 emissions were different from zero. The MIXED procedure was used to analyse repeated measurements along time of GHG fluxes and soil N content, according to a first-order autoregressive structure model AR(1). Although significant interaction treatment x sampling times were detected, the global analysis was possible because the interactions were quantitative. Comparisons among treatments were performed with Tukey’s test. Pearson correlation analysis was used to determine the relationship between N_2O fluxes and soil NO_3^- and NH_4^+ concentrations, soil temperature, and WFPS.

In all tests, the level of significance considered by default was 95%. Statistical analyses were performed using the SAS software University Edition (SAS Institute, Cary, NC).

3. Results

3.1. Soil mineral nitrogen, WFPS, and temperature

The annual pattern of SMN for the 0 to 10 cm soil depth was closely related to the events of the fertiliser applications (Figure 1). Noticeable peaks of SMN were observed in the topsoil following N applications that decreased in the subsequent days. The duration of the SMN peaks ranged from 30 to 53 days. SMN of the stabilised treatments were not directly comparable with those of Urea since the stabilised fertilisers were applied at one time in maize, while Urea was split into two applications. In the one-month period after the single N side-dress application of stabilised fertilisers, in comparison to the other treatments, the DMPP treatment always showed the highest values of soil NH_4^+ concentration in this layer and in four of the six cases, it was significantly different from that of the UIs (Table 3). The DMPP treatment presented the largest permanency of ammonium in the soil compared to that of NBPT and MCDHS, being more effective in Shallow soil, e.g., in Shallow soil during the two maize crops, DMPP maintained an N concentration greater than 70 mg N kg^{-1} soil for at least 18 days (Supplementary material - Figure S2). The behaviour of the NO_3^- concentrations was the opposite of that of NH_4^+, and in general, no significant differences in SMN were found in the topsoil among the stabilised fertilisers in the one-month period that followed fertilisation.

WFPS at a 5-cm depth throughout the whole rotation ranged from 25% to 90% in Deep soil (average of 56%) and from 24% to 72% in Shallow soil (average of 47%) (Figure 2a). WFPS was on average 27% higher from seeding to harvest than during the intercrop period (25% higher in Deep soil and 29% higher in Shallow soil) due to the effect of irrigation. Averaged over the whole rotation, Deep soil presented WFPS values 20% higher than those of Shallow soil ($p<0.0001$). Major differences among soils were found during the wheat crop and during the first intercrop period between maize 1 and maize 2.

Topsoil daily average temperature (5-cm depth) ranged from 0.3 ºC to 33.6 ºC during the three growing seasons (Figure 2b). Small but significant differences in soil temperature were found between the two soil types (daily mean temperature of 16.0 ºC and 16.8 ºC for Deep and Shallow soil, respectively). The largest divergence was found at the end of the rotation, during the wheat crop when the temperature was 9% higher ($p<0.0001$) in Shallow soil than in Deep soil.

3.2. Greenhouse gas emissions

High temporal variability was observed in the N_2O fluxes (Figure 3), with values in the range of -3 to 1,918 g N_2O-N ha^{-1} day^{-1} in Deep soil and from 5 to 2,182 in Shallow soil. Extremely high fluxes were observed after the fertiliser application events (MCDHS reached 1,918 g N_2O-N ha^{-1} day^{-1} in Deep soil, and NBPT reached 2,182 g N_2O-N ha^{-1} day^{-1} in Shallow soil, with both peaks having a firm performance), and very low fluxes were observed during the rest of the year. Averaging over crops and soils, 97% of N_2O was emitted during the crop periods, and the remaining 3% was emitted during the intercrop periods. The accumulated N_2O emissions were highly related to the maximum peak of the N_2O fluxes measured in each lysimeter (maize 1: $R^2=0.49$; maize 2: $R^2=0.92$; wheat: $R^2=0.81$; data not shown).

The repeated measures analysis of N_2O fluxes for the ‘fertilisation period’ showed significant differences among treatments (Figure 3). DMPP showed the lowest N_2O fluxes for the fertilisation period and was significantly different from Urea (except in maize 1, Shallow soil).

The temporal pattern of the CH_4 fluxes was extremely variable (Supplementary material - Figure S3) and not related to crop type, period of the year, fertilisation, or irrigation events. The repeated measures analysis did not show differences among the fertiliser treatments regardless of the soil type or season (data not shown).

The soil type significantly affected direct N_2O emissions from the reference Urea treatment: N_2O emissions were more than double in Deep (6.15 kg N_2O-N ha^{-1}) than in Shallow soil (2.92 kg N_2O-N ha^{-1}) (**¡Error! No se encuentra el origen de la referencia.**). However, considering the four treatments, in comparison to soil type, fertiliser treatment had a greater impact on N_2O emissions (**¡Error! No se encuentra el origen de la referencia.**).

In Deep soil, DMPP significantly reduced cumulative N_2O emissions in comparison to that in Urea in all seasons (with the exception of maize 2). For the whole rotation, DMPP was able to reduce N_2O emissions by 73% (from 6.15 kg N_2O-N ha^{-1} to 1.65 kg N_2O-N ha^{-1}). NBPT and MCDHS were not able to abate N_2O emissions in neither season nor for the whole rotation.

In the Shallow soil, DMPP significantly reduced N_2O emissions in relation to Urea in only the maize 2 season. For the whole rotation, DMPP was able to reduce N_2O emissions by 60% with respect to those in the Urea treatment, although this reduction was significant at $p=0.06$. UIs (NBPT and MCDHS) quantitatively increased N_2O emissions for the whole rotation; i.e., UIs were not able to reduce emissions significantly in relation to Urea.

CH_4 emissions were not affected by soil type or fertiliser treatment (Supplementary material – Table S1). Negative emissions were observed in different periods, with the soil acting as a methane sink, although in six out of the eight cases (4 treatments x 2 soil types) CH_4 emissions during the whole rotation were not significantly different than zero ($p>0.05$).

Estimated indirect N_2O emissions derived from nitrate leaching (Supplementary material - Table S2) did not show differences among fertiliser treatments for any soil type and considered period. Indirect N_2O emissions presented significant differences among soils. Indirect N_2O emissions for the whole rotation were higher in Shallow soil than in Deep soil for the Urea treatment (136%) and for the average of the 4 treatments (83%).

For the whole rotation, indirect N_2O emissions in Deep soil were, on average, 0.24 kg N_2O-N ha^{-1}, whereas direct N_2O emissions were 17 times higher (3.98 kg N_2O-N ha^{-1}). In Shallow soil, the importance of indirect emissions increased; direct N_2O emissions (3.34 kg N_2O-N ha^{-1}) were only 8 times higher than indirect N_2O emissions (0.44 kg N_2O-N ha^{-1}).

In Deep soil, DMPP tended to present lower total N_2O emissions than Urea (Table 4. Average (n=3) of cumulative N_2O emissions for the different seasons[a], fertiliser treatments (Urea, DMPP, NBPT, and MCDHS), and soil types (Deep and Shallow). Different letters within columns indicate significant differences among treatments (Tukey's test, $p<0.05$) for each soil type.

	kg N_2O-N ha^{-1}				
	Maize 1	**Maize 2**	**Wheat**	**Maize 1+2**	**Whole rotation**
	--------------------------Deep soil--------------------------				
Urea	2.20 a	3.32	0.59 a	5.53 a	6.15 a
DMPP	0.84 b	0.52	0.28 b	1.36 b	1.65 b
NBPT	1.51 ab	1.51	0.56 a	3.04 ab	3.63 ab
MCDHS	1.24 ab	2.68	0.57 a	3.91 ab	4.50 ab
	------------------------Shallow soil------------------------				
Urea	1.13 ab	1.56 a	0.22	2.69 ab	2.92
DMPP	0.48 b	0.49 b	0.19	0.98 b	1.18
NBPT	1.02 ab	4.12 a	0.18	5.14 a	5.33
MCDHS	1.30 a	2.41 a	0.23	3.71 ab	3.94
Treatment	<0.001	<0.001	<0.001	0.004	0.003
Soil type	0.006	0.964	<0.001	0.632	0.379
Treat.*Soil	0.091	0.047	<0.001	0.043	0.050

[a]- Maize 1, maize 2 and wheat include the period from sowing to the following sowing. Maize 1+2 includes from maize 1's sowing to wheat's sowing. Whole rotation includes from maize 1's sowing to end September.

Table 5), although the reduction was only significant for wheat. Similarly, in Shallow soil, DMPP presented lower values compared to Urea, although differences were not significant. In comparison with conventional fertiliser, urease inhibitors did not significantly affect total N_2O emissions in any of the three seasons in the two soil types. For the whole rotation, DMPP was able to reduce total N_2O emissions by 71% (Deep soil, significant at p=0.053) and 54% (Shallow soil, not significant) in comparison to the conventional Urea treatment.

Treatments with UIs behaved differently depending on the soil type. In comparison to Urea, UIs showed lower total N_2O emissions in Deep soil, although higher values occurred in Shallow soil when the whole rotation was considered although the differences were not significant in both soil types.

Soil NO_3^- content was the variable with the highest correlation to N_2O fluxes (r=0.46) (Table 6), followed by soil NH_4^+ content (r=0.33). When the correlation analysis was performed separately for the different treatments, a different behaviour was observed in the DMPP treatment. Thus, in this treatment, N_2O fluxes presented a higher correlation with soil NH_4^+ (r=0.31) than with soil NO_3^- (r=0.24). WFPS and soil temperature were the variables with weaker correlation to N_2O fluxes when pooled data of the four treatments were considered, even though for some treatments, the correlation was higher for soil temperature than for soil NH_4^+ content (Urea and NBPT). However, the relation between N_2O fluxes and WFPS was non-linear (Figure 4), maximum N_2O fluxes values were observed at approximately 60% of WFPS, and the highest peaks (>500 g N_2O-N ha^{-1} day^{-1}) of the N_2O fluxes were only observed at approximately 60% WFPS and at extremely high (>100 kg N ha^{-1}) values of topsoil SMN.

3.3. Yield-scaled N_2O emissions, and emission factors

Treatments did not affect yield in the two soil types. The only exception was wheat for Shallow soil, where in comparison to Urea, DMPP presented 10% lower grain production (data not shown).

The fertiliser treatments were more important than the soil type in the yield-scaled N_2O emissions (Table 7). Yield-scaled N_2O emissions showed differences among treatments depending on the considered period and soil type. DMPP presented the lowest values (except Shallow soil during wheat crop) and was significantly different from Urea in Deep soil for all seasons. Considering the whole rotation, all stabilised treatments decreased yield-scaled N_2O emissions compared to those with Urea in Deep soil but no effect of inhibitors was detected in Shallow soil. There was a strong relationship (R^2=0.99, n=69) between the N uptake-scaled N_2O emissions (calculated using the aboveground N uptake as the denominator) and the yield-scaled N_2O emissions (data not shown), and the statistical response to the treatments for the whole rotation was similar for the two variables.

Emission factors ranged from 0.03% to 1.91% (Table), with an average value of 0.54%. Maize 2 presented the highest value (average of 1.03%), whereas wheat had the lowest value (average of 0.12%). Comparing treatments, the DMPP always presented the lowest EFs, although considering the whole rotation, DMPP was only different from Urea in the Deep soil.

4. Discussion

Special care was taken during the experiment to manage the irrigation and the N rates to avoid practices with already well-known negative effects on nitrous oxide emissions. Thus, N fertiliser rates and irrigation management were adjusted to crop needs.

Nevertheless, the observed maximum fluxes in N_2O were notably higher than those measured in the same region for a maize crop by Álvaro-Fuentes et al. (2016). Thus, for the conventional treatment with urea, emissions peaks higher than 200 g N_2O-N ha^{-1} day^{-1} were measured, while in the previously mentioned study the maximum fluxes were approximately 40 g N_2O-N ha^{-1} day^{-1} for a N application of 300 kg N ha^{-1}, split into three applications of 100 kg N ha^{-1}. This difference is noteworthy considering that the N fertiliser rates of urea used in our study for maize crops were quite similar, between 89 and 148 kg N ha^{-1} (depending on the side-dress application and soil type). The important factor is the type of fertiliser; urea was used in this study as opposed to the ammonium nitrate applied in that of Álvaro-Fuentes et al. (2016). Similarly to this study, Guardia et al. (2017) found maximum fluxes of nitrous oxide of 142 N_2O-N ha^{-1} day^{-1} with side-dress applications of urea at 180 kg N ha^{-1} in sprinkler-irrigated maize in the central area of Spain. Additionally, N_2O peaks higher than 200 g N_2O-N ha^{-1} day^{-1} have been described by Martins et al. (2017) with urea rates of 100 kg N ha^{-1} under tropical conditions with air temperatures similar to those found in this study. Also, similar peaks (approximately 200 g N_2O-N ha^{-1} day^{-1}) have been reported by Franco-Luesma et al. (2019) in sprinkler-irrigated maize fertigated with 100 kg N ha^{-1} of N-32 and located on the same experimental farm than this study. The observed variability in the maximum N_2O emissions rates reflects the high number of environmental and management factors that affect N_2O flux. Divergences between the studies could also have been due to the time of day when the N_2O flux was sampled since a diurnal pattern in N_2O has been observed (Xu et al., 2016) under conditions of high mineral N availability (Shurpali et al., 2016); therefore, the selection of sampling time can significantly influence the estimates, especially when fluxes are high.

Treatment with DMPP presented the lowest N_2O emissions for the whole rotation in both soil types. Compiling data from several experiments in Mediterranean areas, Sanz-Cobena et al. (2017) reported reductions in N_2O emissions of 30-50% associated with the use of NIs. Despite the fact that some studies found higher efficiency of NIs to abate N_2O emissions under high fertiliser rates (Yang et al., 2016), in this experiment DMPP allowed mitigation of 73% (Deep soil) and 60% (Shallow soil, $p=0.06$) of N_2O emissions in comparison to Urea, under adjusted N fertiliser rates. The highest mitigation percentages in comparison with values found in the literature could be related to the intrinsic higher N_2O losses that occur when splitting the N fertiliser compared to a single application (Huérfano et al., 2015). Consequently, the single application of urea with DMPP in this study could have inherently lowered N_2O losses when compared with those in the split application of conventional urea.

In comparison to the conventional urea treatment, urea stabilised with the two UIs did not significantly reduce N_2O emissions during any of the studied periods. During maize 2, the high emission peaks measured in the MCDHS (Deep soil) and NBPT (Shallow soil) treatments had a noticeable influence on the accumulated values. The absence of differences contrasts with the positive N_2O mitigation effect of UIs (ranging between 30 and 60%) described in the meta-analysis study of Sanz-Cobena et al. (2017) under Mediterranean climate. For instance, urea with NBPT applied to maize crops in Central Spain reduced N_2O emissions by 54% (Sanz-Cobena et al., 2012) and by 50% (Guardia et al., 2017). The main reason for the failure of UIs to inhibit the N_2O emissions might be the non-direct relation between hydrolysis of urea and N_2O emissions (Akiyama et al., 2010).

Maize crops under tropical conditions (Martins et al., 2017) presented higher N_2O emissions when fertilised with urea+NBPT than with conventional urea, a result similar to that observed in this study for Shallow soil. The authors associated this effect with an extension of nitrification period (Smith et al., 2012), favouring the action of nitrifiers (Christianson et al., 1993) leading to an increase in N_2O emissions.

Microbial processes of N_2O production and consumption are mainly driven by soil factors (Ussiri and Lal, 2013). However, in our study, the emissions patterns of UI treatments did not seem to respond to the soil water content observed by Sanz-Cobena et al. (2012) in a maize crop under Mediterranean conditions where NBPT led to a loss in effectiveness in the abatement of N_2O fluxes when WFPS was higher than 65%. UIs did not show N_2O mitigation although Shallow soil surpassed the topsoil WFPS of 65% during only 0% and 9% of the days of maize crop in seasons 2015 and 2016, respectively; Deep soil surpassed this threshold more frequently (31% and 48%), respectively, and these conditions were less suitable for NBPT efficiency according to the cited study.

In studies under similar climate conditions where urea+NBPT was applied to maize, yield-scaled N_2O values were in the range of the values obtained in our study. Thus, the study by Guardia et al. (2017) showed values between 37 and 87 g Mg^{-1}, and Sanz-Cobena et al. (2012) showed yield scaled N_2O emissions of 52 g Mg^{-1} (in both cases derived from information in grain yield and N_2O emissions). The exception on similarities is maize 2 in Shallow soil, where yield-scaled N_2O emissions were extremely high and related to the highest but consistent emission peak measured after fertiliser application. The values obtained for the Urea treatment in the abovementioned studies (85 and 167 g Mg^{-1} and 130 g Mg^{-1}, respectively) were in agreement with our results, which ranged from 64 to 192 g Mg^{-1}. The single DMPP application in a wheat crop reported lower yield-scaled N_2O emissions than those derived from Huérfano et al. (2016) (69 and 59 g N_2O-N Mg^{-1} grain yield), even though their work was conducted under humid Mediterranean conditions and DMPP was mixed with ammonium sulphate.

In this study, in the one-month period after fertiliser application, urease hydrolysis and nitrification pathways were not affected by the UIs since similar amounts of mineral N (NO_3^-+NH_4^+) were observed in the different treatments. The highest soil NH_4^+ concentrations observed in the DMPP treatment after fertiliser application indicate the expected delay in nitrification, which is consistent with the results of other studies under similar climate conditions; e.g., Díez-López et al. (2008) found a 60-day delay in the nitrification derived from the inhibitory effect of DMPP.

The presence of N in the topsoil governs N_2O emissions because it is the soil factor better explains the variability in N_2O fluxes. Thus, the DMPP treatment showed a different behaviour compared to that of the other treatments, with a higher effect of soil NH_4^+ than NO_3^- content on N_2O fluxes. The delay in nitrification and the SMN content before the fertilisation application could have weakened the NO_3^- contribution compared to that of the other fertiliser treatments. N_2O production is regulated mainly by soil water content and temperature (Barrena et al., 2017). These two factors were positive, although moderately, correlated to N_2O fluxes in our study.

According to Huérfano et al. (2015), the absence of a water table in the root zone and the prevalence of aerobic conditions help soils act as methane sinks. Overall, a zero-balance of CH_4 emissions was observed in our study since in only two treatments (in Deep soil) a significant negative cumulative emission was detected considering the whole 3-year rotation period. Our results indicate that no emission of CH_4 were produced in maize and wheat cropped in sprinkler irrigated fields, that corroborate the results of previous studies (Álvaro-Fuentes et al., 2016; Pareja-Sánchez et al., 2019) under similar climatic and management conditions.

The methodology for N_2O basal emission calculation could have underestimated the EF values since it did not consider some residual SMN compared to an actual unfertilised control. Despite that limitation, the EFs estimated for the N fertiliser with DMPP in wheat were 0.03% (Deep soil) and 0.06% (Shallow soil), which were of the same magnitude as those calculated by Huérfano et al. (2015) for the same crop and inhibitor that ranged from 0.03 to 0.07% depending on the season. The EFs obtained for conventional urea for the wheat crop (individual EFs from 0.06% to 0.30%) were within the range of values for cereals (EF_{Med}: 0.26%, 95% confidence interval (CI): ±0.22%, n=53) shown in the meta-analysis of Cayuela et al. (2017). Estimated EFs for Urea in the maize crop had a broader range for both soil types and seasons (individual EFs from 0.31% to 2.50%) in contrast with the interval presented for maize in Cayuela et al. (2017) (EF_{Med}: 0.83%, 95%CI: ±0.26%, n=47). The EF averages for the whole rotation considering all fertiliser treatments were 0.64% (Deep soil) and 0.51% (Shallow soil) which are in agreement with the IPCC Tier I default value for "all N input in dry climates" (0.5%) (IPCC, 2019). However, it should be remarked the high variability in emission factors found in this study and, therefore, the necessity to progress to more complex models (tier 2 and tier 3) for GHG estimation. In fact, the development of mitigation strategies as pointed out by Henault et al. (2012) relays in a better understanding of the determinism of GHG emissions.

Indirect N_2O emissions associated with nitrate lost through leaching and runoff are very complicated to measure, and their values are probably dependent on the specific situation and final fate of water and are therefore not evaluated in most studies. Averaging over crops and fertiliser treatments, N_2O emissions associated with nitrate leaching were between 12% (Shallow soil) and 6% (Deep soil) of the total N_2O emissions. The optimal N-fertiliser amounts under conditions of efficient irrigation management in our study must have limited the indirect N_2O emissions compared to those in other situations with lower irrigation efficiency (e.g., flooded irrigation systems or mismanaged irrigation schedules) and where higher masses of nitrate are leached from cereal fields (Malik et al., 2019). According to that study, and for the worst scenario of low water retention soils, the actual farmers' sprinkler irrigation and N management practices in the maize crop led to an estimated mass of nitrate leached of 40 kg N ha^{-1} that will produce estimated indirect N_2O emissions of 0.44 g N ha^{-1}. However, the quantification of indirect N_2O losses from agricultural systems is in initial research stages, and more precise estimations of indirect N_2O emissions are necessary (Tian et al., 2019) to refine the IPCC guidelines and avoid incongruities in the estimations. Accordingly, in the recent IPCC revision, default emission factors have been updated (IPCC, 2019).

5. Conclusions

N_2O emissions and the effect of the three inhibitors (DMPP, NBPT and MCDHS) on N_2O emission were soil type-dependent. The results show that in Deep soil, a single side-dress application of urea with DMPP abated total N_2O emissions in comparison with that in the traditional urea application (split in two applications in maize) at the same N rate. The behaviour of urease inhibitors was completely different in the two soil types, and recommendations should be established in relation to soil characteristics. Thus, in Deep soil, urease inhibitors were able to abate yield-scaled N_2O emissions, while in Shallow soil, UIs increased N_2O and yield-scaled N_2O emissions. Farmers could afford the extra cost of the inhibitor with the savings associated with the suppression of one fertiliser application.

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8. Tables and Figures

Table 1. Main physical-chemical soil characteristics of Deep and Shallow soil at different depths.

Soil characteristics	**-----------------Deep soil-----------------**			**-------Shallow soil-------**	
	0-30 cm	**30-60 cm**	**60-125 cm**	**0-25 cm**	**25-50 cm**
Texture	Clay-loam	Clay-loam	Loam	Clay-loam	Clay-loam
Sand (%)	29	31	33	24	30
Silt (%)	52	51	48	40	36
Clay (%)	19	18	19	36	34
Stoniness (%$_{vol.}$)	3.1	0.9	7.0	11.4	15.2
Available water (mm)	54.5	54.5	114.3	32.1	31.1
P (Olsen) (mg kg^{-1})	30.7	7.8	12.4	14.5	17.5
K (NH_4Ac) (mg kg^{-1})	499	236	72	225	202
Organic matter (%)	1.46	0.94	0.79	2.04	1.24
pH (1:2.5$_{H2O}$)	8.27	8.65	8.04	7.71	7.65

Table 2. Crop management practices for the whole three-year rotation experiment.

	Maize 1	**Maize 2**	**Wheat**
Sowing date	04/05/2015	14/04/2016	10/11/2016
Harvest date	05/10/2015	13/09/2016	03/07/2017
Plant density (plants ha^{-1})	88083	87000	286[1]
Date N pre-planting	30/04/2015	13/04/2016	-
Date N side-dress 1	15/06/2015	06/06/2016	27/02/2017
Date N side-dress 2	20/07/2015	05/07/2016	-
Total N applied (kg N ha^{-1})			
Deep soil	211	173	150
Shallow soil	236	211	150
Irrigation + Rain (mm)	985	945	609
Crop E.T. (mm)	918	866	578

[1] kg seed ha^{-1}.

Table 3. Average topsoil (0-10 cm depth) nitrate, ammonium, and total mineral N concentrations (mg N kg^{-1} soil) during the one-month period that followed side-dress fertilisation in the stabilised fertiliser treatments[a] (DMPP, NBPT, and MCDHS) and for the two soil types (Deep and Shallow). Values followed by the same letter are not significantly different (p>0.05).

	Maize 1			**Maize 2**			**Wheat**		
	NO_3^-	**NH_4^+**	**Nmin**	**NO_3^-**	**NH_4^+**	**Nmin**	**NO_3^-**	**NH_4^+**	**Nmin**
-----Deep soil-----									
DMPP	31.6 b	39.3 a	70.9	22.8 ab	13.7 a	36.5	9.4 b	21.6 a	31.0
NBPT	69.3 a	0.5 b	69.8	44.9 a	7.6 ab	52.6	16.9 a	10.8 b	27.7
MCDHS	59.4 a	0.6 b	60.1	21.3 b	4.6 b	26.0	14.8 ab	18.4 b	33.1
Treatment	0.001	0.002	0.161	0.042	0.013	0.054	0.014	0.018	0.672
Sampling	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.020	<0.001	0.007
Treat.*Samp.	0.001	0.003	0.022	0.389	0.004	0.740	0.333	0.092	0.689
-----Shallow soil-----									
DMPP	23.3 b	87.0 a	110.3 a	27.0	49.1 a	76.1	10.7 b	63.3	73.9
NBPT	53.7 a	27.1 b	80.8 ab	32.5	15.3 b	47.8	26.0 a	34.7	60.8
MCDHS	58.2 a	6.0 b	64.2 b	36.6	14.2 b	50.8	17.6 ab	31.1	48.7
Treatment	0.001	0.001	0.040	0.308	0.014	0.070	0.042	0.054	0.191
Sampling	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.165	0.039
Treat.*Samp.	0.002	<0.001	0.132	0.101	0.016	0.063	0.097	0.416	0.610

[a]- Fertiliser treatment Urea was not considered in the analysis since it was managed in a different way: splitting application.

Table 4. Average (n=3) of cumulative N_2O emissions for the different seasons[a], fertiliser treatments (Urea, DMPP, NBPT, and MCDHS), and soil types (Deep and Shallow). Different letters within columns indicate significant differences among treatments (Tukey's test, $p<0.05$) for each soil type.

	kg N_2O-N ha^{-1}				
	Maize 1	**Maize 2**	**Wheat**	**Maize 1+2**	**Whole rotation**
	---------------------------Deep soil---------------------------				
Urea	2.20 a	3.32	0.59 a	5.53 a	6.15 a
DMPP	0.84 b	0.52	0.28 b	1.36 b	1.65 b
NBPT	1.51 ab	1.51	0.56 a	3.04 ab	3.63 ab
MCDHS	1.24 ab	2.68	0.57 a	3.91 ab	4.50 ab
	------------------------Shallow soil------------------------				
Urea	1.13 ab	1.56 a	0.22	2.69 ab	2.92
DMPP	0.48 b	0.49 b	0.19	0.98 b	1.18
NBPT	1.02 ab	4.12 a	0.18	5.14 a	5.33
MCDHS	1.30 a	2.41 a	0.23	3.71 ab	3.94
Treatment	<0.001	<0.001	<0.001	0.004	0.003
Soil type	0.006	0.964	<0.001	0.632	0.379
Treat.*Soil	0.091	0.047	<0.001	0.043	0.050

[a]- Maize 1, maize 2 and wheat include the period from sowing to the following sowing. Maize 1+2 includes from maize 1's sowing to wheat's sowing. Whole rotation includes from maize 1's sowing to end September.

Table 5. Total (Direct+Indirect) N_2O emissions (kg N_2O-N ha^{-1}) for the different treatments (Urea, DMPP, NBPT, and MCDHS), seasons[a], and soil type (Deep and Shallow). Different letters within the columns indicate significant differences among treatments ($p<0.05$).

	Maize 1	**Maize 2**	**Wheat**	**Maize 1+2**	**Whole rotation**
			-----------------------------Deep soil-----------------------------		
Urea	2.27	3.41	0.62 a	5.70	6.35
DMPP	0.91	0.60	0.32 b	1.52	1.85
NBPT	1.68	1.60	0.57 a	3.30	3.90
MCDHS	1.36	2.80	0.61 a	4.16	4.79
			---------------------------Shallow soil---------------------------		
Urea	1.34 ab	1.77	0.27	3.12 ab	3.40 ab
DMPP	0.64 b	0.67	0.24	1.32 b	1.57 b
NBPT	1.30 ab	4.33	0.24	5.64 a	5.88 a
MCDHS	1.46 a	2.56	0.27	4.02 ab	4.29 ab
Treatment	0.005	0.026	0.005	0.007	0.006
Soil type	0.044	0.667	<0.001	0.809	0.485
Treat.*S.type	0.234	0.062	0.016	0.073	0.085

[a]- Maize 1, maize 2 and wheat include the period from sowing to the following sowing. Maize 1+2 includes from maize 1's sowing to wheat's sowing. Whole rotation includes from maize 1's sowing to end September.

Table 6. Pearson correlation coefficient between N_2O fluxes and soil NO_3^-, soil NH_4^+, soil WFPS, and soil temperature measured in the topsoil (0-10 cm depth). The analysis was performed independently for the different treatments and for the whole dataset.

		Pearson's r			
Treatment	**n**	**NO_3^-**	**NH_4^+**	**WFPS**	**Soil T**
Urea	210	0.49	0.21	0.23	0.35
DMPP	210	0.24	0.31	0.21	0.26
NBPT	210	0.47	0.25	0.26	0.34
MCDHS	210	0.53	0.35	ns	0.34
Pooled data	840	0.46	0.33	0.19	0.32

ns: not significant.

Table 7. Range of the average grain yield (Mg ha^{-1}) by treatment and average yield-scaled N_2O emissions (g N_2O-N Mg^{-1} grain) for the different treatments in different seasons[a] depending on the soil type (Deep and Shallow). Different letters within the columns indicate significant differences in yield-scaled N_2O emissions among treatments ($p<0.05$).

	Maize 1	**Maize 2**	**Wheat**	**Maize 1+2**	**Whole rotation**
	------------------------------**Deep soil**------------------------------				
Yield range	20.1-21.1	16.3-18.0	8.5-8.9	36.3-39.1	-
Urea	106 a	192 a	69 a	145 a	131 a
DMPP	40 b	33 b	31 b	37 b	36 b
NBPT	71 ab	84 ab	63 a	78 b	76 b
MCDHS	62 ab	89 ab	67 a	68 b	68 b
	----------------------------**Shallow soil**----------------------------				
Yield range	17.3-19.6	12.4-15.4	6.0-6.7	29.7-34.8	-
Urea	64	108 a	33	84 ab	76 ab
DMPP	28	34 b	31	31 b	31 b
NBPT	60	257 a	29	188 a	164 a
MCDHS	75	198 a	37	126 a	110 ab
Treatment	0.007	0.001	0.001	0.001	0.001
Soil type	0.128	<0.001	<0.001	0.141	0.234
Treat.*S.type	0.149	0.005	0.025	0.003	0.004

[a]- Maize 1, maize 2 and wheat include the period from sowing to the following sowing. Maize 1+2 includes from maize 1's sowing to wheat's sowing. Whole rotation includes from maize 1's sowing to end September.

Table 8. Average emission factor (%) for the different treatments, seasons[a], and soil types (Deep and Shallow). Different letters within the columns indicate significant differences among treatments ($p<0.05$).

	Maize 1	**Maize 2**	**Wheat**	**Whole rotation**
	---------------------Deep soil---------------------			
Urea	0.95 a	1.85	0.24 a	1.04 a
DMPP	0.30 b	0.23	0.03 b	0.20 b
NBPT	0.63 ab	0.80	0.22 a	0.57 ab
MCDHS	0.49 ab	1.47	0.23 a	0.73 ab
	-------------------Shallow soil-------------------			
Urea	0.43 ab	0.69	0.08	0.43
DMPP	0.15 b	0.19	0.06	0.14
NBPT	0.38 ab	1.91	0.05	0.84
MCDHS	0.50 a	1.09	0.08	0.61
Treatment	0.002	0.021	0.002	0.004
Soil type	0.004	0.657	<0.001	0.214
Treat.*S.type	0.071	0.053	0.007	0.052

[a]- Maize 1, maize 2 and wheat include the period from sowing to the following sowing. Whole rotation includes from maize 1's sowing to end September.

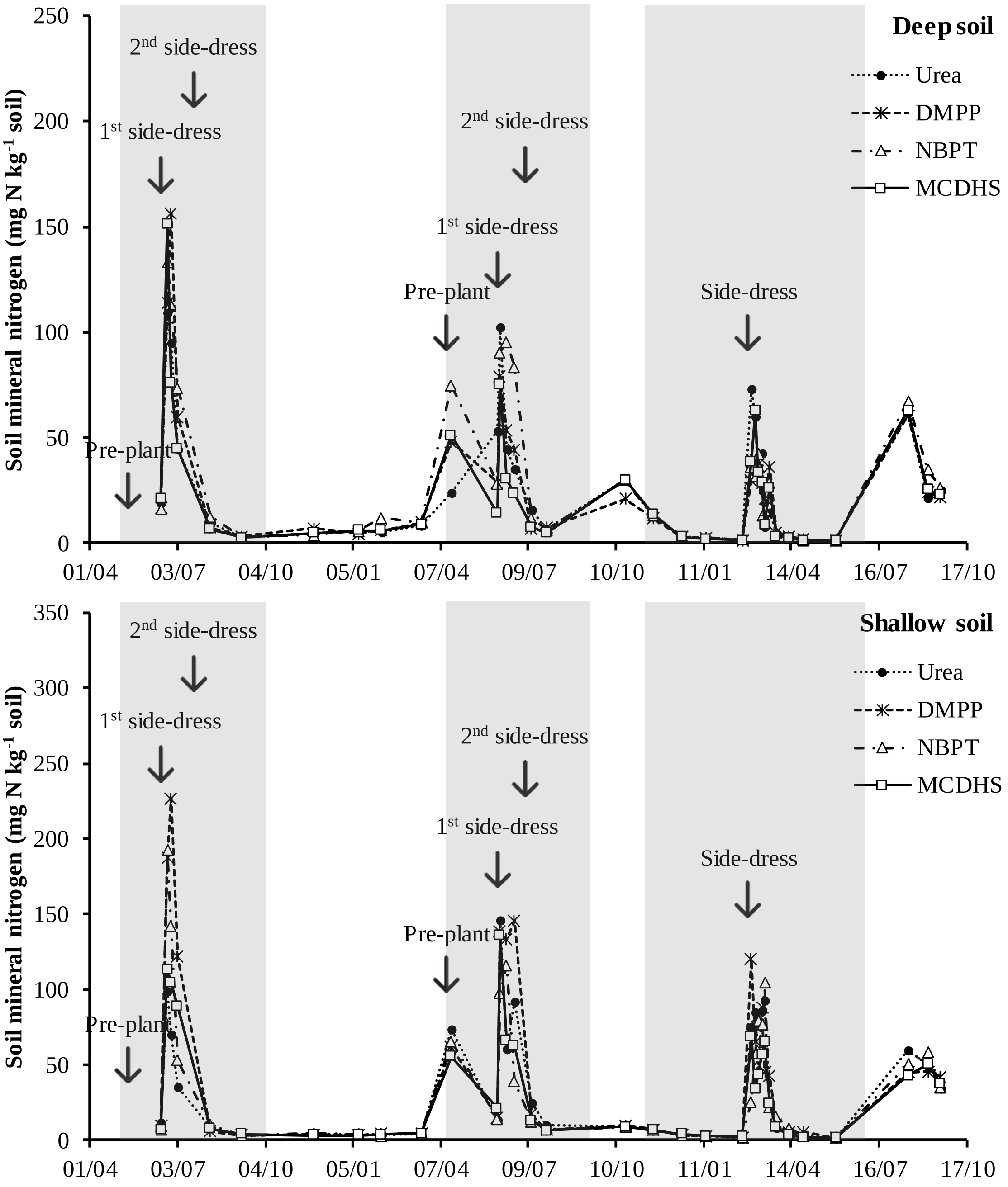
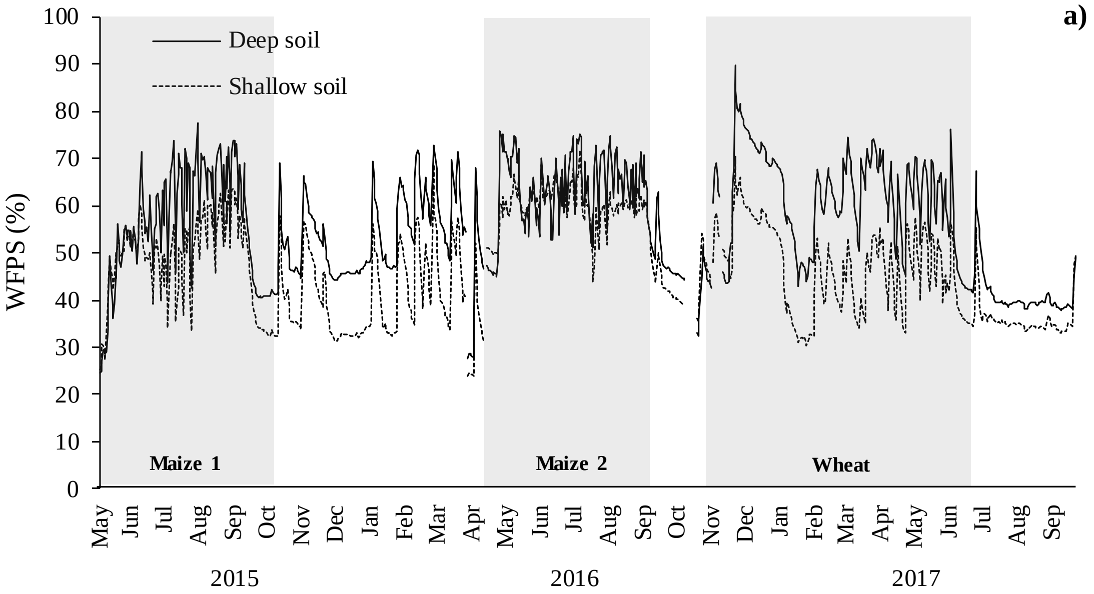


Figure 1. Temporal changes of average soil mineral nitrogen (mg N kg^{-1} soil) (n=3) from 0 to 10 cm depth for each fertiliser treatment (Urea, DMPP, NBPT, and MCDHS) and soil type (Deep and Shallow). The three shadow areas correspond to the period between seeding and harvest of each crop (2015: maize 1, 2016: maize 2, 2017: wheat) within the rotation. Arrows indicate fertiliser applications.



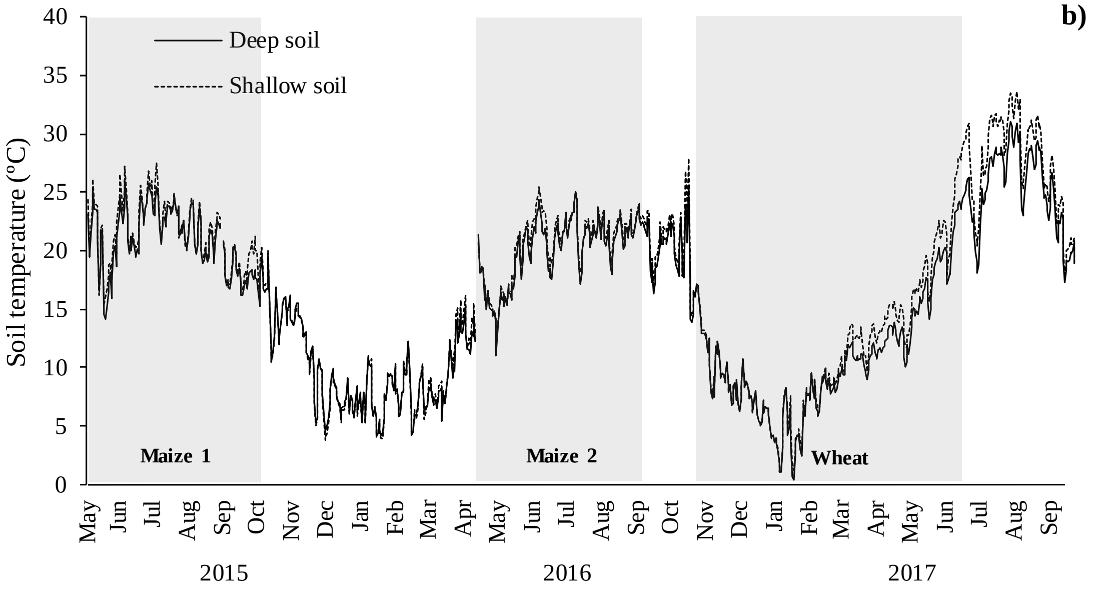


Figure 2. Temporal changes of daily average water-filled pore space (WFPS) (a) and soil temperature (b) at a 5-cm depth for each soil type (Deep and Shallow). The shadow area shows the period between seeding and harvest of each crop.

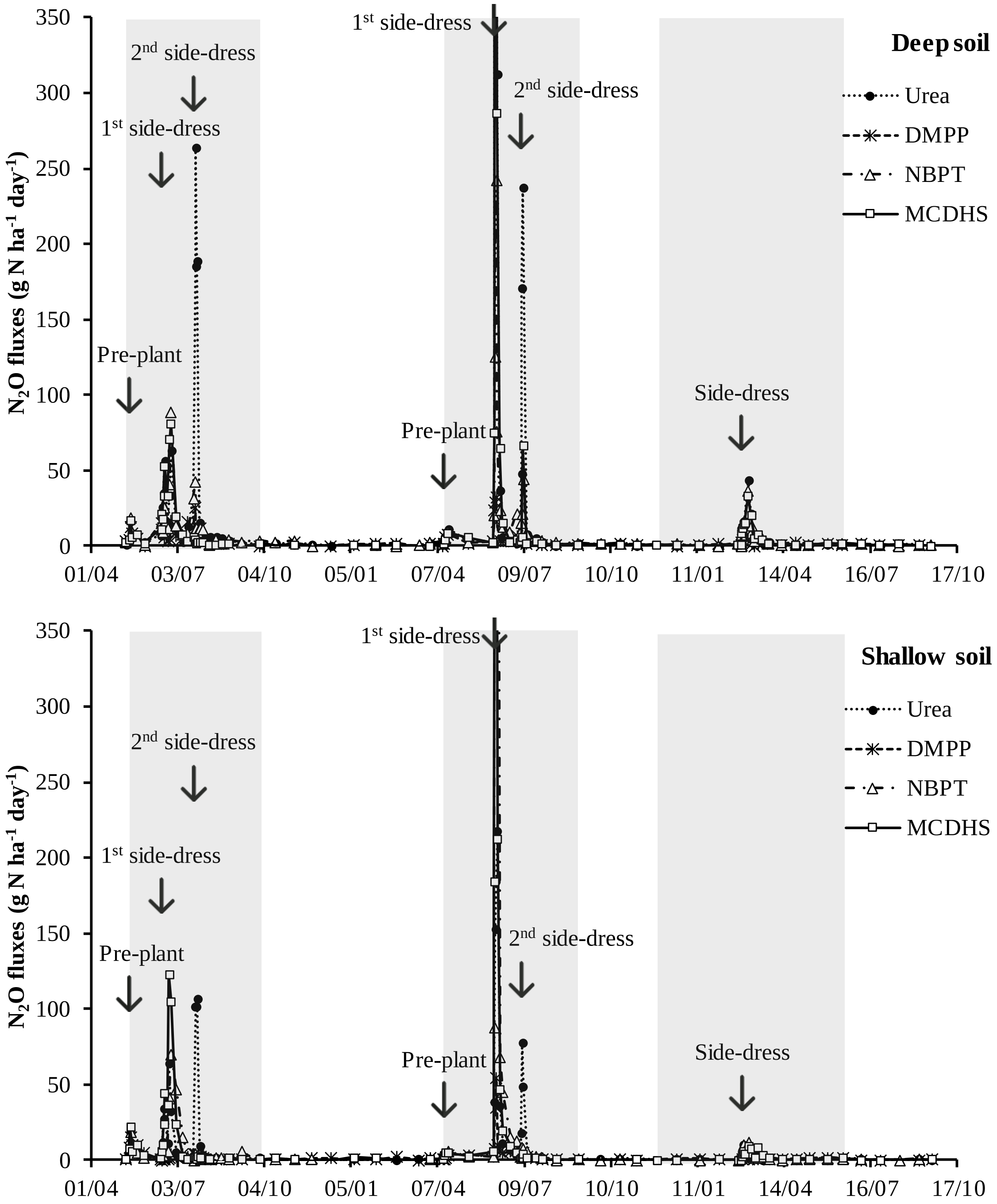


Figure 3. Temporal changes of average N_2O fluxes (g N ha^{-1} day^{-1}) (n=3) for each fertiliser (Urea, DMPP, NBPT, and MCDHS) treatment during the three growing seasons (maize 1, maize 2, and wheat) and for the two soil types (Deep and Shallow). The shadow area shows the period between seeding and harvest of each crop. Arrows show fertiliser applications.

The performance of N_2O emissions peaks did not allow breaking of the Y-axis. Urea and MCDHS reached 656 and 756 g N ha^{-1} day^{-1}, respectively, in Deep soil. NBPT and MCDHS reached 1014 and 596 g N ha^{-1} day^{-1}, respectively, in Shallow soil.

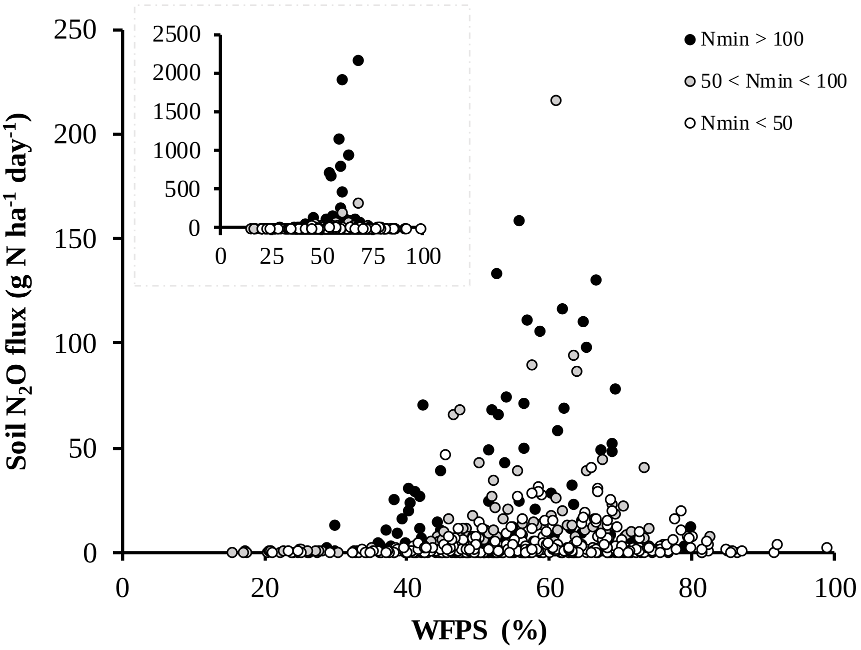


Figure 4. Effect of water-filled pore space (WFPS, %) and soil mineral N (Nmin, kg N ha^{-1}) in the topsoil (5-cm depth) on N_2O fluxes (g N ha^{-1} day^{-1}). The whole dataset (n=840) is also presented with a different Y-scale to show the maximum N_2O fluxes observed.

Supplementary material

Table S1. Average (n=3) of cumulative CH_4 emissions (g CH_4-C ha^{-1}) for the different seasons[a], fertiliser treatments (Urea, DMPP, NBPT, and MCDHS), and soil types (Deep and Shallow). Different letters within columns indicate significant differences among treatments (Tukey's test, $p<0.05$) for each soil type.

	Maize 1	Maize 2	Wheat	Maize 1+2	Whole rotation
	----------------------------**Deep soil**----------------------------				
Urea	-422*	-35	-481	-403	-1021*
DMPP	-544	-242*	-179	-831*	-1101
NBPT	-349*	-246	765	-594*	191
MCDHS	-708*	41	-502	-676*	-1074*
	--------------------------**Shallow soil**--------------------------				
Urea	21	-181*	-462	-139	-622
DMPP	-388*	139	-523	-265	-763
NBPT	-130	159	-236	36	-151
MCDHS	-8	-243*	293	-268	84
Treatment	0.542	0.768	0.482	0.754	0.329
Soil type	0.322	0.401	0.774	0.296	0.712
Treat.*S.type	0.823	0.083	0.232	0.835	0.447

[a]- Maize 1, maize 2 and wheat include the period from sowing to the following sowing. Maize 1+2 includes from maize 1's sowing to wheat's sowing. Whole rotation includes from maize 1's sowing to end September.

*- Asterisk indicates cumulative CH_4 emissions different from zero.

Table S2. Estimated indirect N_2O emissions (kg N_2O-N ha^{-1}) associated with N leaching for the different treatments (Urea, DMPP, NBPT, and MCDHS), seasons[a], and soil type (Deep and Shallow). Different letters within columns indicate significant differences among treatments ($p<0.05$).

	Maize 1	**Maize 2**	**Wheat**	**Maize 1+2**	**Whole rotation**
			----------------------------Deep soil----------------------------		
Urea	0.07	0.09	0.04	0.17	0.20
DMPP	0.08	0.08	0.04	0.16	0.20
NBPT	0.17	0.09	0.02	0.25	0.27
MCDHS	0.13	0.13	0.04	0.25	0.29
			--------------------------Shallow soil--------------------------		
Urea	0.22	0.21	0.05	0.43	0.48
DMPP	0.16	0.18	0.05	0.34	0.39
NBPT	0.28	0.22	0.05	0.50	0.55
MCDHS	0.16	0.15	0.04	0.31	0.35
Treatment	0.439	0.933	0.739	0.594	0.668
Soil type	0.070	0.002	0.021	0.013	0.010
Treat.*S.type	0.851	0.436	0.387	0.681	0.636

Maize 1, maize 2 and wheat include the period from sowing to the following sowing. Maize 1+2 includes from maize 1's sowing to wheat's sowing. Whole rotation includes from maize 1's sowing to end September.

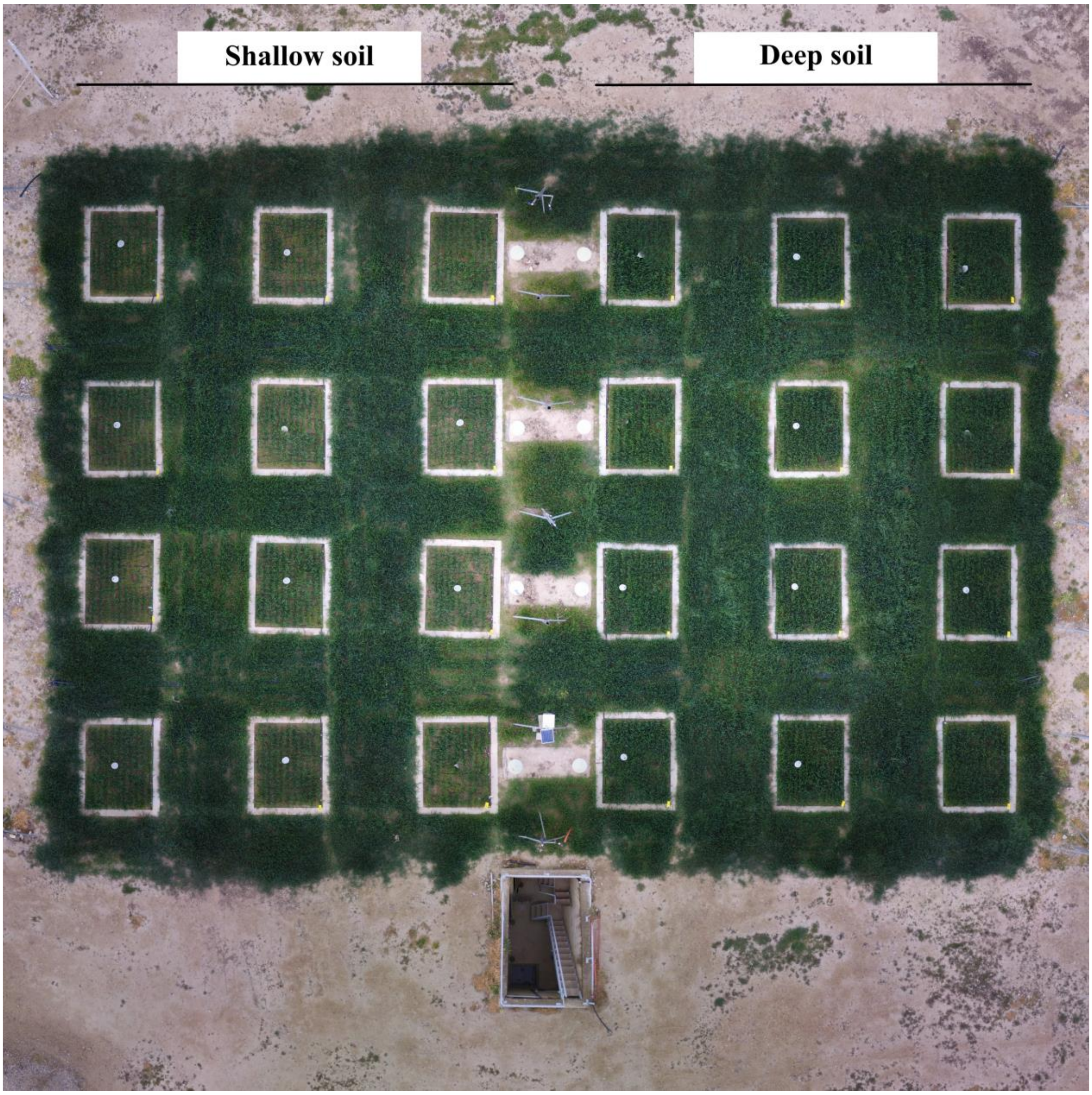


Figure S1. Aerial photography of the lysimeter station. Twelve lysimeters (right side) are those with Deep soil, and twelve lysimeters (left) are those with Shallow soil.

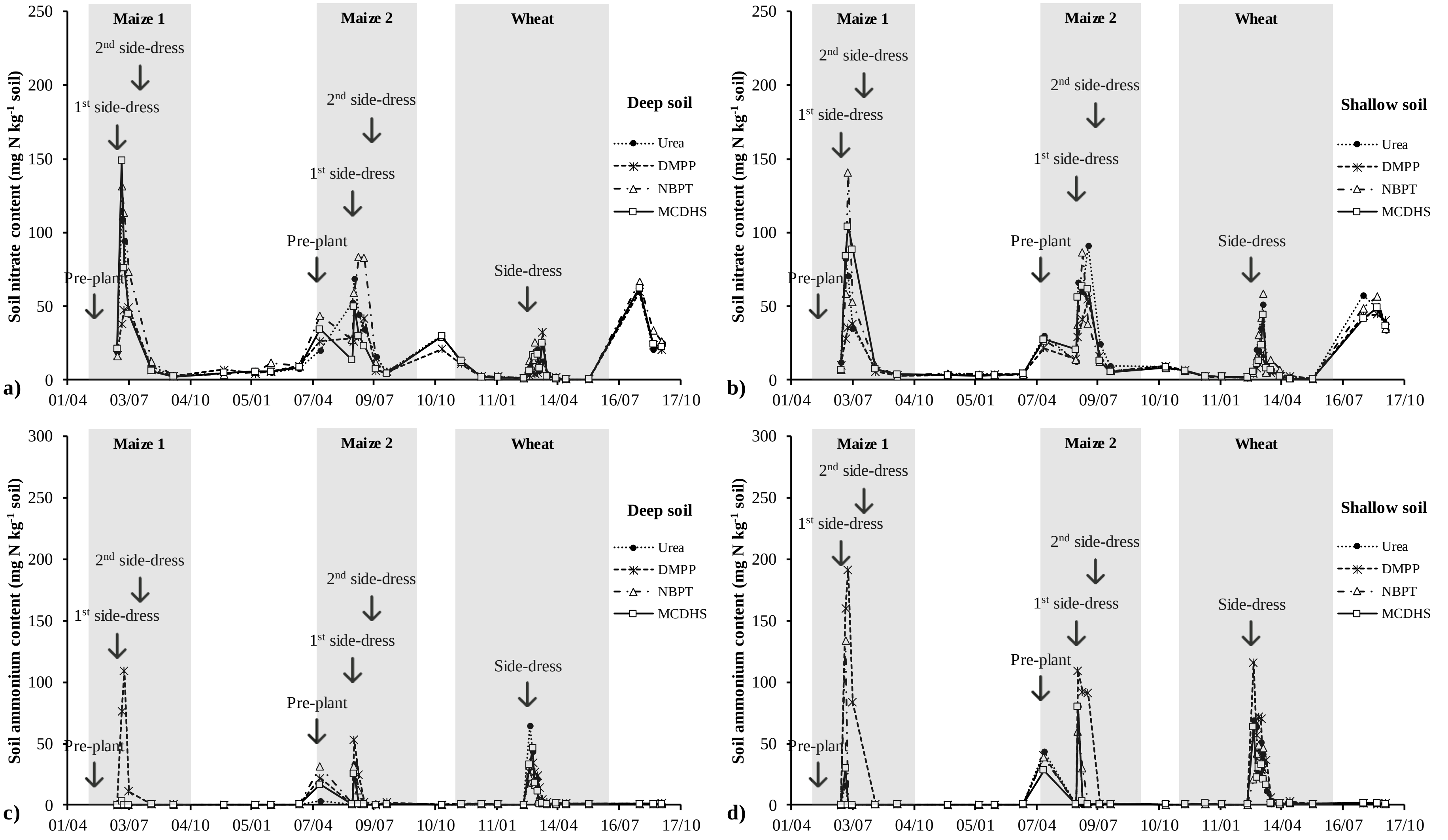


Figure S2. Temporal changes of the average (n=3) of soil nitrate (Fig. S2a, S2b) and soil ammonium (Fig. S2c S2d) content (mg N kg^{-1} soil) from 0 to 10 cm depth for each fertiliser treatment (Urea, DMPP, NBPT, and MCDHS) and soil type (Deep and Shallow). The three shadow areas correspond to the period between seeding and harvest of each crop (2015: maize 1, 2016: maize 2, 2017: wheat) within the rotation. Arrows indicate fertiliser applications.

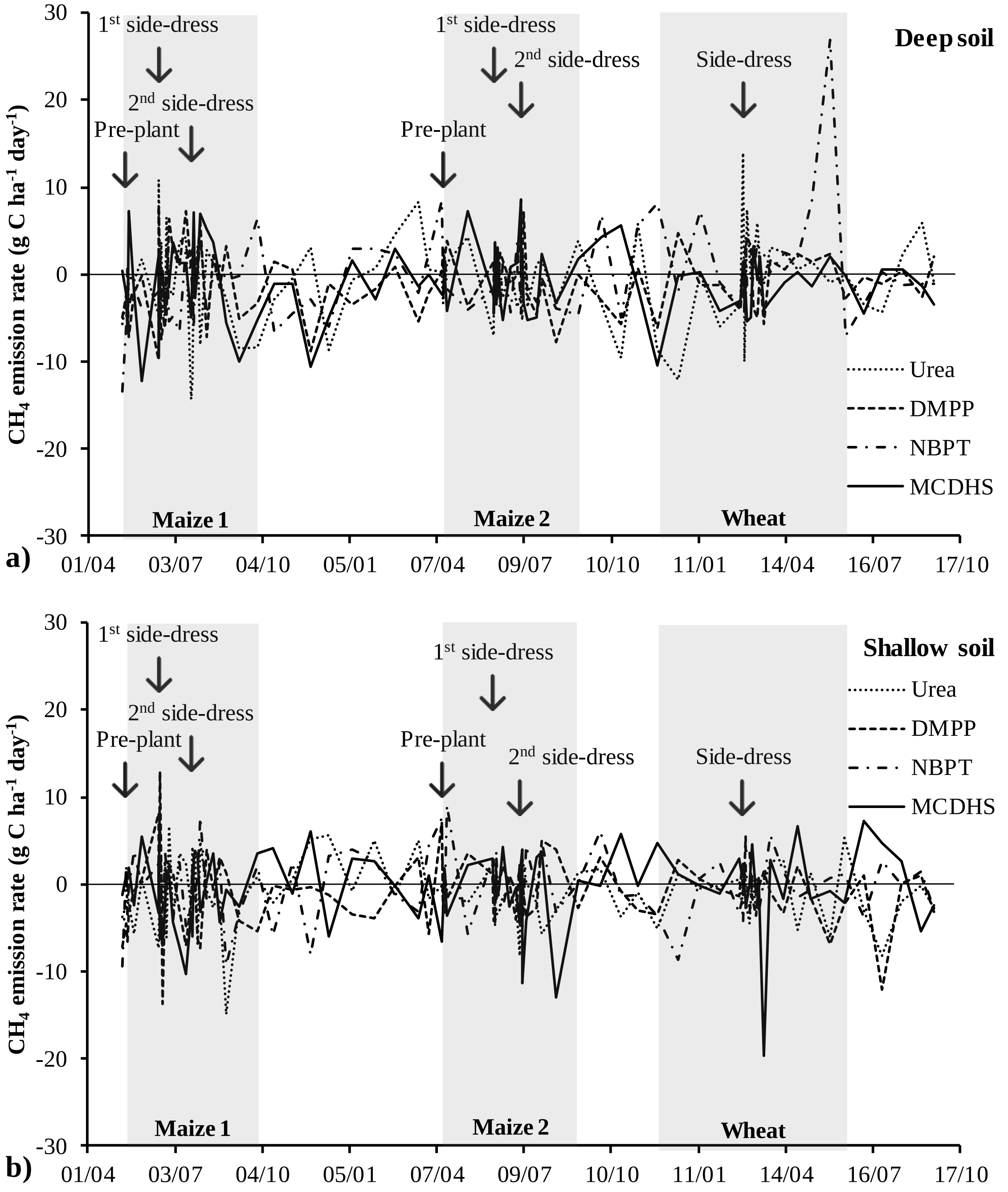


Figure S3. Temporal changes of soil CH_4 flux (g C ha^{-1} day^{-1}) for each fertiliser treatment along the three growing seasons (maize 1, maize 2, wheat) and for the two soil types (Deep and Shallow). The shadow area shows the period between seeding and harvest of each crop. Arrows show fertiliser applications.