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Comparison of grain yields and N_2O emissions on Oxisol and Vertisol soils in response to fertiliser N applied as urea or urea coated with the nitrification inhibitor 3,4-dimethylpyrazole phosphate

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Abstract

The potential for elevated N_2O losses is high in subtropical cereal cropping systems in northeast Australia, where the fertiliser N input is supplied in one single application at or prior to planting due to the unpredictability of in-season rainfall patterns. The use of urea coated with the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) has been reported by several studies to substantially decrease N_2O emissions and increase crop yields in humid, high-intensity rainfall environments. However, it is still uncertain whether this product can be used with the same effectiveness in Vertisols and Oxisols, two of the main soil types in the cropping region of northeast Australia. In this study the grain yield response of sorghum (*Sorghum bicolor L. Moench*) to rates of fertiliser N applied as urea or urea coated with DMPP were compared in crops grown on a Vertisol and an Oxisol in southern Queensland. Seasonal N_2O emissions were monitored on selected treatments for the duration of the cropping season and the early stages of a subsequent fallow period using a fully automated high frequency greenhouse gas measuring system. On each soil the tested treatments included an unfertilised control (0N kg N ha^{-1}) and two fertilised treatments chosen on the basis of delivering at least 90% of seasonal potential grain yield (160 kg N ha^{-1} and 120 kg N ha^{-1} on the Vertisol and Oxisol, respectively) or at a common (suboptimal) rate at each site (80 kg N ha^{-1}). During this study DMPP had a similar impact at both sites, clearly inhibiting nitrification for up to 8 weeks after fertiliser application, while differences in seasonal moisture conditions and irrigation frequency had much smaller impacts on soil mineral N dynamics. Despite the relatively dry seasonal conditions experienced during most of the monitoring period, DMPP was effective in abating N_2O emissions on both soils and on average reduced seasonal N_2O emissions by 60% compared to conventional urea at fertiliser N rates equivalent to those producing 90% of site maximum grain yield.. The significant abatement of N_2O emissions observed with DMPP however did not translate into significant yield gains or improvements in agronomic efficiencies of fertiliser N use. These results may be due to the relatively dry growing season conditions prior to the bulk of crop N acquisition, which limited the exposure of fertiliser N to large losses due to leaching and denitrification.

DMPP might be expected to increase the agronomic efficiency of urea in summer seasons with high rainfall rates, such as during *la Niña* phases of the El Niño Southern Oscillation (ENSO) cycle.

Keywords: nitrogen response, grain yield, Vertosol, Oxisol, automated greenhouse gas measuring system

Introduction

Vertisols and Oxisols are amongst the main soil types in subtropical regions (Buol and Eswaran 1999; Syers *et al.* 2001) and contribute significant amounts of global cereal production (Sant'Anna 1993; Webb *et al.* 1997; Fageria and Baligar 2008). Although characterised by high clay contents (Eswaran and Cook 1988; von Uexküll and Mutert 1995), decreases in soil organic matter and mineralisable nitrogen (N) stocks have often been observed in both soil types due to intensive cropping (Dalal *et al.* 1997). This reduction in native soil fertility has led farmers to increase synthetic fertiliser rates to achieve maximum yield potential. For example, fertiliser N rates in Australian cereal cropping systems on Vertisols and Oxisols have been observed to increase from negligible to over 100 kg N ha^{-1} over the last few decades (Bell *et al.* 1995; Lester *et al.* 2009).

The application of high fertiliser N rates can, however, lead to low plant N use efficiency and increased risk of high N losses if the timing of those applications results in less synchrony between plant N demand and fertiliser supply (Crews and Peoples 2005). The potential for N losses is further exacerbated in subtropical cereal cropping systems in northeast Australia, where fertiliser N is typically supplied in one single application at or prior to planting, due to the unpredictability of in-season rainfall patterns (Bell *et al.* 2015).

N losses can pose severe threats to the environment, amongst which the emission of significant amounts of nitrous oxide (N_2O) is arguably one of the most important. The environmental relevance of N_2O emissions resides both in terms of its elevated global warming potential (298 times that of carbon dioxide over a 100 year time horizon (Myhre *et al.* 2013)) and its contribution to the depletion of the ozone layer in the stratosphere (Ravishankara *et al.* 2009). Importantly, numerous studies on agricultural soils have proven a clear correlation between N_2O emissions and N fertilisation. Increasing N_2O fluxes have been shown to correspond to increasing N fertilisation rates, with emissions typically increasing exponentially where N rates exceed crop N requirements (McSwiney and Robertson 2005; Hoben *et al.* 2011; Kim *et al.* 2013; Shcherbak *et al.* 2014; Scheer *et al.* 2016).

One of the most promising methods to reduce N_2O emissions and decrease overall N losses is the addition of nitrification inhibitors to NH_4^+-based fertilisers (Linzmeier *et al.* 2001b; Pasda *et al.* 2001; Kawakami *et al.* 2012). Nitrification inhibitors are antibiotics that slow the activity of the *Nitrosomonas sp.* bacteria, the genus responsible for the oxidation of NH_4^+ to NO_2^-. Maintaining fertiliser N in the NH_4^+ form reduces the chances of N being lost via leaching or denitrification when soil moisture conditions are elevated. Nitrification inhibitor-coated urea has been reported by several studies to substantially decrease N_2O emissions and increase crop yields in humid, high rainfall environments (Prasad and Power 1995; Linzmeier *et al.* 2001a; Pasda *et al.* 2001; Hatch *et al.* 2005), which are the environmental conditions that are prevalent during subtropical summers. Among nitrification inhibitors, 3,4-dimethylpyrazole phosphate (DMPP) has been reported by many authors as the most efficient in slowing nitrification and reducing N_2O losses (Weiske *et al.* 2001b; Liu *et al.* 2013; Lester *et al.* 2016 in press).

While DMPP was shown to efficiently reduce N_2O emissions on Oxisol soils in subtropical cropping systems in northeast Australia (De Antoni Migliorati *et al.* 2014), it is still uncertain whether DMPP can be used with the same effectiveness in Vertisols – the dominant cropping soils in the region. The overall aims of this study were therefore to determine whether: i) the different soil properties of Vertisols and Oxisols can affect the potential of DMPP to reduce N_2O losses from urea applications and ii) DMPP can increase grain yields through limiting fertiliser N losses or improving synchronisation between fertiliser N supply and plant demand.

In this study, grain yields and N_2O emissions from a cereal crop (sorghum) grown on a Vertisol and an Oxisol were monitored for the duration of the cropping season and for a portion of the subsequent fallow period using a fully automated high frequency greenhouse gas measuring system. The results of this study will help define fertilisation strategies that maximise the efficient use of fertiliser N while minimizing environmental impacts in subtropical summer cereal cropping systems.

Materials and Methods

STUDY SITES

The study was conducted at two sites with contrasting soil types. One field trial was located at the Kingsthorpe research station, situated in the Darling Downs region about 140 km west of Brisbane (27°31’S, 151°47’E, 431 m above mean sea level). The soil at the site is classified as a self-mulching, torrert Vertisol (USDA Soil Taxonomy, USDA (1998)) or as a haplic, black Vertisol (Australian Soil Classification (Isbell 2002)). It has a heavy clay texture (67% clay) in the 1.5 m root zone profile, with a distinct change in soil colour from brownish black (10YR22) in the top 90 cm to dark brown (7.5YR33) deeper in the profile. The soil was formed in an alluvial fan of basalt rock origin with a surface slope of about 0.5%, is slowly permeable and has a plant available water holding capacity (PAWC) of 210-230 mm for wheat. Physical and chemical characteristics of the soil profile are shown in Table 1.

The other field trial was located at the J. Bjelke Petersen Research Station at Taabinga (26°34’54,3’’ S, 151°49’43.3’’ E, altitude 441 m above mean sea level), near Kingaroy, in the southern inland Burnett region of southeast Queensland, Australia. The soil is classified as Tropeptic Eutrustox Oxisol (USDA Soil Taxonomy, USDA (1998)) or as a Brown Ferrosol (Australian Soil Classification, (Isbell 2002)), is moderately permeable, with a high clay content (50-65% clay) in 1.2 m of effective rooting zone and a PAWC of 100-110 mm in maize-peanut rotations. Physical and chemical soil properties are listed in Table 1.

At both sites the climate is classified as subtropical, with warm, humid summers and mild winters. Monthly mean minimum and maximum temperatures at the Vertisol site (Kingsthorpe) are 16.3 °C and 27.2 °C in summer, and 5.9 °C and 17.0 °C in winter, respectively. Mean annual precipitation is 630 mm (1990-2010), where most of the rainfall occurs between October and March, during the summer crop growing season. At the Oxisol site (Kingaroy), monthly mean minimum and maximum temperatures are 16.5 °C and 29.6 °C in summer, and 4.0°C and 18.9°C in winter, respectively. Mean annual precipitation is 776.2 mm, with most also occurring in the spring-summer period, and varies from a minimum of 28.6 mm in August to a maximum of 114.1 mm in January (Australian Bureau of Meteorology).

EXPERIMENTAL DESIGN

Experiments were sown to sorghum (*Sorghum bicolor* L.) during the 2013/14 summer season, with cv. Pacific MR43 planted 10 December 2013 and machine-harvested 5 May 2014 at the Vertisol site, while at the Oxisol site cv. Pioneer G22 was planted on 27 November 2013 and machine-harvested on 10 April 2014. The Vertisol site had been cropped to sorghum in 2012/13 with green manure winter cereals (barley and wheat) grown during the 2012 and 2013 winter seasons and removed as a forage crop to maintain low soil mineral N status. The Oxisol site had grown sorghum in 2011/12 season, with a winter fallow, 2012/13 summer peanut (*Arachis hypogaea* L.) and 2013 winter forage barley crops, respectively.

Briefly, treatments were organised in a randomized complete block design with four replicates at the Vertisol site and in a split plot design (fertilizer products as main plots and N rates as sub plots) with three replicates at the Oxisol site. The Vertisol site was direct sown into forage residue sprayed out after forage removal, while the Oxisol site was prepared using conventional tillage (chisel plough (20 cm) and two passes with offset discs (15 cm). Crop row spacing was 1 m and 0.9 m at the Vertisol and Oxisol sites, respectively, with six plant rows in each treatment. Plots at the Vertisol and Oxisol sites measured 6 m x 12 m and 5.4 m x 13 m, respectively, with buffer areas of 1-2 m between plots. Further information on the experimental details is outlined in full in Lester *et al.* (2016 in press)

Both sites utilized supplementary irrigation using overhead sprinkler application. At the Vertisol site this consisted of a 30 mm irrigation immediately after sowing, to ensure uniform crop establishment, followed by two 25mm irrigations during the early stages of crop establishment. At the Oxisol site however, lack of profile moisture and the low PAWC of this soil type necessitated more frequent irrigations, with a total of 168 mm applied in five irrigation events from early January to mid-February 2014 (Table 2).

At each site, treatments consisted of a range of N rates supplied as either urea or DMPP urea, with rates chosen to cover the full yield-N response surface at each location. In addition to an unfertilized control (0N added), N rates supplied as urea or DMPP urea ranged from 40-160 kg N ha^{-1} on the Vertisol and 40-240 kg N ha^{-1} on the Oxisol. Fertilizer was banded between 10 and 15cm away from the crop row at sowing at both sites.

Crop growth and N accumulation was assessed by a total crop biomass sampling at physiological maturity (two crop rows each 1m in length and at two locations in each plot) on 8 April 2014 at the Vertisol site and 10 March 2014 in the Oxisol site, with samples oven dried (60°C for 72h) before mulching and grinding and subsequent analysis for N concentration. Grain yields were determined by a combine harvester after a 1m buffer area was removed from either end of the plot (2 crop rows by the length of the experimental plot), with grain moisture determined and used to adjust yields and grain N concentration to a dry weight basis.

Emissions were monitored from four treatments during the monitoring period, with treatments chosen to both allow a direct comparison between soil types at a common N rate, and to also allow a comparison between urea and DMPP urea at a rate estimated to deliver maximum crop yields on each soil type. These were:

- Control (CNT)- no N fertiliser applied: to quantify background N_2O emissions and baseline yields in each soil type;
- Urea (UREA) and DMPP urea (DMPP): the different fertilizer products were compared at N rates estimated to produce maximum grain yields at each site. These were 160 kg N ha^{-1} on the Vertisol and 120 kg N ha^{-1} on the Oxisol. These rates were *ca.* 30% higher than standard farmer practice (approximately 120 kg N ha^{-1} and 90 kg N ha^{-1} on the Vertisol and Oxisol, respectively), but considered appropriate due to the preceding very wet summer with large denitrification losses (see De Antoni Migliorati *et al*. 2015; Scheer *et al* this issue) and the use of winter forage crops to ensure low starting profile N.

- Urea (UREA-R): in both soils conventional urea was applied at a reduced rate (80 kg N ha^{-1}) that was more comparable to standard farming practice in each region. The N rate was reduced to assess crop response and N_2O emissions at sub-optimal N rates.

CONTINUOUS N_2O MEASUREMENTS

At both sites N_2O fluxes were measured over 198 days, from 11 December 2013 to 26 June 2014 on the Vertisol and from 6 December 2013 to 21 June 2013 on the Oxisol. N_2O measurements were taken from every plot of the target treatments in the field trials using two fully automated measuring systems similar to the one described in De Antoni Migliorati *et al.* (2015). Each system consisted of twelve chambers, linked to a computerized sampling unit and an *in situ* gas chromatograph (SRI GC 8610C) equipped with a ^{63}Ni electron capture detector (ECD) for N_2O concentration analysis.

Briefly, chambers were closed airtight with lids made of transparent acrylic panels operated by pneumatic actuators. Chambers measured 50 cm x 50 cm x 15 cm and were attached via a rubber seal to stainless steel frames inserted 10 cm into the ground. During a measurement cycle a set of four chambers closed for 60 min with each chamber sampled 4 times for 3 min. A certified gas standard of 500 ppb N_2O (BOC – Munich, Germany and Air Liquide – Dallas, TX, USA) was pumped into the gas chromatograph every 15 min. At the end of the cycle the chambers reopened and the next set of four chambers closed for sampling. Measurements in one complete cycle of twelve chambers lasted 3 hours, during which each chamber was sampling for 1 hour and then remained opened for 2 hours to restore ambient conditions. This method enabled the determination of up to 8 single fluxes per chamber per day. The detection limit of the system was approximately 1.0 μg N_2O-N m^{-2} hour^{-1} for N_2O; both systems were regularly checked for leaks throughout the season, making sample dilution due to leakage negligible.

All chambers were positioned next to the plant rows to account for N_2O emissions from a localized source (banded fertiliser) with background emissions from residual soil N derived from unfertilized plots. The measuring systems were deployed soon after fertilizer application and planting and retrieved 4-6 weeks after harvesting.

ANCILLARY MEASUREMENTS

Chamber air temperatures and topsoil temperatures (buried at 10 cm in the proximities of three chambers) were measured every 5 minutes using resistance temperature detectors (RTD, Temperature Controls Pty Ltd, Australia). An electronic weather station recording rainfall was installed at each research site.

At the beginning of the cropping seasons, soil samples (0-20 cm) were collected from every plot with a manual open-faced bucket auger (10 cm diameter) and analysed for texture (hydrometer method as described by (Kroetsch and Wang 2008)). Other soil analyses were conducted using standard methodology described in Rayment and Higginson (1992), including total carbon (C%) and total nitrogen (N%) by Dumas combustion pH (1:5 soil:water), Cation Exchange Capacity and NH_4-N and NO_3-N. The latter were determined on extracts collected from the soil samples after adding 100 mL of 1M KCl to 20g of soil and shaking the solution for 1 hour. The solution was then filtered and stored in a freezer until analysed colorimetrically for NH_4-N and NO_3-N using method 7c2 (Rayment and Higginson, 1992).

Soil sampling was conducted at intervals of 3-4 weeks at each site by collecting topsoil samples (0-20 cm) in each plot and analysing them for NH_4-N and NO_3-N. In each plot, soil samplings were systematically collected to represent the chamber area on which emissions monitoring was conducted in fertilised treatments, and in equivalent positions relative to the crop row in the Control treatment. This represented three replicate samples collected 5 cm, 15 cm and 20 cm from the plant row, with replicate samples thoroughly mixed and the sub-sample analysed.

FLUX CALCULATIONS AND STATISTICAL ANALYSIS

Hourly N_2O fluxes were calculated with the method described by (Nguyen *et al.* 2014), determining the slope of the linear increase or decrease of the four gas concentrations measured during the 60 minute period of chamber closure. The obtained data were corrected for internal air temperature, atmospheric pressure and ratio of chamber volume and soil area. Measurements were quality-checked using the

Pearson correlation and fluxes above the detection limit discarded if the regression coefficient (r^2) was < 0.80, while those below the detection limit were assumed to be zero.

To account for the spatial variability between two crop rows (0.9 m - 1 m) imposed by banding the fertiliser, mean daily fluxes for each fertilised treatment were calculated with the methodology established by Kusa *et al.* (2006) and Parkin and Kaspar (2006). Using this approach, hourly fluxes from the three replicate chambers of each fertilised treatment (covering 50 cm on the side of the crop row where the fertiliser was banded) were averaged. The obtained mean flux was then averaged with the mean of hourly fluxes measured in the control treatment (covering 50 cm on the side of the crop row without any fertiliser) for the Vertisol site. For the Oxisol site the weighted average consisted of 55% of the chamber over the fertilizer band and 45% of that with no applied fertilizer.

Cumulative N_2O fluxes [kg N_2O-N ha^{-1}] were determined by summing hourly fluxes to produce daily flux totals and then summing daily N_2O fluxes measured during the study period. Emission factors were corrected for background emissions (Kroeze *et al.* 1997) using the following:

$$EF\ \% = \frac{N_2O\ (Fert) - N_2O\ (Unfert)}{N\ fertiliser\ input} \cdot 100$$

where *EF %* is the emission factor reported as a percentage of *N fertiliser input* (kg N ha^{-1} $season^{-1}$) lost as N_2O-N, $N_2O\ (Fert)$ and $N_2O\ (Unfert)$ (kg N ha^{-1} $season^{-1}$) are the cumulative N_2O-N emissions measured in the fertilised and non-fertilised treatments with the same cropping history, respectively.

Agronomic efficiency (AE) was calculated as:

$$AE\ = \frac{Grain\ (Fert) - Grain\ (Unfert)}{N\ fertiliser\ input}$$

where *AE* is the agronomic efficiency (kg grain kg N $applied^{-1}$), *Grain Fert* and *Grain Unfert* (kg ha^{-1}) are the quantities of grain harvested in the fertilised and unfertilised treatment, respectively, and N fertiliser input is the amount of fertiliser N applied (kg N ha^{-1}).

Daily N_2O fluxes missing due to occasional brief (< 4 days) failures of the measuring system were estimated by linear interpolation. Statistical analyses were undertaken in the R environment (R Core Team 2015). Benjamini and Hochberg (BH) adjustment (Benjamini and Hochberg 1995) was performed to assess significant differences on total cumulative N_2O emissions within and across sites. Tukey post hoc test was performed to determine the influence of N fertilisation rate or soil type on grain yields and agronomic efficiency within and between sites. Post hoc tests were performed only when the analysis of variance (ANOVA) yielded P values <0.05. The shape of the grain yield-N fertilizer rate response surface was determined using linear (Vertisol) and mitserlich (Oxisol) regression functions in Genstat (VSN International 2014) and the fitted response functions were used to estimate the N fertilizer rate that was required to produce 90% of the site maximum yield.

Results

ENVIRONMENTAL AND SOIL CONDITIONS

Seasonal precipitation measured during this study tended to be lower than the 30-year historic summer averages (December to June) recorded at the Vertisol (493 mm) and Oxisol (464 mm) sites. At the Vertisol site rainfall over the study amounted to 241 mm (with an additional 80 mm of early season irrigation), however ~40% (90 mm) of the total rainfall occurred in a rainfall event that took place late in the cropping season (27 and 30 March 2014) (Figure 1). Rainfall at the Oxisol site was more evenly distributed (Figure 1) but amounted to only 212 mm, equal to less than 46% of the growing season historic average. Accounting for irrigation, in-season total water supply at the Oxisol site amounted to 371 mm and at the Vertisol site it was 321 mm (Table 2).

Mean soil temperature (0-10 cm) at the Vertisol site was 20.7 °C and ranged between 4.8 °C (June 2014) and 29.7 °C (January 2014), while at the Oxisol site soil temperature averaged 21.4 °C and varied from 10.8 °C (June 2014) to 30.3 °C (December 2013) (Figure 1).

Mineral N dynamics in the fertiliser band of the high N rate treatments varied substantially between fertilizer products and, to a lesser extent, sites. At the Vertisol site soil NH_4^+ concentrations in the UREA treatment followed a relatively steady decline throughout the season, decreasing from an initial value of 100 mg N kg^{-1} on 23 December 2013 to a low of 15-25 mg N kg^{-1} during March 2014, although there was a slight increase in the sample taken on 10 April 2014 (near harvest) to 40 mg N kg^{-1}. Soil NO_3^- concentration in the top 20 cm increased until the first half of February (105-110 mg N kg^{-1}) and then rapidly declined to a minimum of <10 mg N kg^{-1} in March after 90mm mm of rain fell over the trial in late March 2014. Soil NH_4^+ and NO_3^- contents in the UREA-R treatment showed the same temporal pattern of those in the UREA treatment, although declined to low concentrations by late February 2014.

Different patterns were observed in the DMPP treatment. While NH_4^+ concentrations declined steadily to reach a minimum in the sampling in mid-March 2014, they remained much higher than in the UREA treatment (

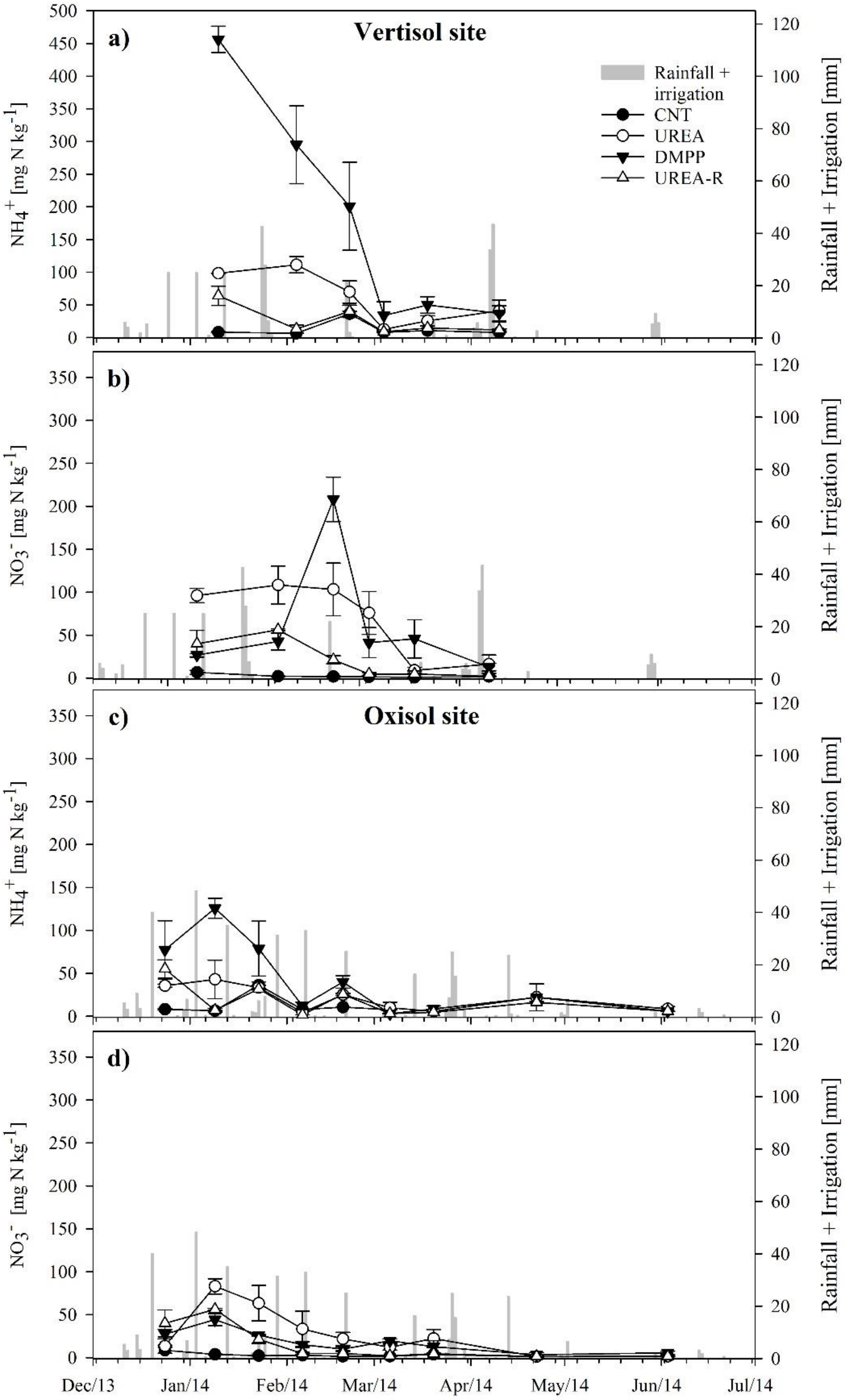

Figure 2). Conversely, NO_3^- concentrations were constrained to between 25% and 50% of those recorded in the UREA treatment until the inhibitor effect degraded in early February 2014. This then resulted in a sharp increase in NO_3^- concentrations (reaching a maximum of 208 mg N kg^{-1} on 21 February 2014, 10 weeks after planting) followed by a rapid decline to values similar to that in the UREA treatment for the rest of the season.

At the Oxisol site, a similar pattern of mineral N dynamics in the UREA and DMPP treatments was observed during the period of nitrification inhibition, which was evident until early February 2014. Soil NH_4^+ levels peaked 6 weeks after planting (9 January 2014) in both the UREA (43 mg N kg^{-1}) and DMPP (125 mg N kg^{-1}) treatments, when the UREA-R treatment showed soil NH_4^+ values similar to CNT treatment. Soil NO_3^- concentrations followed a similar pattern, peaking 6 weeks after planting (83 mg N kg^{-1} in UREA, 56 mg N kg^{-1} in UREA-R and 44 mg N kg^{-1} in DMPP) before

304 gradually declining (

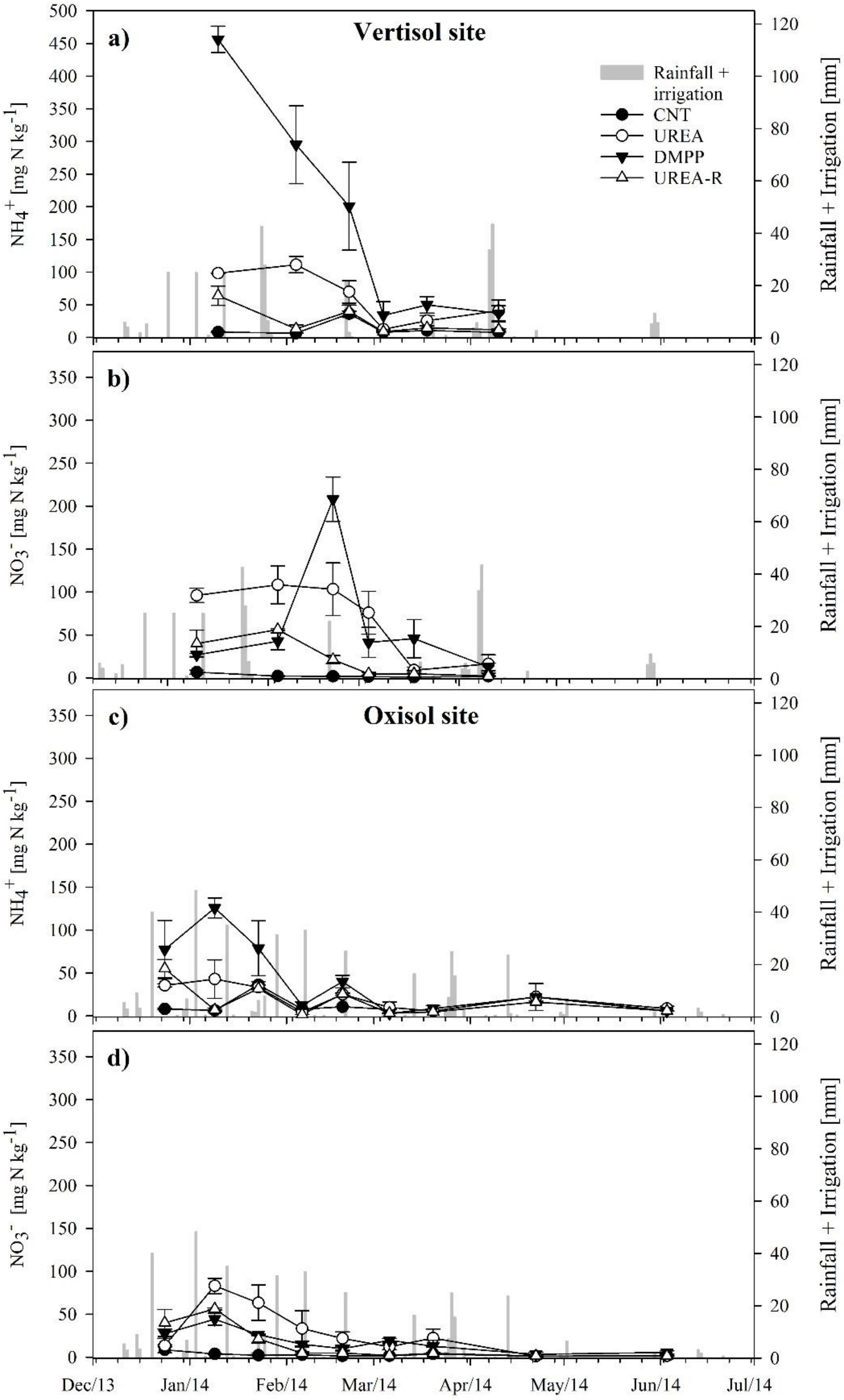

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Figure 2). Unlike the Vertisol site, there was no sharp increase in NO_3^- concentrations once the inhibitory effect in the DMPP treatment was eroded, possibly due to more extensive crop uptake and/or leaching into deeper soil layers in response to the regular irrigation events.

Soil mineral N levels in the CNT treatments did not vary substantially at either site, although there was evidence of a flush of N mineralization at each site in response to a rainfall event in mid-February on the Vertisol and a combination of rainfall and an irrigation event in mid-January on the Oxisol (

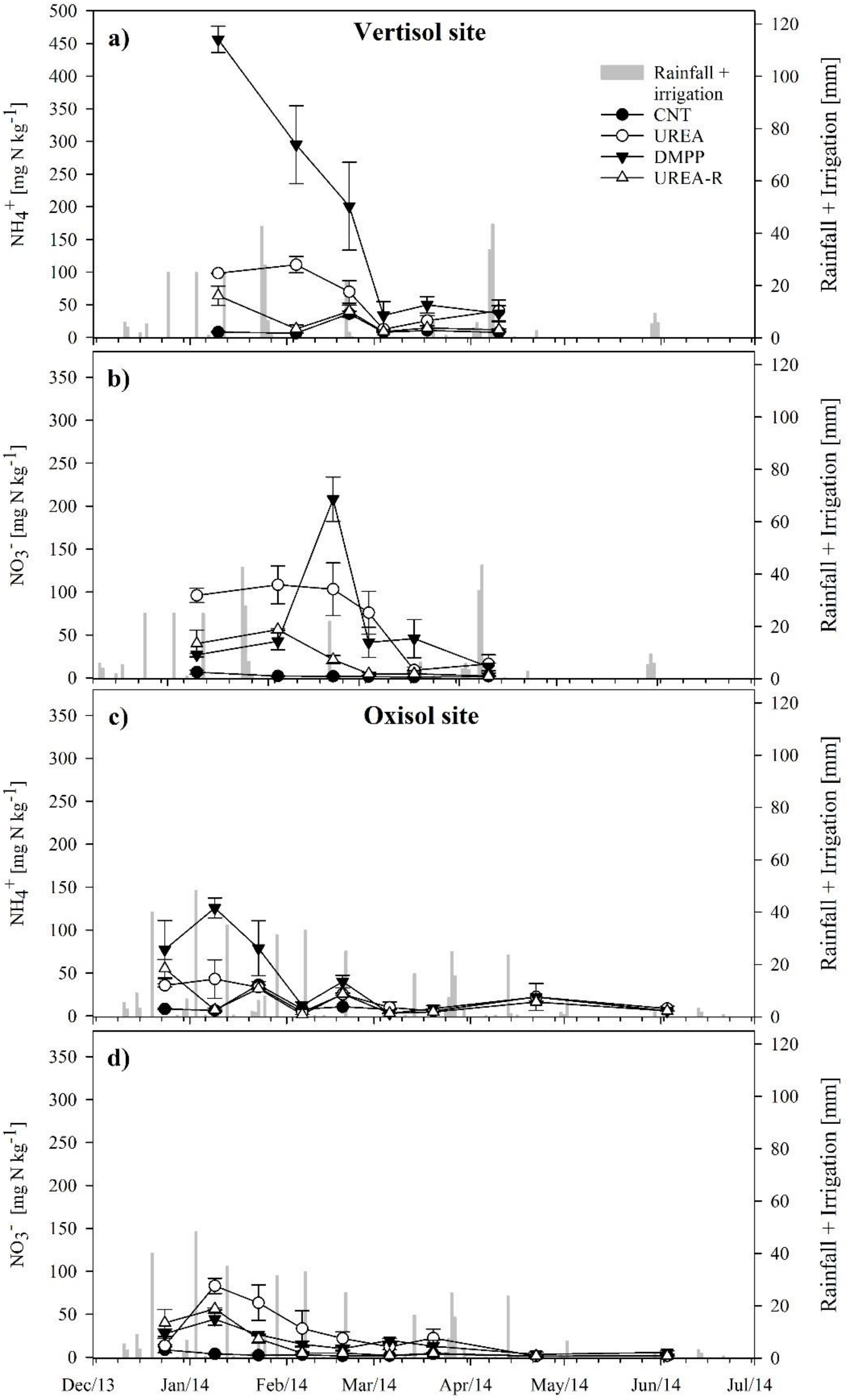


Figure 2).

N_2O EMISSIONS AND PLANT RESPONSE TO FERTILISATION TREATMENTS

At both sites there were strong responses to applied N fertilizer (Fig. 3), with grain yield in the unfertilized treatments ranging from 20% (Oxisol) to 40% (Vertisol) of the yields achieved with the highest N rates at each site. The shape of the grain yield-N response relationship was clearly curvilinear on the Oxisol, with a calculated maximum yield (Y_{max}) in response to applied N of 6900 and 6650 kg ha^{-1} for the DMPP and UREA treatments, respectively. The response functions fitted to yield-applied N relationship showed the fertilizer N rate needed to achieve 90% of the maximum grain yield ($Y_{90\%}$) would have been 100 (DMPP) to 125 (UREA) kg N ha^{-1} - very similar to the rates chosen to compare the emissions from these two fertilisers (120 kg N ha^{-1}).

Unfortunately at the Vertisol site the response to applied N was linear across the treatment range (Fig 3), and so a derivation of Y_{max} or the fertilizer N rate required to achieve $Y_{90\%}$ was not able to be undertaken. However data suggest that greater yields would have been achieved with higher fertiliser N rates, and so the 160 kg N ha^{-1} rate chosen to compare emissions from UREA and DMPP would also seem to be appropriate for this particular site and season.

On both soil types grain yields in the DMPP treatments tended to be higher than in UREA, although differences were never statistically significant ($p < 0.05$) (Table 3). Similar results were obtained analysing the agronomic efficiency of the two fertilisation treatments. Both grain yields and agronomic efficiencies tended to be higher at the Oxisol site where UREA-R treatment showed the highest agronomic efficiency value across sites (Table 3).

As with soil mineral N, N_2O emissions differed substantially across treatments while some commonalities could be observed between sites. In both soil types, seasonal N_2O losses from the UREA treatments were significantly higher than in the UREA-R, CNT and DMPP treatments (Table 3). Compared to UREA, DMPP reduced seasonal N_2O emissions by 66.4% in the Vertisol and 61% in the Oxisol. At the Vertisol site N_2O emissions from DMPP did not differ significantly from those in the UREA-R and CNT. Emissions factors for UREA were 0.7% and 0.6% for Vertisol and Oxisol sites, respectively, while much lower emissions factors were observed for DMPP on the Vertisol (0.1%) and

Oxisol (0.2%). Across treatments, seasonal N_2O emissions on the Vertisol tended to be higher than in the Oxisol (Table 3).

The majority of N_2O emissions from the UREA treatments took place within three months from fertiliser application, accounting for 63% and 95% of seasonal N_2O losses at the Vertisol and Oxisol sites, respectively. In all treatments on the Vertisol over 30% of N_2O-N losses were due to the emission pulses that took place in late March 2014 in response to a major rain event that delivered 90mm of rain from 27 - 30 March (**Error! Reference source not found.**). On the Oxisol, N_2O emissions from the DMPP treatments were concentrated in the first three months of the season, while in the Vertisol the majority of N_2O from the DMPP plots was lost through the late-March emission pulse (**Error! Reference source not found.**). On both soils N_2O emission pulses from the DMPP treatments lasted for much shorter periods (< 6 days) compared to the UREA treatments

Discussion

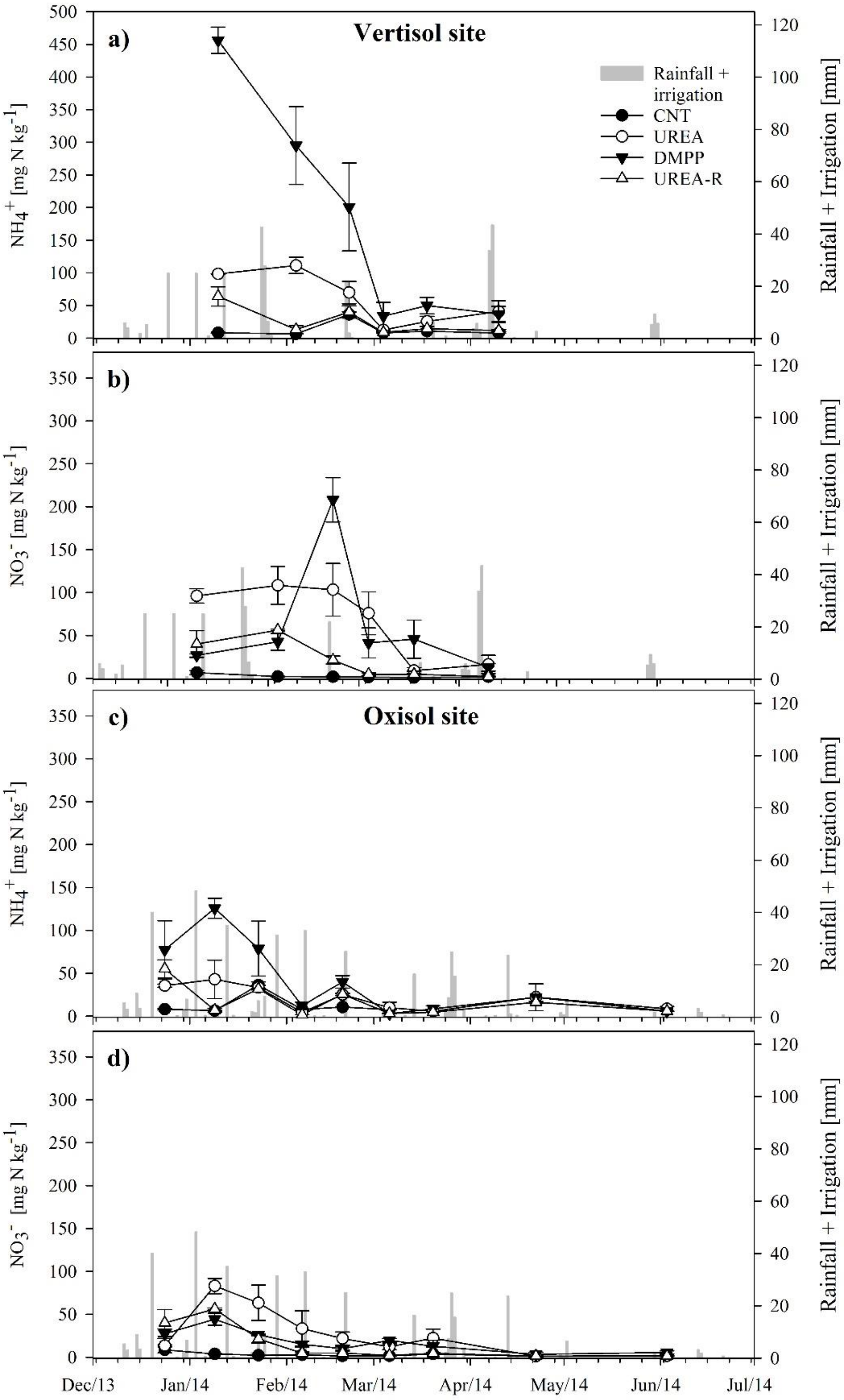
EFFECTS OF WEATHER EVENTS ON SEASONAL N DYNAMICS

The results of this research highlight how the frequency and intensity of rainfall and irrigation events, linked with intrinsic soil characteristics such as drainable porosity and hydraulic conductivity, can exert a substantial influence on seasonal N dynamics and N_2O emissions in subtropical cereal cropping systems.

Changes in soil mineral N concentrations, N_2O emissions and grain yields were largely influenced by the substantially different rainfall patterns observed at the two sites. Accounting for irrigation, the Oxisol site received a total of 240 mm uniformly distributed over the first three months of the cropping season. While the Vertisol site received only slightly less (125 mm of rainfall and 80 mm of irrigation) over the same three month duration, all the irrigation was applied in the first month to ensure good crop establishment and 66% (78 mm) of the rain that fell occurred in a single rainfall event over two days in late January (Figure 1). Subsequently, there was only a single fall of 23 mm in the latter half of February to break the drying trend that persisted until the rain event in late March.

The uniform distribution of the rainfall/irrigation events, at the Oxisol site guaranteed a constant water supply to soil microorganisms, which is likely to have promoted relatively rapid nitrification rates (Bouwman 1998; Kiese and Butterbach-Bahl 2002). The rapid decline of NH_4^+ concentrations and the concurrent increase of NO_3^- levels observed in both the UREA and DMPP, and to a lesser

372 extent UREA-R, treatments support this hypothesis (



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374 Figure 2).

As a result, the majority of NH_4^+ derived from the urea hydrolysis was transformed into NO_3^- within approximately eight weeks from fertilisation in the Oxisol (

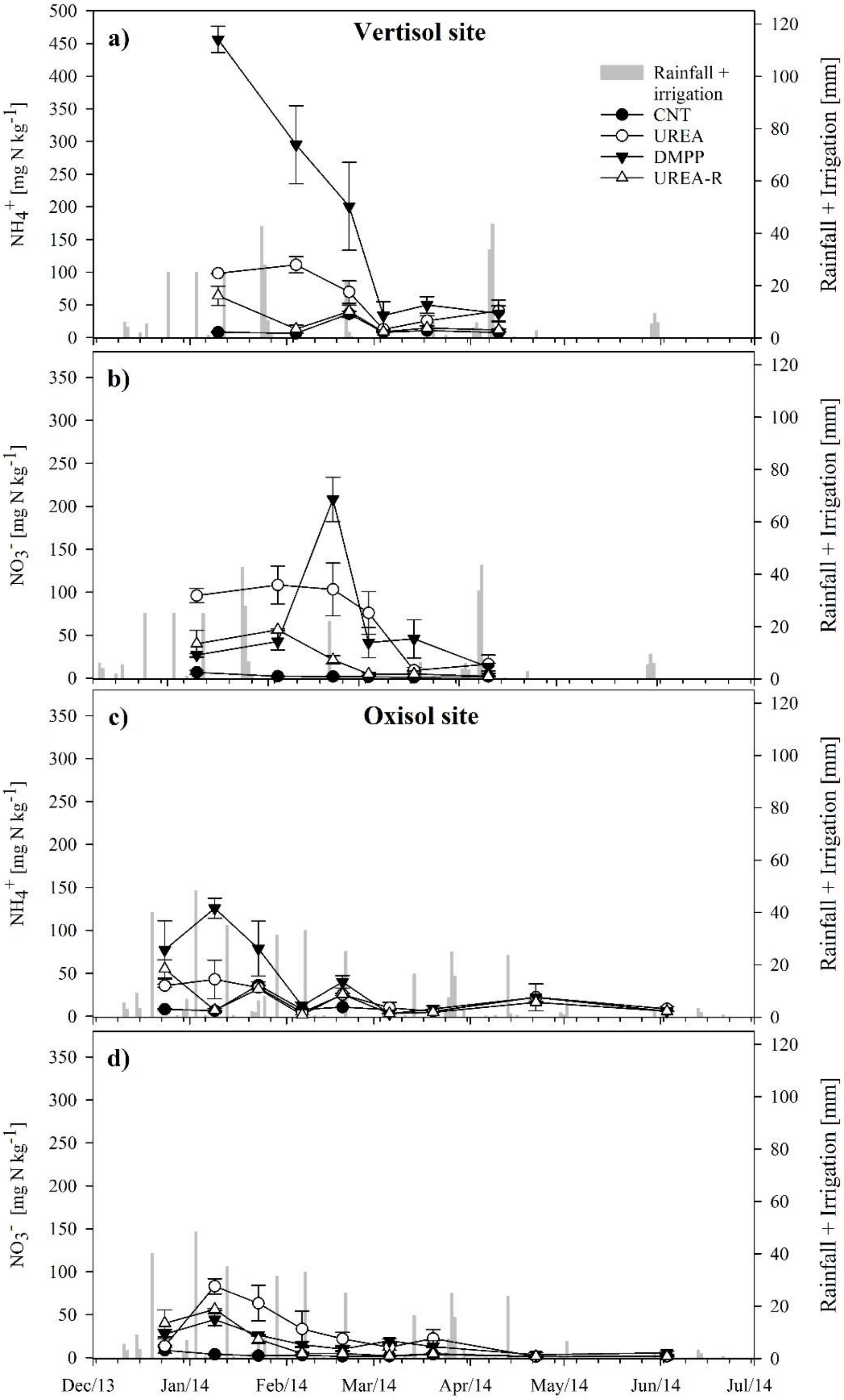

Figure 2), ensuring substantial amounts of NO_3^- available in the soil during the period of maximum N uptake of sorghum (Blum 2004). The free-draining nature of this soil (Bell *et al.* 2005) was illustrated by the rapid drainage after rainfall and irrigation events (Fig. 1), and combined with the frequent irrigation events, was likely to have contributed to some leaching of that NO_3-N into soil layers below the top 20cm monitored during the growing season. This contributed to absence of sharp peaks in NO_3-N accumulation at this site (Fig2a).

N_2O emissions pulses were triggered by rainfall or irrigation events in all N fertilised treatments and were concentrated during the first three months after fertilisation (**Error! Reference source not found.**4). Conditions during this period were characterised by high soil temperatures, moist soils and

387 elevated mineral N levels in the top soil (Figure 1 and

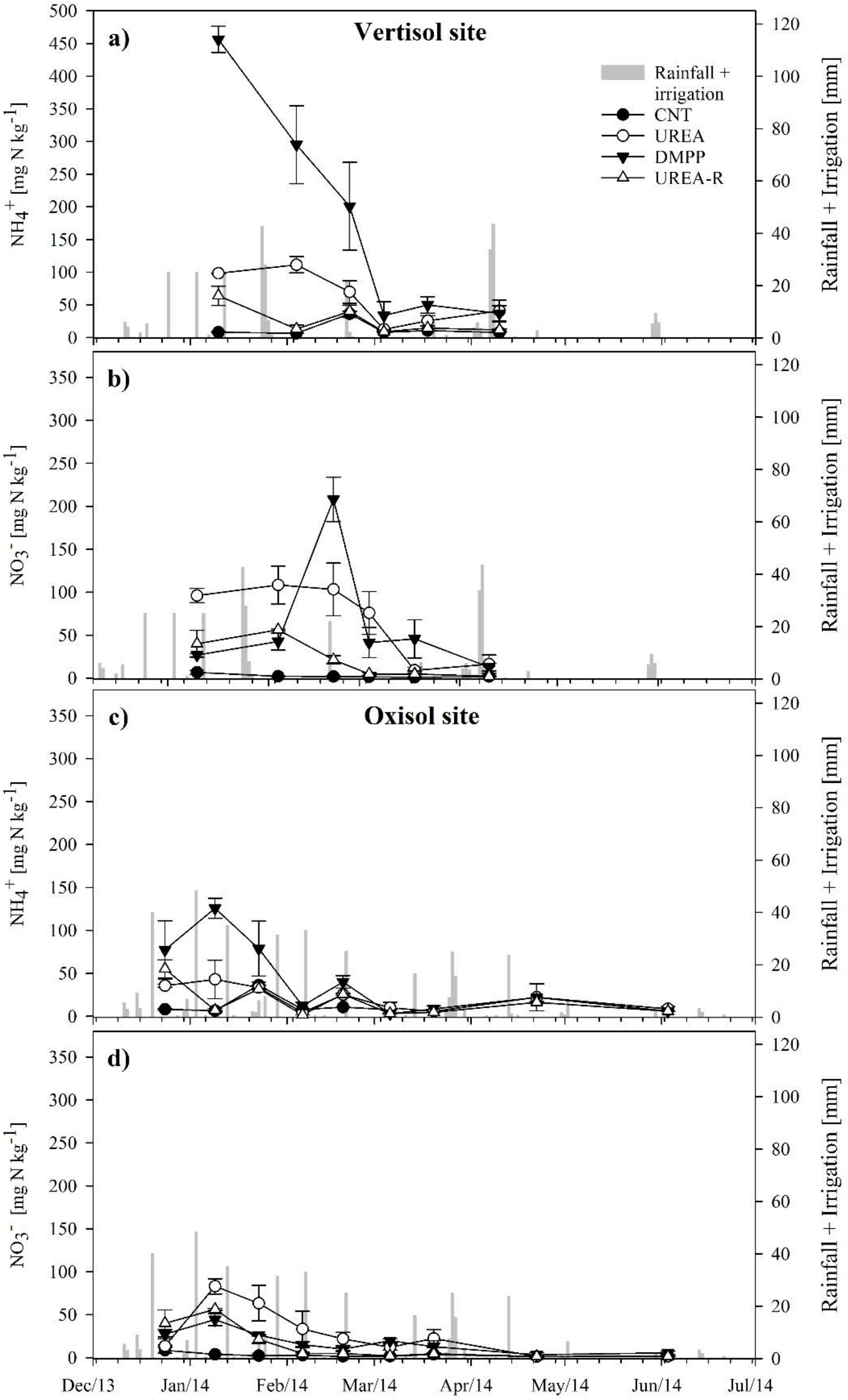

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Figure 2). Notably, substantial rainfall events that occurred later in the cropping season (a total of 178 mm fell from mid-February to mid-April 2014 at the Oxisol site) did not generate high N_2O emissions, indicating that by then most of the applied N was probably taken by the plants, immobilized by microbes, lost to the environment or deeper in the soil profile. These observations of the majority of N_2O emissions being recorded within 90 days from fertilisation are in good agreement with the results reported in other studies on Australian sub-tropical summer cropping systems on Vertisols and Oxisols (Scheer *et al.* 2013; De Antoni Migliorati *et al.* 2014; Scheer *et al.* 2016 in press).

At the Vertisol site, the imbalance of the rainfall distribution over the first 3 months of the growing season and the relatively dry soil conditions that persisted until the late season event at the end of March 2014 were likely to have limited nitrification rates (Stark and Firestone 1995). This was confirmed by the NH_4^+ concentrations, which remained high in all fertilised treatments in the Vertisol until late February 2014 (Fig. 2a, b), a substantially longer period compared to that observed at the

Oxisol site (

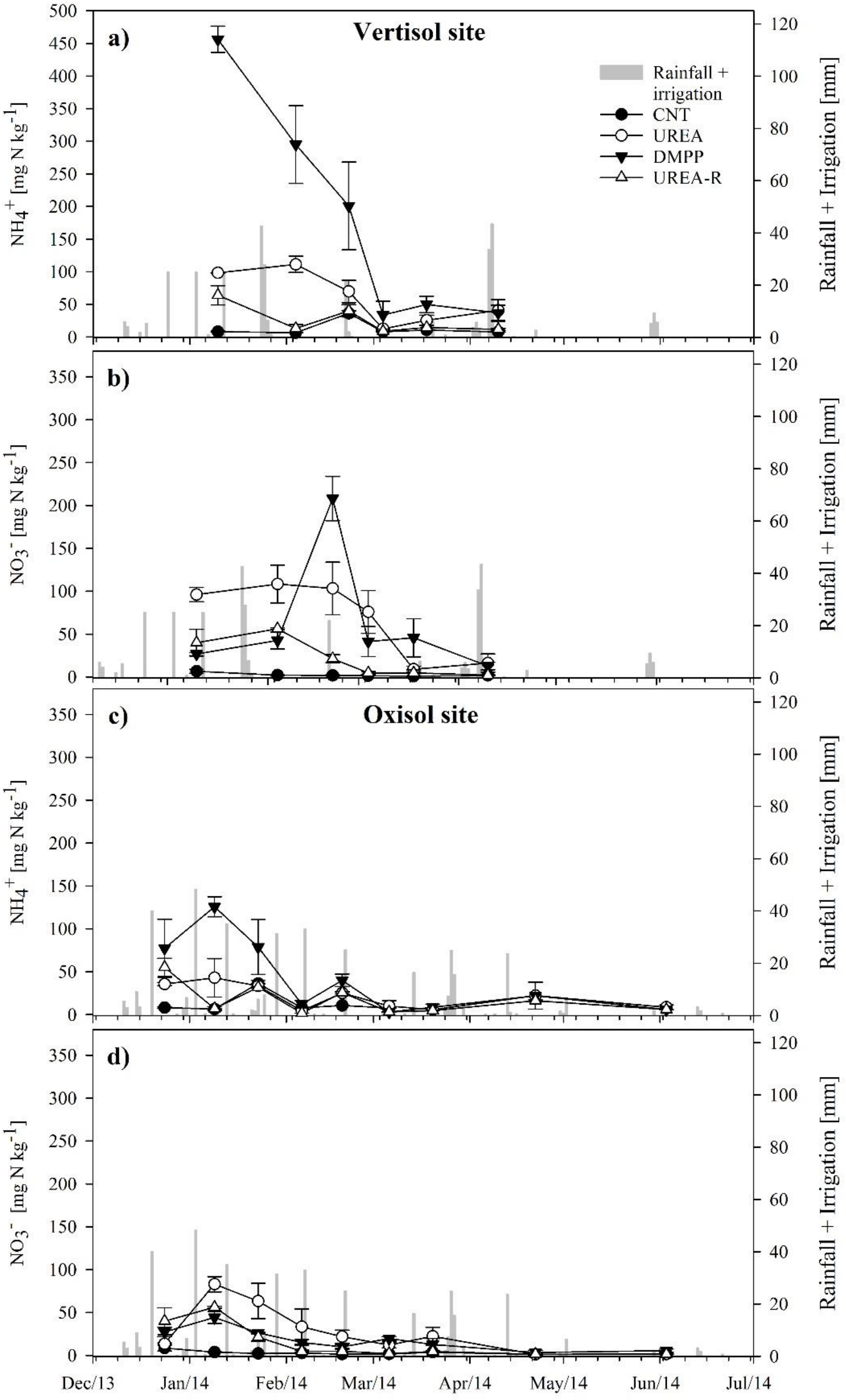
a)
Vertisol site
Rainfall + irrigation
CNT
UREA
DMPP
UREA-R
NH_4^+ [mg N kg^{-1}]
Rainfall + Irrigation [mm]
0
50
100
150
200
250
300
350
400
450
500
0
20
40
60
80
100
120
b)
NO_3^- [mg N kg^{-1}]
c)
Oxisol site
d)
Dec/13
Jan/14
Feb/14
Mar/14
Apr/14
May/14
Jun/14
Jul/14

Figure 2c, d). Soil NO_3^- concentrations in the Vertisol increased and remained high until early March 2014, indicating that plant N assimilation from the top 20cm of the profile was probably limited by the low water availability (Poorter and Nagel 2000).

The heterogeneous distribution of rainfall at the Vertisol site caused short periods of high soil water availability and relatively long period of water limitation (Figs. 1, 4). Plant access to N was therefore limited to short windows of opportunity and resulted in lower agronomic efficiency and higher N_2O emissions when compared to the Oxisol site (Table 3, Fig. 3). This result is particularly significant when comparing crop responses to applied N fertilizer (Fig. 3) between sites. Despite similar starting profile mineral N contents at sowing (60-62 kg N ha^{-1} – Table 2) the AE of fertiliser N use at suboptimal N rates was consistently higher in the Oxisol than the Vertisol. Using the same N fertilizer rate across soil types (UREA-R, or 80 kg N ha^{-1}) as an example, the AE on the Oxisol was 50 kg additional grain produced kg of N $applied^{-1}$, compared to 19 kg additional grain produced kg of N $applied^{-1}$ on the Vertisol (Table 3). Further evidence includes the linearity of the N response up to 160 kg N ha^{-1} (the highest rate tested) on the Vertisol, compared to the asymptotic response on the Oxisol with optimum N rates to achieve $Y_{90\%}$ at 100-120 kg N ha^{-1} (Fig. 3). Even though significant amounts of N_2O were lost during the first months after fertilisation, the presence of substantial amounts of mineral N still left in the Vertisol in the later stages of the season was confirmed by the significant N_2O emission pulse recorded after 70 mm of rain fell on the trial on 27 and 30 March 2014 (**Error! Reference source not found.**).

In summary, the nitrification inhibition was clearly effective in both soil types, with decreased NO_3^- and elevated NH_4^+ concentrations in the DMPP compared to the UREA treatment for *ca.* 8 weeks. However at the end of this period the breakdown of the inhibitory effect was demonstrated quite clearly in the Vertisol, with NO_3^- concentrations in the DMPP treatment changing from half those in the UREA treatment to more than double in the space of a two week period. The effects were not as evident at the Oxisol site, where the more frequent and effective irrigations in the freely draining soil resulted in a much shorter duration of high NO_3^- concentrations in the UREA treatment – presumably due to more rapid crop uptake and some movement into deeper profile layers than those monitored and reported here.

EFFECTS OF DMPP ON N_2O EMISSIONS AND GRAIN YIELDS

In both soils the application of DMPP urea influenced the dynamics of mineral N in the top soil (0-20 cm). DMPP was effective in inhibiting the oxidation of NH_4^+ to NO_3^- and extended the longevity of N fertiliser in the NH_4^+ form compared to conventional urea in both the Vertisol and Oxisol (

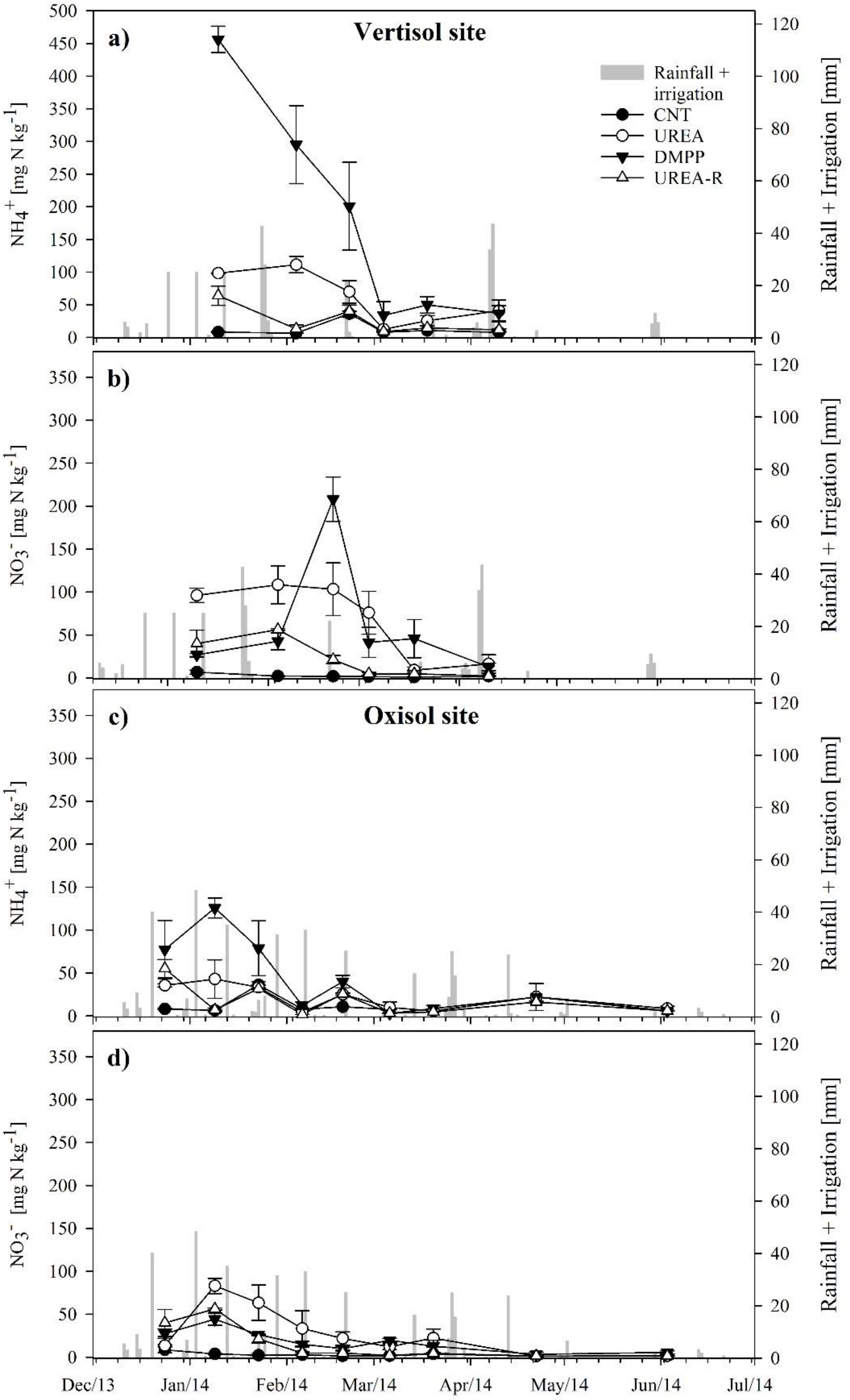

Figure 2a and

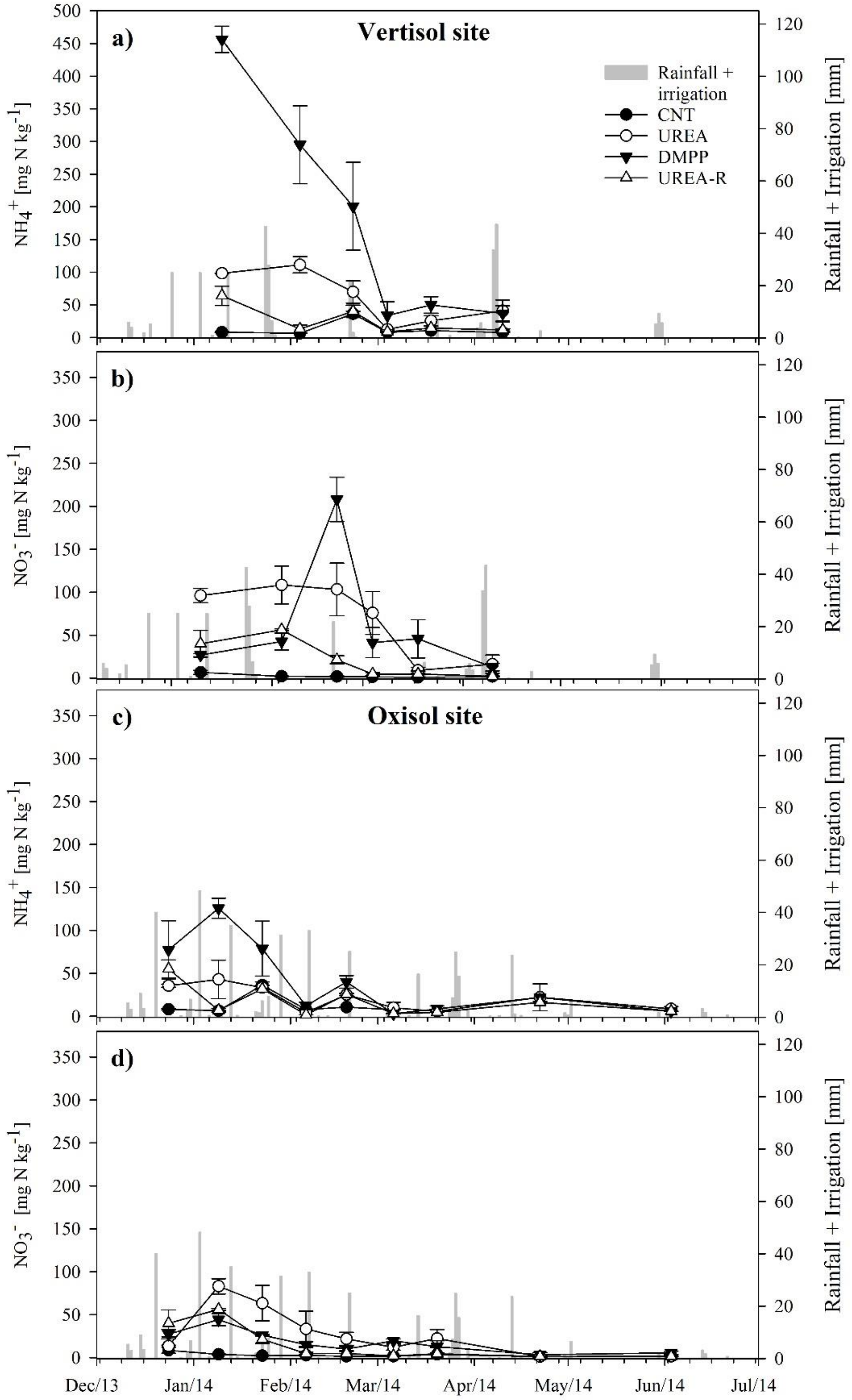

Figure 2c). Significantly, the results of this study indicate that the different rainfall conditions measured at the two sites had little impact on the duration of the inhibitory effect, which lasted for approximately eight weeks.

At both sites the NH_4^+ levels in the DMPP treatments started to decline from early January. The increased nitrification rates after eight weeks from fertilisation were particularly evident on the Vertisol, where the decrease in soil NH_4^+ concentrations was accompanied by a sudden spike in NO_3^-

concentrations in the samples collected in late February 2014 (

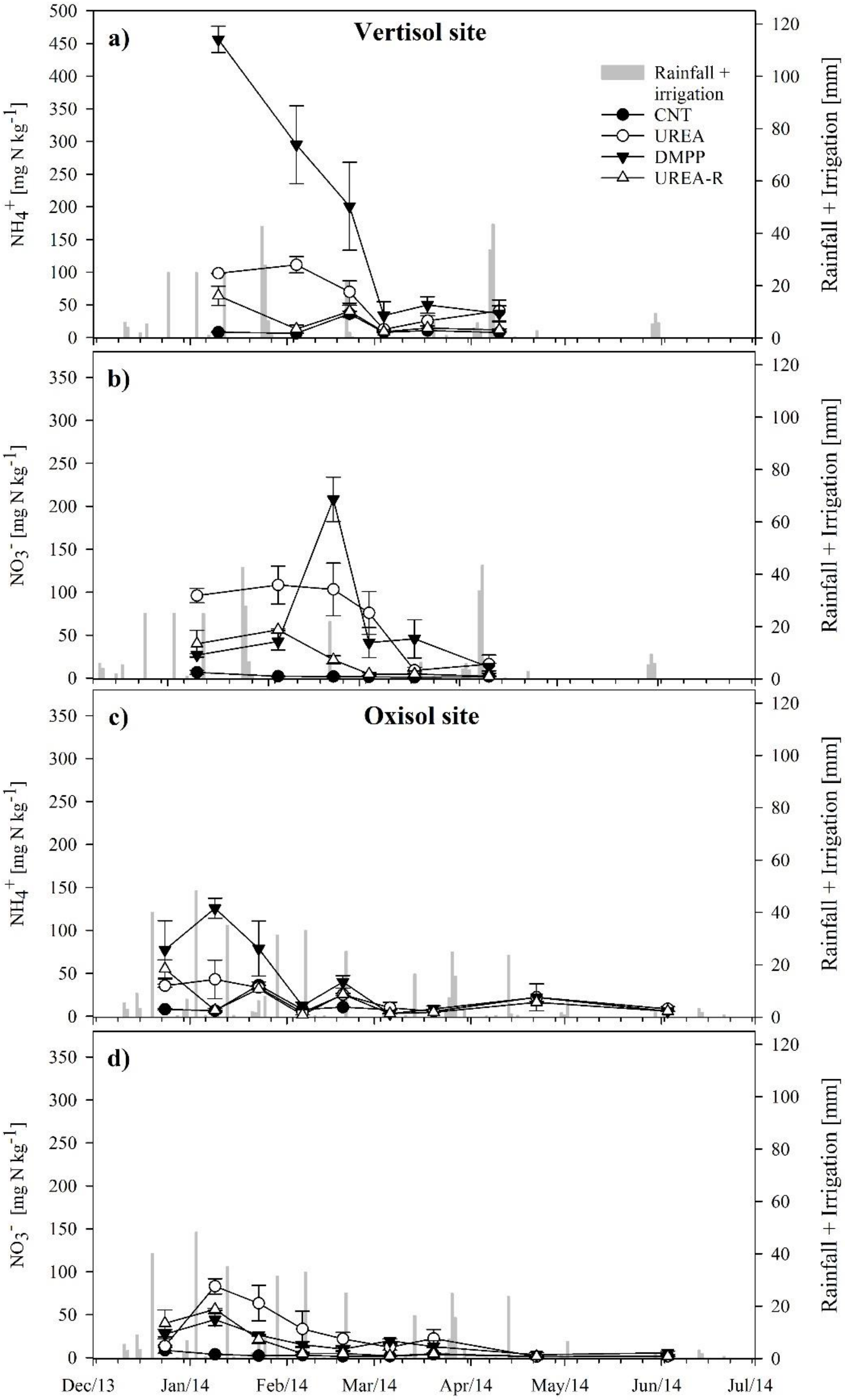

Figure 2b). This dynamic was less obvious at the Oxisol site, where the delayed rise of NO_3^- levels was likely to have been due to a combination of plant uptake and leaching into deeper profile layers.

The longevity of DMPP was reflected also in the N_2O emissions patterns, with these effects particularly evident on the Vertisol (Fig. 4). At this site the dry soil conditions that characterised the beginning of the cropping season limited the potential for N losses and plant N uptake, but there was a consistent pattern of higher emissions pulses in the UREA treatment during each of the irrigation and rainfall events that occurred up until early-mid February 2014. The drier conditions resulted in relatively high amounts of NO_3^- still present in the soil in early March, so that when the 90mm of rainfall event occurred in late March a further emissions pulse was recorded. However by this stage the inhibitory effect of DMPP was largely expired and the magnitude of the N_2O emission pulse measured in the DMPP treatment on this occasion was comparable to that measured in the UREA treatment. Significantly, this event alone caused the majority (64%) of seasonal N_2O losses in the DMPP treatment, while it contributed a much lesser proportion (36%) to overall N_2O emissions in the UREA plots.

On the Oxisol, significant rainfall events during the first eight weeks triggered much shorter duration, and generally lower, N_2O emissions pulses in the DMPP treatment than those measured in the UREA treatment (**Error! Reference source not found.**4), again consistent with the lower NO_3^- concentrations evident in the top 20cm of the profile at that time (Fig. 2d). In late February however, when the trial was irrigated with 20 mm, the N_2O emission pulse from the DMPP treatment was comparable to those in UREA. Even though the magnitude of these last emission pulses was limited

466 due to the low concentrations of mineral N left in the soil (

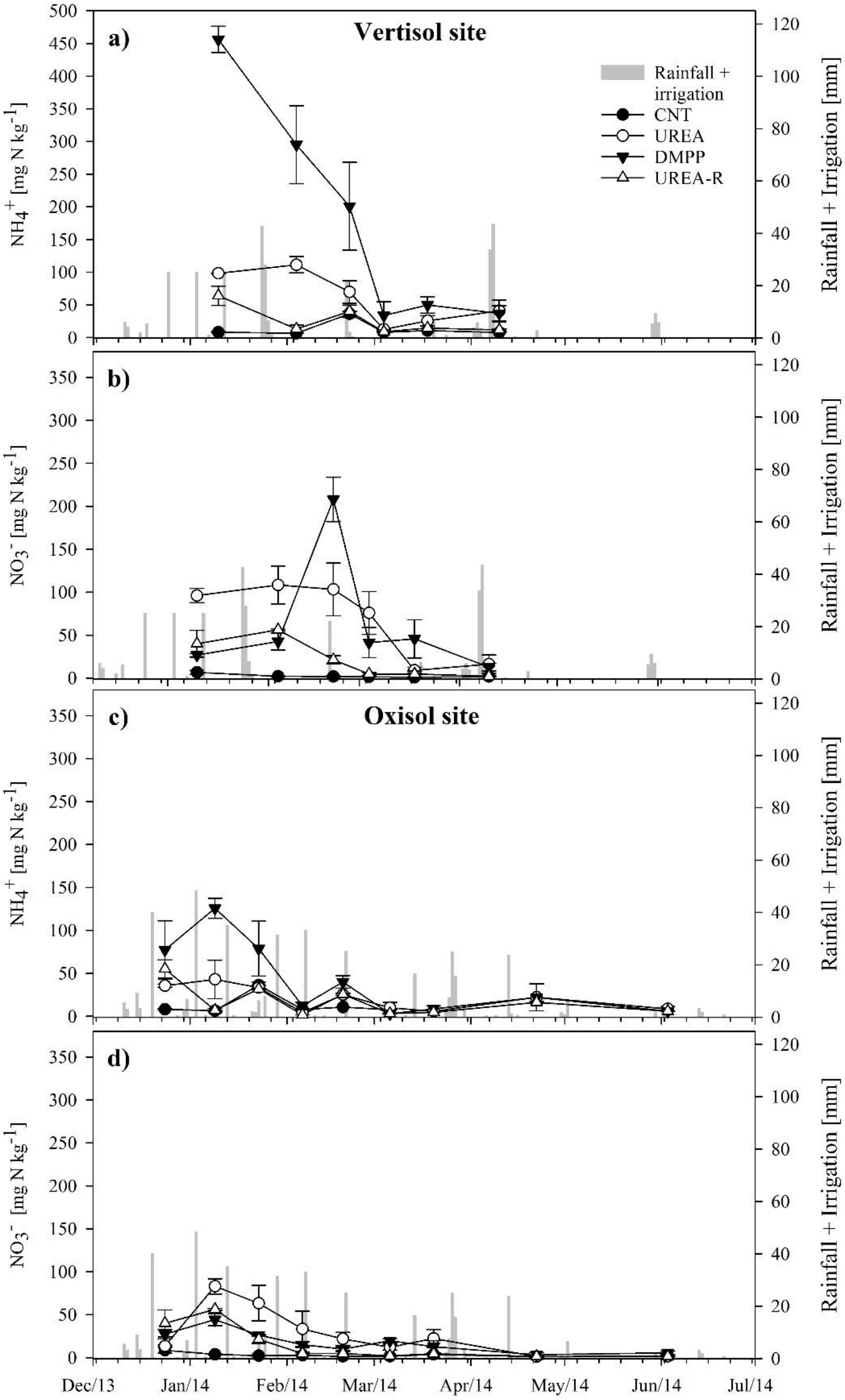

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Figure 2c and

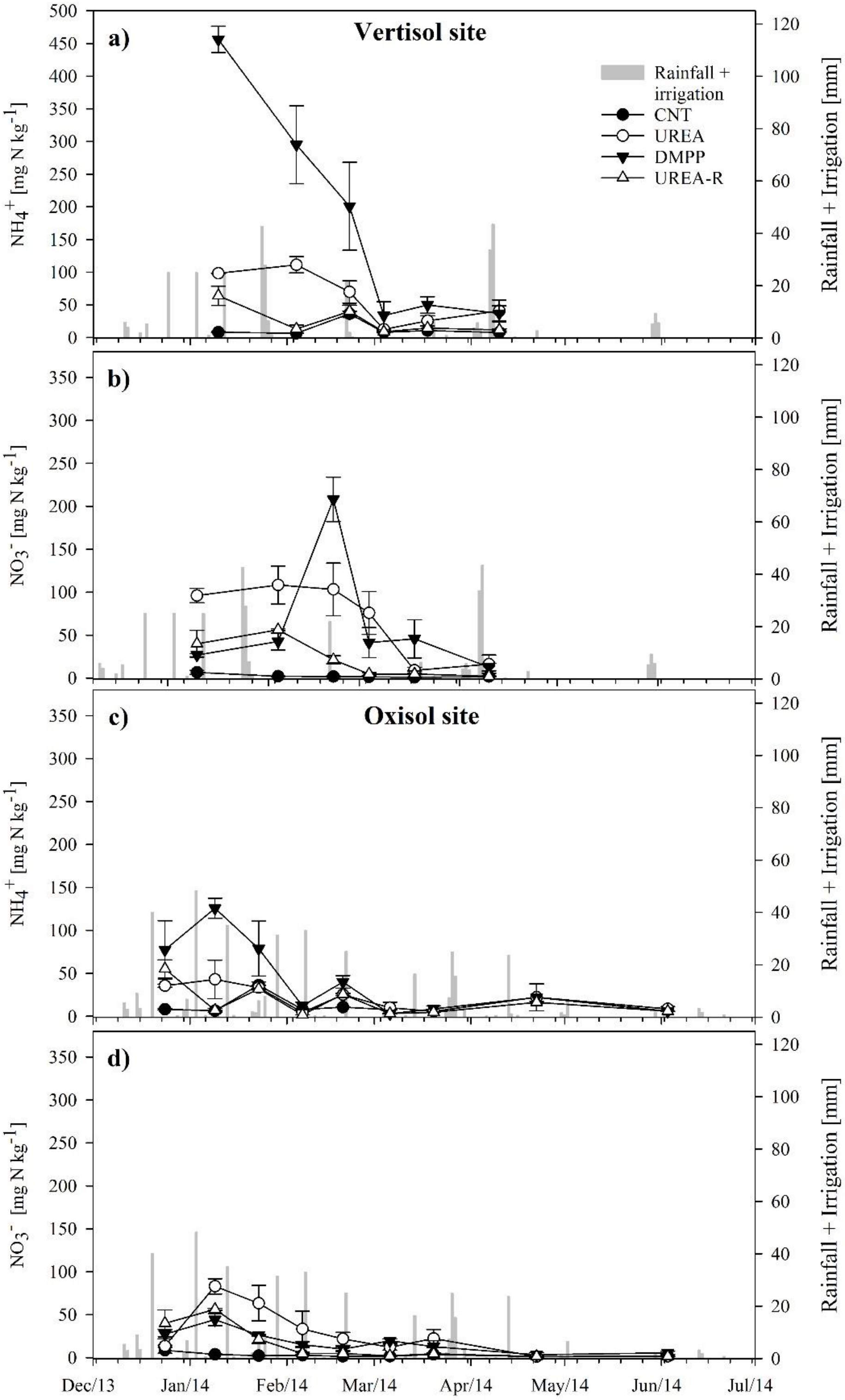

Figure 2d), the absence of substantial difference between the two N_2O peaks again suggests that by this stage the inhibitory effect of DMPP had ended.

Our results were consistent with those reported from other studies using DMPP on similar soil types in this region (De Antoni Migliorati *et al.* 2014; Scheer *et al.* 2014; Scheer *et al.* 2016 in press) and from other climates and production systems (Pasda *et al.* 2001; Chaves *et al.* 2006; Benckiser *et al.* 2013). All have consistently reported effective nitrification inhibition periods varying between 60 and 90 days.

Overall, DMPP reduced the amount of N_2O losses by over 60% in both the Vertisol and Oxisol, a result consistent with the 40-60% abatement rates reported in field trials and incubation studies by De Antoni Migliorati *et al.* (2014), Chen *et al.* (2010); Suter *et al.* (2010) and Liu *et al.* (2013). The efficiency of DMPP in inhibiting N_2O losses was reflected at both sites by the emission factors and emission intensities, which on average were reduced by 70% compared to conventional urea (Table 3). Emission factors from the UREA treatments (0.7% and 0.4% on the Vertisol and Oxisol, respectively) were higher than values recorded in the sub-optimal UREA-R treatments (0.5% and 0.3%, respectively), but tended to be lower than the default values of 1% of applied N suggested by the International Panel on Climate Change (De Klein *et al.* 2006) and intermediate between the dryland (0.2%) and irrigated (0.85%) default values adopted in the Australian Greenhouse Gas Inventory submission (Anon 2015). This was consistent with the largely supplementary use of irrigation in these studies. The significant reduction in N_2O emissions achieved through the use of DMPP showed that emissions factors can be reduced to well below even the dryland standard of 0.2%, albeit in a season without large rainfall events in the vulnerable early parts of the growing season. More research is advocated to investigate the benefits of DMPP when combined with high fertilizer rates under varying climatic conditions.

Despite the significant abatement of N_2O emissions observed with DMPP, there did not appear to have been substantial improvements in fertilizer NUE or the amount of fertilizer required to achieve a given yield target (i.e. $Y_{90\%}$). While there were suggestions of slight improvements in AE in the DMPP compared to UREA treatments in Table 3 (by 6% and 19% on the Oxisol and Vertisol, respectively), these differences were not statistically significant. Similarly, where the experiment was able to adequately estimate a site yield potential in response to applied N (the Oxisol site – Fig. 3b) there was a suggestion of a lower critical N rate for the DMPP (100 kg N ha^{-1}) compared to the urea (125 kg N ha^{-1}) in order to achieve $Y_{90\%}$,. The consistency of these trends across a broader range of sites and seasons is reported in Lester *et al.* (2016 in press), with this study also suggesting only small agronomic benefits from use of DMPP in summer sorghum cropping.

These results, similar to those reported by Díez López and Hernaiz (2008), Weiske *et al.* (2001a) and De Antoni Migliorati *et al.* (2014), are likely to be due to the absence of prolonged periods with extremely wet soils in these environments, especially early in the growing season (e.g. Fig.1). These conditions therefore limit the number of opportunities for fertiliser N to leach or denitrify, and so limit the potential benefits from employing products like DMPP. In addition, while the fertiliser N rates at which the UREA and DMPP treatments were compared were appropriate for the seasonal conditions and soil N availability at both sites (Fig. 3), it is also worth noting the relatively low incremental AE for additional N application on this part of the yield response curve. The incremental AE of increasing N rates from 100 to 120 kg N ha^{-1} on the Oxisol or from 120 to 160 kg N ha^{-1} on the Vertisol (Fig. 3) averaged 14-16 kg grain for each kg additional N applied. This relatively low incremental AE suggests large amounts of N would need to be lost before a statistically significant yield penalty would be detected from using urea rather than the DMPP-coated product.

As concluded by Lester *et al.* (2016 in press), DMPP might have a greater scope to increase agronomic efficiency of urea in higher rainfall or irrigated production regions, or when high rates of N fertilizer are required to meet seasonal yield potential under high-intensity cropping situations. Examples of the latter would include double cropping from a winter cereal to summer sorghum in a high rainfall year, where systems are characterised by high amounts of crop residues and low levels of soil N - conditions that require high fertiliser N rates to prevent severe crop N deficiency.

Conclusions

Data gathered in this study illustrated the importance of rainfall patterns in affecting N dynamics in subtropical cereal cropping systems. Even though the lack of extreme rainfall events early in the growing season minimised the opportunities for differences in soil water holding and drainage characteristics between the two soils to be expressed in terms of potential N losses, DMPP proved to be a reliable tool to abate N_2O emissions from these systems. Importantly, DMPP displayed consistent capacity to inhibit nitrification for a similar duration in different soil types, weather conditions, fertiliser N rates and ranges of soil water availability.

Despite this effectiveness, the use of DMPP urea did not lead to significant yield increases compared to conventional urea. Limited moisture availability during the study constrained crop growth, especially at the Vertisol site, and at both sites conditions were not conducive to high leaching or denitrification losses for extended periods, which is likely to have contributed to masking the potential for DMPP to reduce N losses in these systems. DMPP might therefore have a greater scope to increase the agronomic efficiency of urea in summer seasons expected to have high rainfall rates, such as in *la Niña* phases of the El Niño Southern Oscillation (ENSO) cycle (Australian Bureau of Meteorology 2016) – especially under double crop situations where surface residue amounts from the previous crop are high. Further research is required to clarify the conditions where DMPP might have a substantial scope to increase grain yields in subtropical cereal cropping systems.

Acknowledgements

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List of Tables

Table 1 - Main soil physical and chemical properties for the top 30 cm (means ± SE, n=3) at the Kingsthorpe and Kingaroy research stations, Queensland, Australia. Respective soil types are reported within brackets. LL15, DUL and SAT are the volumetric water contents (m^3 m^{-3}) corresponding to the lower limit of crop water extraction, the drained upper limit and at saturation, respectively, for the research sites (Mielenz *et al.* 2016).

Soil Property (0-30 cm)	**Kingsthorpe (Vertisol)**	**Kingaroy (Oxisol)**
pH (H_2O)	7.1 ± 0.2	5.00 ± 0.7
Total C (%)	1.7 ± 0.1	1.3 ± 0.1
Total N (mg kg^{-1})	1150 ± 80	980 ± 63
Bulk density 0-30 cm (g cm-3)	0.98 ± 0.1	1.18 ± 0.1
PAWC (mm)	210-230	100-110
LL15 (m^3 m^{-3})	0.33	0.24
DUL ((m^3 m^{-3})	0.53	0.37
SAT (m^3 m^{-3})	0.61	0.51
Texture (USDA)	Clay	Clay
Clay (%)	67	55
Silt (%)	22	14
Sand (%)	11	31

Table 2 – N fertilization rates on which N_2O emissions monitoring were undertaken, profile mineral N at sowing (kg ha^{-1} to 120cm) and in-season rainfall and irrigation totals during the sorghum cropping seasons at the Vertisol and Oxisol sites in 2013 -2014.

Site	**Fertilization [kg-N ha^{-1}]**				**Profile mineral N (kg ha^{-1})**	**Rainfall [mm]**	**Irrigation [mm]**
	CNT	**UREA-R**	**UREA**	**DMPP**			
Vertisol	0	80	160	160	62	241	80
Oxisol	0	80	120	120	60	203	168

Table 3 - Cumulative N_2O fluxes, N_2O emission factors, grain yields (expressed as dry matter), agronomic efficiencies and N_2O intensities (mean ± SE, n=3) as a function of the six treatments. Numbers in the Treatment column indicate seasonal fertiliser N rates (kg N ha^{-1}). Means denoted by a different lower–case letter indicate significant differences between treatments ($p<0.05$) within the same site. Means denoted by a different upper–case letter indicate significant differences between treatments ($p<0.05$) across the two sites.

Site	**Treatment**	**N_2O emissions [kg N_2O-N ha^{-1}]**	**Emission Factor [%]**	**Grain yield [t ha^{-1}]**	**Agronomic Efficiency [kg extra grain kg N $applied^{-1}$]**	**Emissions intensity [kg-N_2O-N t $yield^{-1}$]**
Vertisol	**CNT**	0.24 ± 0.17 $^{a, A}$		1.91 ± 0.13$^{a, BA}$		
	UREA-R (80)	0.63 ±0.05$^{b, BC}$	0.5	3.20±0.36$^{ab, CB}$	18.54±5.24$^{a, A}$	0.19
	UREA (160)	1.30 ± 0.13 $^{c, D}$	0.7	4.19 ± 0.30$^{b, DC}$	15.94 ± 4.17$^{a, A}$	0.31
	DMPP (160)	0.44 ± 0.04$^{ab , AB}$	0.1	4.26 ± 0.58$^{b, CDE}$	16.94 ± 4.11 $^{a, A}$	0.10
Oxisol	**CNT**	0.11 ± 0.02 $^{a, A}$		1.08 ± 0.21$^{a, A}$		
	UREA-R (80)	0.33 ± 0.1$^{a, AB}$	0.3	4.71 ± 0.37$^{b, CDE}$	50.37 ± 2.50$^{b, B}$	0.07
	UREA (120)	0.81 ±0.19 $^{a, C}$	0.4	5.27 ± 0.07$^{b, ED}$	38.91 ± 3.0 $^{a, B}$	0.15
	DMPP (120)	0.31 ± 0.09 $^{b, AB}$	0.1	5.83 ± 0.15$^{b, E}$	46.20 ± 1.30 $^{ab, B}$	0.05

List of Figures

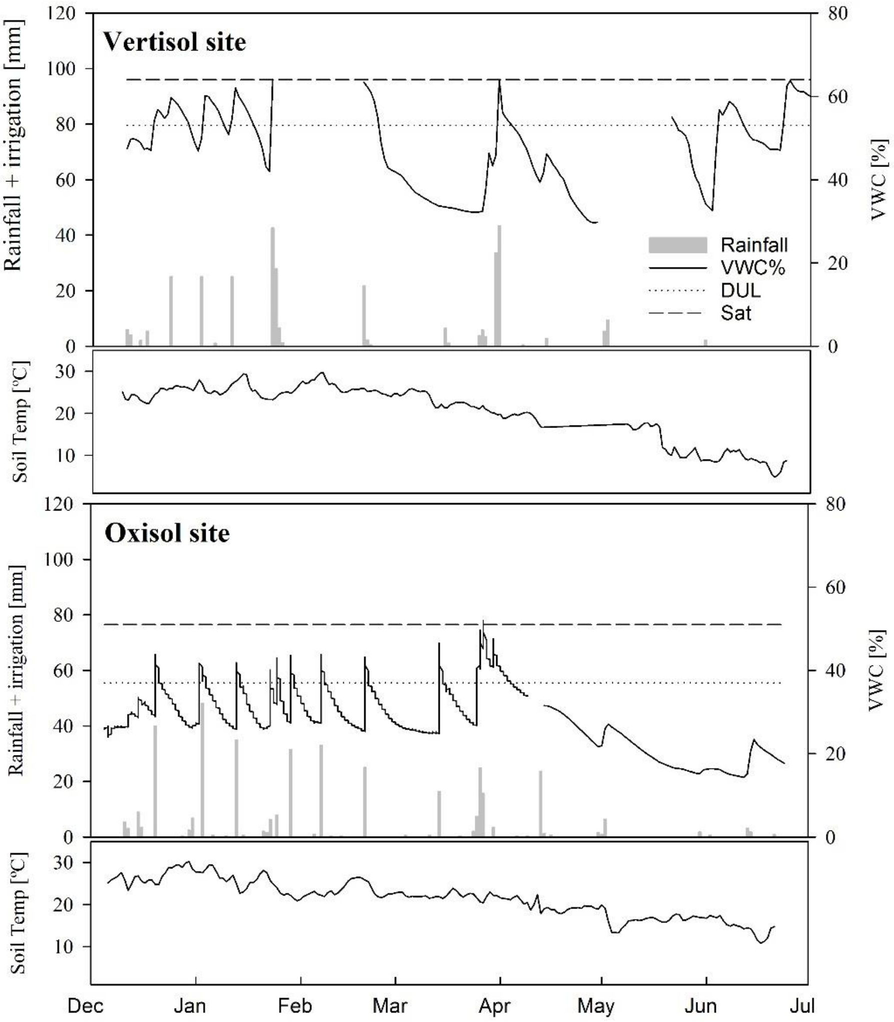

Figure 1– Daily (rainfall + irrigation) and average daily volumetric soil water content (m^3m^{-3}) and soil temperatures (°C) in the top 10 cm at the Vertisol (top) and Oxisol (bottom) sites during the 2013/14 sorghum cropping season. The dotted and dashed lines represent the volumetric moisture contents pertaining to the Drained Upper Limit and Saturation, respectively. Soil moisture data were not available at the Vertisol site during the month of February 2014 due to equipment malfunction.

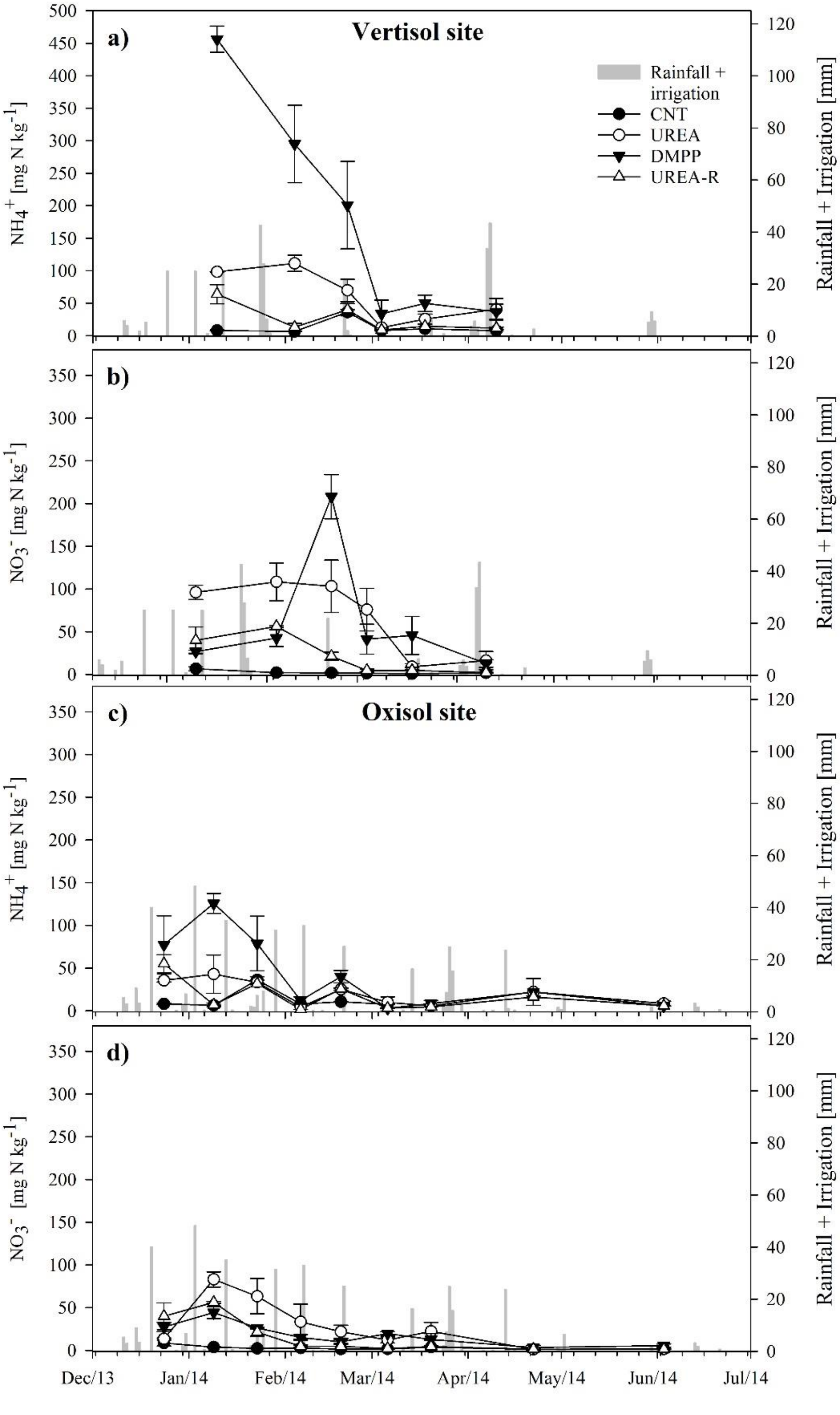

Figure 2 – Variation in soil ammonium and nitrate concentrations (0-20 cm) and daily rainfall and irrigation for the three treatments at the Vertisol (a, b) and Oxisol (c, d) sites during the 2013/14 sorghum cropping season.

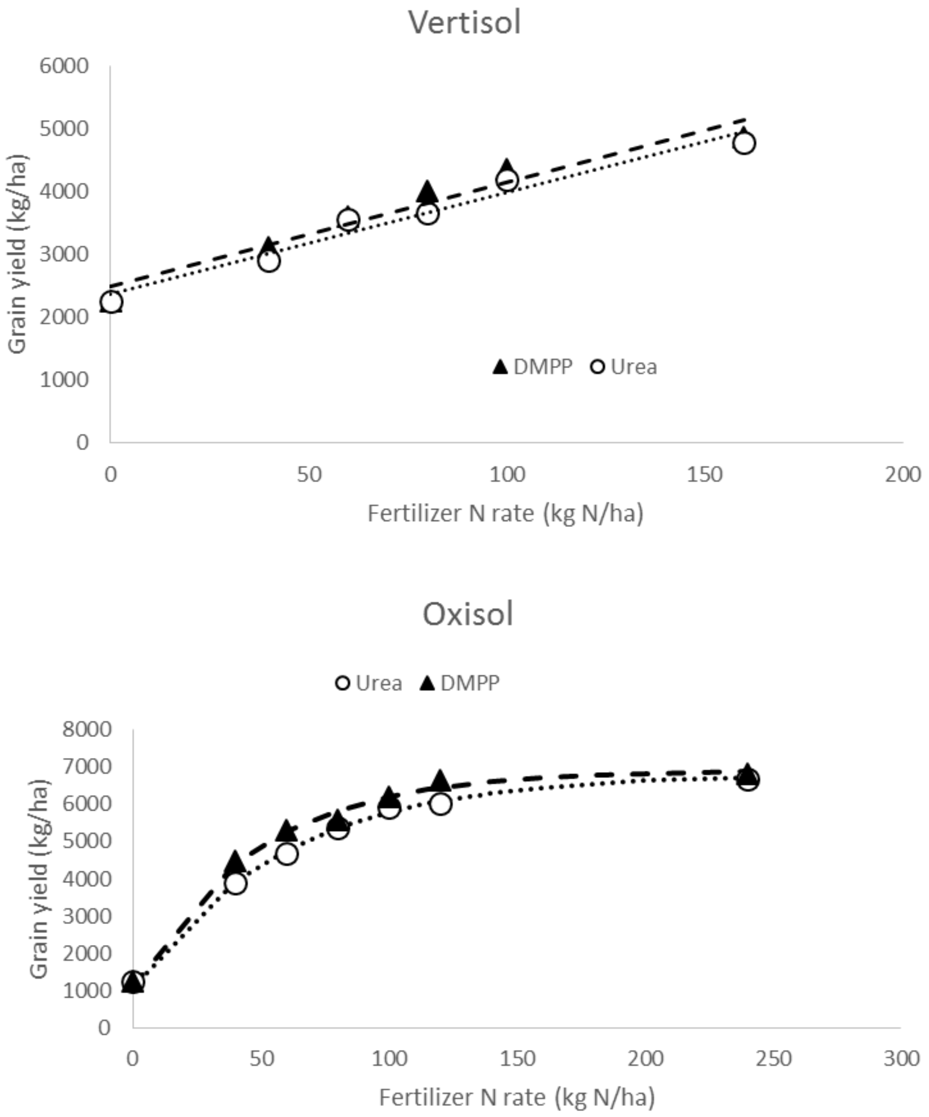

Figure 3 - Relationship between applied fertilizer N (as urea or urea with DMPP) and grain yield at the Vertisol and Oxisol sites in 2013/14. The N rates to produce 90% of N-unlimited grain yields were 100 (Entec) to 120 (urea) kg N/ha on the Oxisol and >160 kg N/ha for both products on the Vertisol.

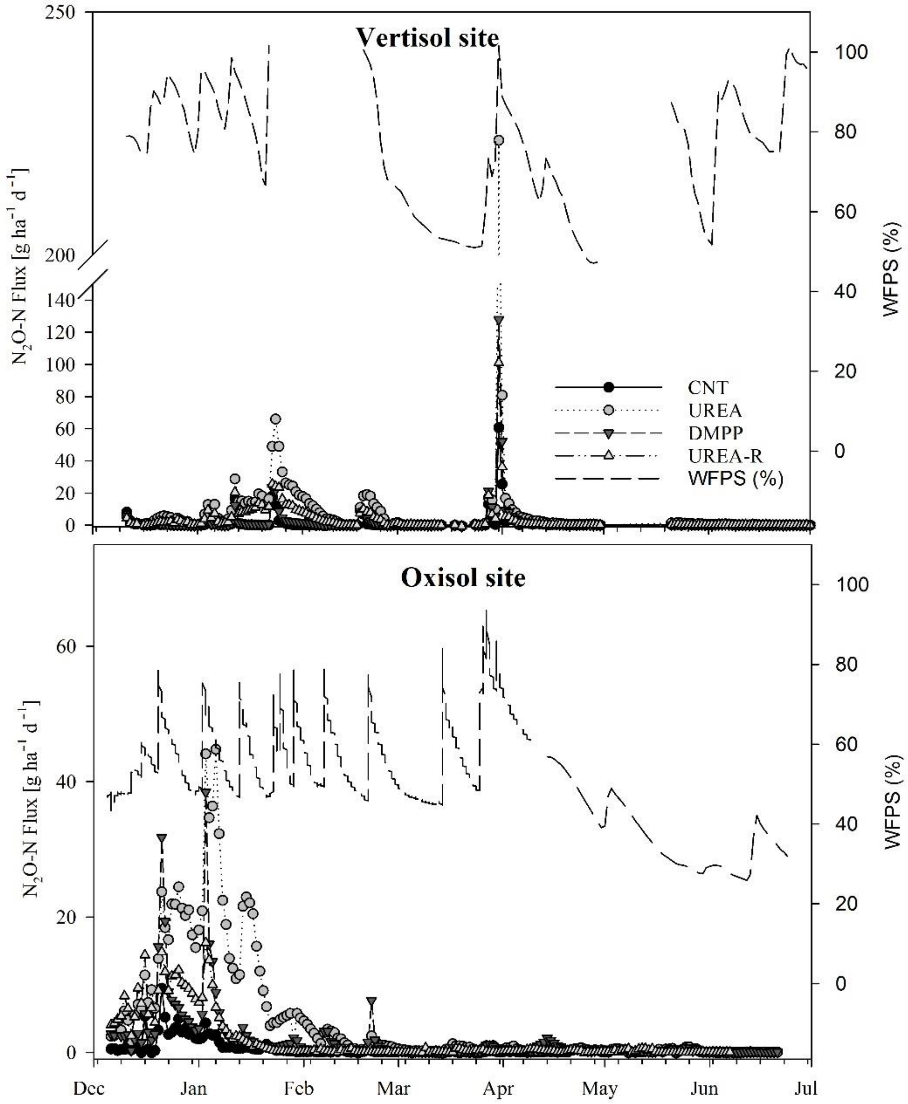

Figure 4 - Daily soil N_2O fluxes and water-filled pore space (WFPS, %) for the three treatments at the Vertisol (top) and Oxisol (bottom) sites during the 2013/14 sorghum cropping season. N_2O emissions in the two panels are reported using different scales.