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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 nitrous oxide (N_2O) losses is high in subtropical cereal cropping systems in north-east Australia, where the fertiliser nitrogen (N) input is one single application at or before planting. The use of urea coated with the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) has been reported to substantially decrease N_2O emissions and increase crop yields in humid, high-intensity rainfall environments. However, it is still uncertain whether this product is similarly effective in contrasting soil types in the cropping region of north-east 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 (0 kg N ha^{-1}) and two fertilised treatments chosen on the basis of delivering at least 90% of seasonal potential grain yield (160 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. Despite the relatively dry seasonal conditions 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 with 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 before the bulk of crop N acquisition, which limited the exposure of fertiliser N to large losses due to leaching and denitrification.

Additional keywords: automated greenhouse gas measuring system, denitrification, nitrogen response.

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Introduction

Vertisols and Oxisols are among 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 are often 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 increased from negligible to >100 kg N ha^{-1} over the last few decades (Bell *et al*. 1995; Lester *et al*. 2010).

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 north-east Australia, where fertiliser N is typically added in one single application at or before planting, due to the unpredictability of in-season rainfall patterns (Bell *et al*. 2015).

N losses can pose severe threats to the environment, among 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 shown 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*a*).

One of the most promising methods to reduce N_2O emissions and decrease overall N losses is the addition of nitrification inhibitors to ammonium (NH_4^+)-based fertilisers (Linzmeier *et al*. 2001*b*; Pasda *et al*. 2001; Kawakami *et al*. 2012). Nitrification inhibitors are antibiotics that slow the activity of the *Nitrosomonas* spp. bacteria, responsible for the oxidation of NH_4^+ to nitrite. 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 in several studies to substantially decrease N_2O emissions and increase crop yields in humid, high rainfall environments (Prasad and Power 1995; Linzmeier *et al*. 2001*a*; Pasda *et al*. 2001; Hatch *et al*. 2005), which are the prevalent environmental conditions during subtropical summers. Among nitrification inhibitors, DMPP (3,4-dimethylpyrazole phosphate) has been reported by many authors as the most efficient in slowing nitrification and reducing N_2O losses (Weiske *et al*. 2001*b*; Liu *et al*. 2013; Lester *et al*. 2016).

While DMPP was shown to efficiently reduce N_2O emissions on Oxisol soils in subtropical cropping systems in north-east Australia (De Antoni Migliorati *et al*. 2014), it is still uncertain whether it has 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 minimising 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 ~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 in USDA Soil Taxonomy (Soil Survey Staff 1998) or as a haplic, black Vertosol in the 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 ~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 south-east Queensland, Australia. The soil is classified as a Tropeptic Eutrustox Oxisol in USDA Soil Taxonomy (Soil Survey Staff 1998) or as a Brown Ferrosol in the 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 and 27.2°C in summer, and 5.9 and 17.0°C in winter respectively. Mean annual precipitation is 630 mm (1990–2010), with most rainfall in October–March, during the summer crop growing season. At the Oxisol site (Kingaroy), monthly mean minimum and maximum temperatures are 16.5 and 29.6°C in summer, and 4.0 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

Table 1. Main soil physical and chemical properties for the top 30 cm (means ± s.e., $n = 3$) 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, and PAWC is plant available water holding capacity, 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

a maximum of 114.1 mm in January (Australian Bureau of Meteorology).

Experimental design

Experiments were sown to sorghum (*Sorghum bicolor* L. Moench) during the 2013–14 summer season, with cv. Pacific MR43 planted on 10 December 2013 and machine-harvested on 5 May 2014 at the Vertisol site; at the Oxisol site, cv. Pioneer G22 was planted on 27 November 2013 and machine-harvested on 10 April 2014. The Vertisol site was 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.

Briefly, treatments were organised in a randomised complete block design with four replicates at the Vertisol site and in a split plot design (fertiliser 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 at 20 cm) and two passes with offset discs (15 cm). Crop row spacing was 1.0 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 each measured 6 m × 12 m and 5.4 m × 13 m, with buffer areas of 1–2 m between plots. Further information on the experimental details is outlined in full in Lester *et al.* (2016).

Both sites utilised supplementary irrigation using overhead sprinkler application. At the Vertisol site this consisted of 30 mm of irrigation immediately after sowing, to ensure uniform crop establishment, followed by two 25-mm 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 unfertilised control (0 N added), N rates supplied as urea or DMPP urea were in the ranges of 40–160 and 40–240 kg N ha^{-1} on the Vertisol and Oxisol respectively. Fertiliser was banded at 10–15 cm 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 1 m 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 72 h) before mulching and grinding and subsequent analysis for N concentration. Grain yields were determined following harvesting with a combine after a 1-m buffer area was removed from either end of the plot (two crop rows by the length of the experimental plot), with grain moisture 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 fertiliser products were compared at N rates estimated to produce maximum grain yields at each site. These were 160 and 120 kg N ha^{-1} on the Vertisol and Oxisol respectively. These rates were ~30% higher than standard farmer practice (~120 and 90 kg N ha^{-1} respectively), but considered appropriate due to the preceding very wet summer with large denitrification losses (De Antoni Migliorati *et al.* 2015; Scheer *et al.* 2016*b*) 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 suboptimal 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 2014 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 12 chambers, linked to a computerised sampling unit and an *in situ* gas chromatograph (SRI GC 8610C) equipped with a ^{63}Ni electron capture detector 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 × 50 cm × 15 cm and were attached

Table 2. N fertilisation rates on which N_2O emissions monitoring was undertaken, profile mineral N at sowing (kg ha^{-1} to 120 cm) and in-season rainfall and irrigation totals during the sorghum cropping seasons at the Vertisol and Oxisol sites in 2013–14

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

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 four 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 12 chambers lasted 3 h, during which each chamber was sampled for 1 h and then remained opened for 2 h to restore ambient conditions. This method enabled the determination of up to eight single fluxes per chamber per day. The detection limit of the system was ~1.0 μg N_2O-N m^{-2} h^{-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 localised source (banded fertiliser) with background emissions from residual soil N derived from unfertilised plots. The measuring systems were deployed soon after fertiliser 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 min using resistance temperature detectors (Temperature Controls Pty Ltd, Brisbane, 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 by the 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 of 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 1 M potassium chloride to 20 g of soil and shaking the solution for 1 h. The solution was then filtered and stored in a freezer until analysed colourimetrically 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 CNT treatment. This represented three replicate samples collected 5, 15 and 20 cm from the plant row, with replicate samples thoroughly mixed and a subsample 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-min period of chamber closure. The obtained data were corrected for internal air temperature, atmospheric pressure and the ratio of chamber volume and soil area. Measurements were quality-checked using the Pearson correlation and fluxes above the detection limit were 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 (0.9–1.0 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 fertiliser band and 45% of that with no applied fertiliser.

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:

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

where *EF* (%) is the emission factor of *N fertiliser input* (kg N ha^{-1} $season^{-1}$) lost as N_2O-N, and 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 (in kg grain kg N $applied^{-1}$) as:

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

where *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 adjustment (Benjamini and Hochberg 1995) was performed to assess significant differences in 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 *AE* within and between sites. *Post hoc* tests were performed only when the analysis of variance yielded P values <0.05. The shape of the grain yield–N fertiliser 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 fertiliser rate 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–June) recorded at the Vertisol (493 mm) and Oxisol (464 mm) sites. At the Vertisol site, rainfall during the study was 241 mm (with an additional 80 mm of early season irrigation); however, ~40% (90 mm) of the total rainfall occurred in a rainfall event late in the cropping season (27 and 30 March 2014) (Fig. 1). Rainfall at the Oxisol site was more evenly distributed (Fig. 1) but was 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 was 371 mm and at the Vertisol site 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) (Fig. 1).

Mineral N dynamics in the fertiliser band of the high N rate treatments varied substantially between fertiliser products and, to a lesser extent, sites. At the Vertisol site soil, NH_4^+ concentrations in the UREA treatment declined relatively steadily 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

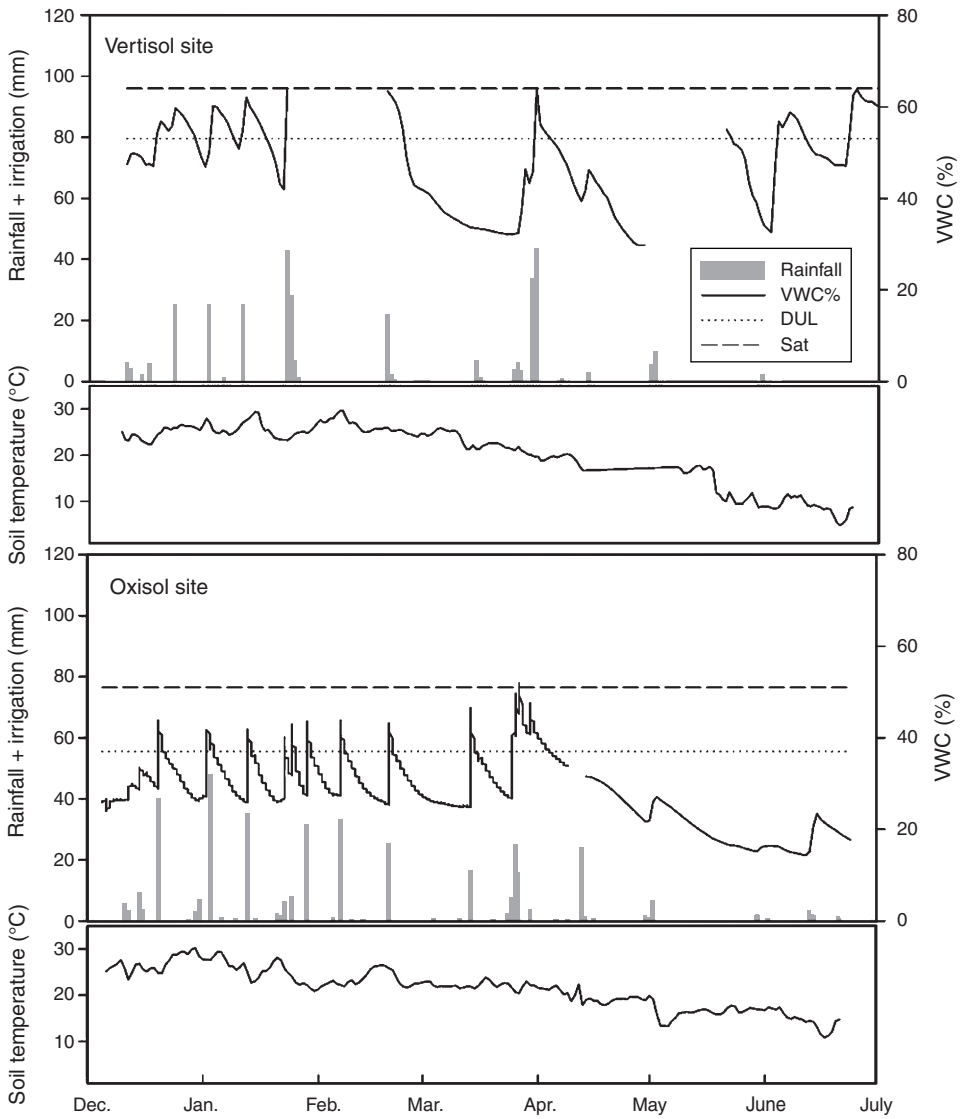

Fig. 1. Daily (rainfall + irrigation) and average daily volumetric soil water content (VWC, $m^3 m^{-3}$) and soil temperatures (°C) in the top 10 cm at the Vertisol (top) and Oxisol (bottom) sites during the 2013–14 sorghum cropping season. The dotted and dashed lines represent the volumetric moisture contents pertaining to the drained upper limit (DUL) and saturation (Sat) respectively. Soil moisture data were not available at the Vertisol site during the February 2014 due to equipment malfunction.

(105–110 mg N kg^{-1}) and then rapidly declined to a minimum of <10 mg N kg^{-1} in March after 90 mm of rain on the trial in late March 2014. Soil NH_4^+ and NO_3^- concentrations in the UREA-R treatment showed the same temporal pattern as for the UREA treatment, but 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 mid-March 2014, they remained much higher than in the UREA treatment (Fig. 2). Conversely, NO_3^- concentrations were constrained to within 25–50% of those recorded in the UREA treatment until the inhibitor effect degraded in early February 2014. The NO_3^- concentrations then sharply increased (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, there was a similar pattern of mineral N dynamics in the UREA and DMPP treatments 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 the CNT treatment. Soil NO_3^- concentrations followed a similar pattern, peaking 6 weeks after planting (83, 56 and 44 mg N kg^{-1} in UREA, UREA-R and DMPP respectively) before gradually declining (Fig. 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 mineralisation 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 (Fig. 2).

N_2O emissions and plant response to fertilisation treatments

At both sites there were strong responses to applied N fertiliser (Fig. 3), with grain yield in the unfertilised 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 N ha^{-1} for the DMPP and UREA treatments respectively. The response functions fitted to yield–applied N relationship showed that the fertiliser N rate needed to achieve 90% of the maximum grain yield ($Y_{90\%}$) was 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 fertiliser N rate required to achieve $Y_{90\%}$ was not possible. However, the data suggest that greater yields were likely with higher fertiliser N rates, and so the 160 kg N ha^{-1} rate chosen to compare emissions from UREA and DMPP seemed appropriate for this particular site and season.

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

As with soil mineral N, N_2O emissions differed substantially across treatments but with some commonalities between sites. In both soil types, seasonal N_2O losses were significantly higher from the UREA than the UREA-R, CNT and DMPP treatments (Table 3). Compared with 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 there were much lower emissions factors for DMPP on the Vertisol (0.1%) and Oxisol (0.2%). Across treatments, seasonal N_2O emissions tended to be higher on the Vertisol than the Oxisol (Table 3).

The majority of N_2O emissions from the UREA treatments occurred 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, >30% of N_2O-N losses were due to emission pulses in response to a major rain event that delivered 90 mm during 27–30 March 2014 (Fig. 3). 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 (Fig. 4). On both soils, N_2O emission pulses from the DMPP treatments lasted for much shorter periods (<6 days) than for 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 substantially influence 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 for 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 within the first month to ensure good crop establishment and 66% (78 mm) of the rainfall was in a single event over two days in late January (Fig. 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 and irrigation events at the Oxisol site guaranteed a constant water supply to soil microorganisms, which was likely to have promoted relatively rapid nitrification rates (Bouwman 1998; Kiese and Butterbach-Bahl 2002). The rapid decline of NH_4^+ concentrations and the

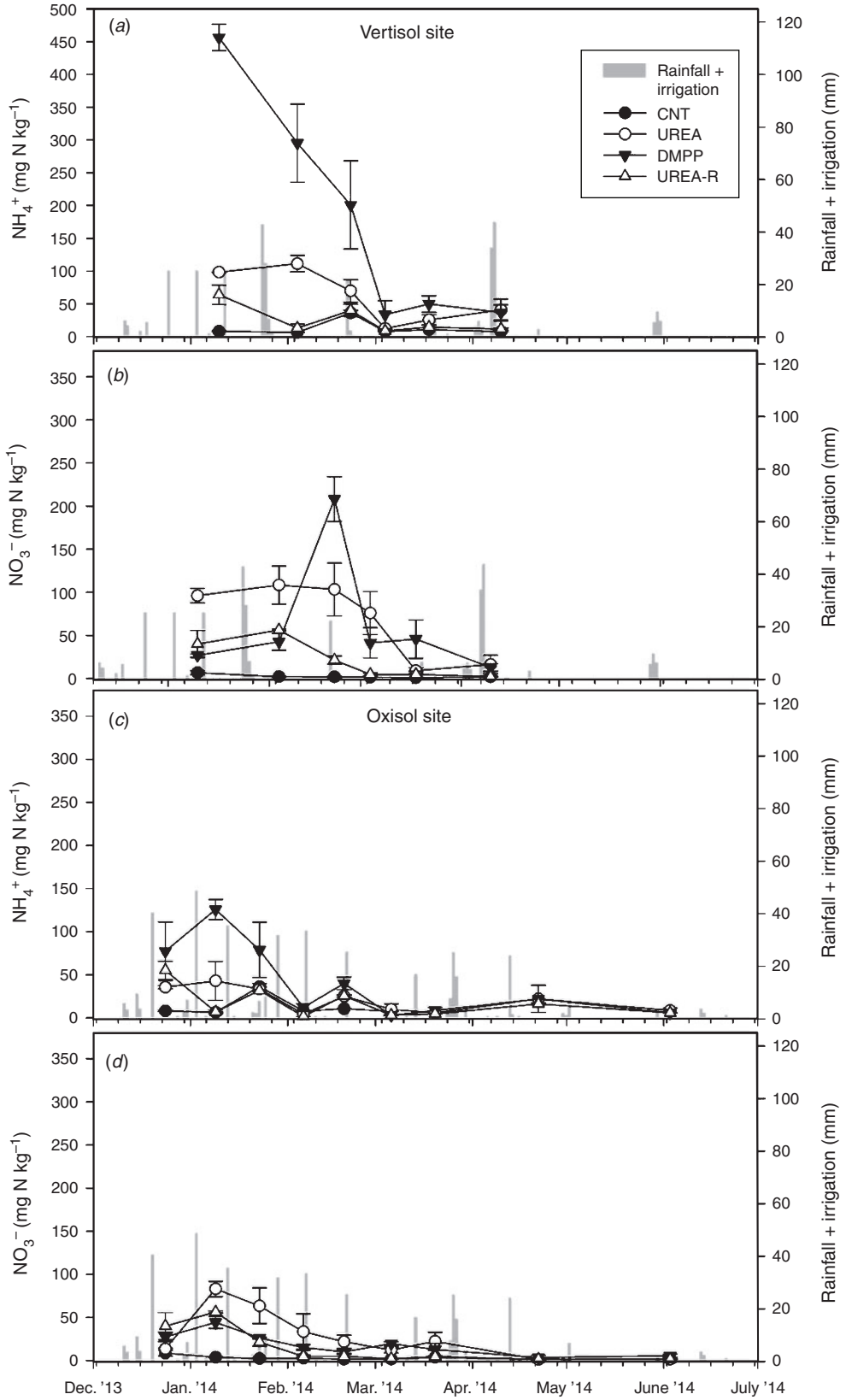

Fig. 2. Variation in soil ammonium (NH_4^+) and nitrate (NO_3^-) concentrations (0–20 cm) and daily rainfall and irrigation for the three treatments at the Vertisol (*a*, *b*) and Oxisol (*c*, *d*) sites during the 2013–14 sorghum cropping season.

concurrent increase of NO_3^- concentrations in both the UREA and DMPP, and to a lesser extent UREA-R, treatments support this hypothesis (Fig. 2).

As a result, the majority of NH_4^+ derived from urea hydrolysis was transformed into NO_3^- within ~8 weeks from fertilisation in the Oxisol (Fig. 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 NO_3-N into soil layers below the top 20 cm that was monitored during the growing season. This contributed to the absence of sharp peaks in NO_3-N accumulation at this site (Fig. 2*a*).

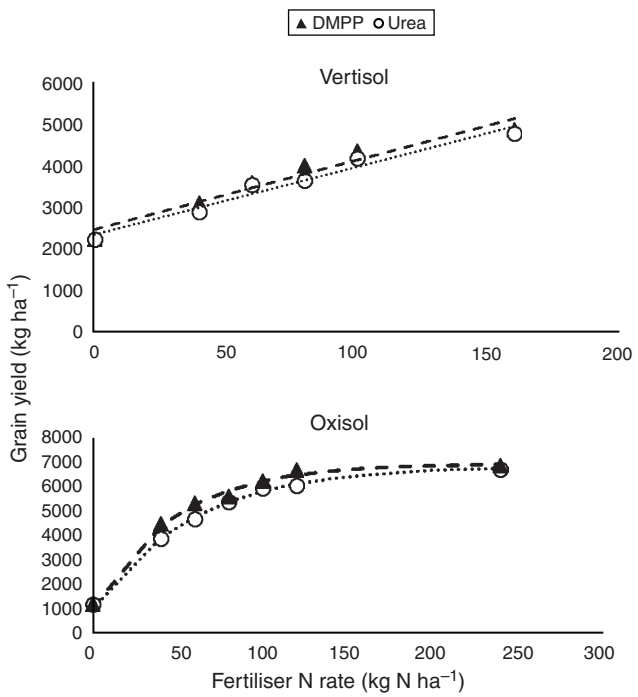

Fig. 3. Relationship between applied fertiliser N (as urea or urea with DMPP) and grain yield at the Vertisol and Oxisol sites in 2013–14. The N rates to produce 90% of N-unlimited grain yields were 100 (DMPP) to 120 (urea) kg N ha^{-1} on the Oxisol and >160 kg N ha^{-1} for both products on the Vertisol.

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 (Fig. 4). Conditions during this period were characterised by high soil temperatures, moist soils and elevated mineral N levels in the topsoil (Figs 1, 2). Notably, the substantial rainfall events later in the cropping season (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 up by plants, immobilised 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 of other studies on Australian subtropical summer cropping systems on Vertisols and Oxisols (Scheer *et al*. 2013, 2016*b*; De Antoni Migliorati *et al*. 2014).

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 the 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. 2*a*, *b*), a substantially longer period compared with that observed at the Oxisol site (Fig. 2*c*, *d*). Soil NO_3^- concentrations in the Vertisol increased and remained high until early March 2014, indicating that plant N assimilation from the top 20 cm 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 a 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 *AE* and higher N_2O emissions compared with the Oxisol site (Table 3, Fig. 3). This result is particularly significant when comparing crop responses to applied N fertiliser between sites (Fig. 3). Despite similar starting profile mineral N contents at sowing (60–62 kg N ha^{-1}; Table 2) the *AE*

Table 3. Cumulative N_2O fluxes, N_2O emission factors, grain yields (expressed as dry matter), agronomic efficiencies and N_2O intensities (mean ± s.e., $n = 3$) 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 lowercase letter indicate significant differences between treatments ($P < 0.05$) within the same site. Means denoted by a different lowercase letter set in italic 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 ± 0.17a, *a*		1.91 ± 0.13a, *ba*		
	UREA-R (80)	0.63 ± 0.05b, *bc*	0.5	3.20 ± 0.36ab, *cb*	18.54 ± 5.24a, *a*	0.19
	UREA (160)	1.30 ± 0.13c, *d*	0.7	4.19 ± 0.30b, *dc*	15.94 ± 4.17a, *a*	0.31
	DMPP (160)	0.44 ± 0.04ab, *ab*	0.1	4.26 ± 0.58b, *cde*	16.94 ± 4.11a, *a*	0.10
Oxisol	CNT	0.11 ± 0.02 a, *a*		1.08 ± 0.21a, *a*		
	UREA-R (80)	0.33 ± 0.1a, *ab*	0.3	4.71 ± 0.37b, *cde*	50.37 ± 2.50b, *b*	0.07
	UREA (120)	0.81 ± 0.19 a, *c*	0.4	5.27 ± 0.07b, *ed*	38.91 ± 3.0a, *b*	0.15
	DMPP (120)	0.31 ± 0.09 b, *ab*	0.1	5.83 ± 0.15b, *e*	46.20 ± 1.30ab, *b*	0.05

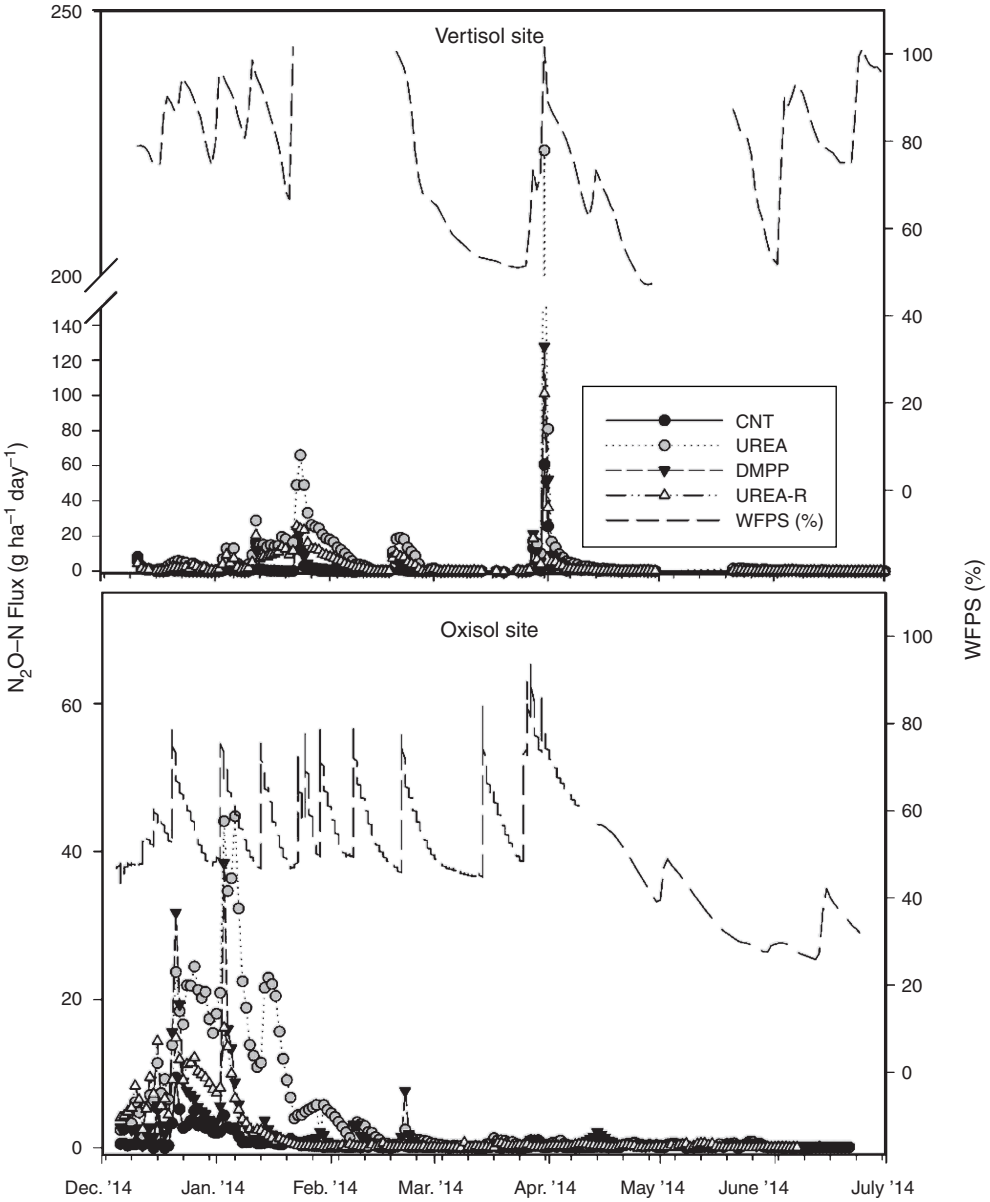

Fig. 4. Daily soil N_2O fluxes and water-filled pore space (WFPS, %) for the three treatments at the Vertisol (top) and Oxisol (bottom) sites during the 2013–14 sorghum cropping season. N_2O emissions in the two panels are reported using different scales.

of fertiliser N use at suboptimal N rates was consistently higher in the Oxisol than the Vertisol. Using the same N fertiliser rate across soil types (UREA-R, or 80 kg N ha^{-1}) as an example, the *AE* on the Oxisol was 50 kg of additional grain produced per kg of N applied, compared with 19 kg of additional grain produced 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 with the asymptotic response on the Oxisol with optimum N rates to achieve $Y_{90\%}$ at 100–120 kg N ha^{-1} (Fig. 3). Although significant amounts of N_2O were lost during the first months after fertilisation, the 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 (Fig. 4).

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 with the UREA treatment for ~8 weeks. However, at the end of this period the inhibitory effect clearly broke down in the Vertisol, with NO_3^- concentrations in the DMPP treatment changing from half those in the UREA treatment to more than double within a 2-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 topsoil (0–20 cm). DMPP effectively inhibited the oxidation of NH_4^+ to NO_3^- and extended the longevity of N fertiliser in the NH_4^+ form compared with conventional urea in both the Vertisol and Oxisol (Fig. 2*a*, *c*). Significantly, the results indicate that the different rainfall conditions at the two sites had little impact on the duration of the inhibitory effect, which lasted for ~8 weeks.

At both sites the NH_4^+ levels in the DMPP treatments started to decline from early January. The increased nitrification rates after 8 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 (Fig. 2*b*). This dynamic was less obvious at the Oxisol site, where the delayed rise of NO_3^- levels was likely due to a combination of plant uptake and leaching into deeper profile layers.

The longevity of DMPP was also reflected in the N_2O emissions patterns, and was 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 up until early to 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 90 mm of rainfall occurred in late March a further emissions pulse was recorded. However, by this stage the inhibitory effect of DMPP had largely expired and the magnitude of the N_2O emission pulse measured in the DMPP treatment on this occasion was comparable to 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 8 weeks triggered much shorter duration, and generally lower, N_2O emissions pulses in the DMPP than in the UREA treatment (Fig. 4), again consistent with the lower NO_3^- concentrations evident in the top 20 cm of the profile at that time (Fig. 2*d*). In late February, however, when the trial was irrigated with 20 mm, the N_2O emission pulse from the DMPP was comparable to that in UREA treatment. Even though the magnitude of these last emission pulses was limited due to the low concentrations of mineral N left in the soil (Fig. 2*c*, *d*), the absence of a 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 from other studies using DMPP on similar soil types in this region (De Antoni Migliorati *et al*. 2014; Scheer *et al*. 2014, 2016*a*) 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 of 60–90 days.

Overall, DMPP reduced the amount of N_2O losses by >60% in both the Vertisol and Oxisol, a result consistent with the 40–60% abatement rates reported in field trials and incubation studies (De Antoni Migliorati *et al*. 2014; Chen *et al*. 2010; Suter *et al*. 2010; 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 with conventional urea (Table 3). Emission factors from the UREA treatments (0.7 and 0.4% on the Vertisol and Oxisol respectively) were higher than for the suboptimal 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 (Australian Bureau of Meteorology 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 fertiliser 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 fertiliser N use efficiency or the amount of fertiliser required to achieve a given yield target (i.e. $Y_{90\%}$). There were slight improvements in *AE* in the DMPP compared with UREA treatments (by 6 and 19% on the Oxisol and Vertisol respectively; Table 3), but these differences were not significant. Similarly, where the experiment was able to adequately estimate a site yield potential in response to applied N (the Oxisol site; Fig. 3*b*) there was a suggestion of a lower critical N rate for the DMPP (100 kg N ha^{-1}) compared with 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), 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*. (2001*a*) 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 of grain for each kg of additional N

applied. This relatively low incremental *AE* suggests large amounts of N would need to be lost before a significant yield penalty would be detected from using urea rather than the DMPP-coated product.

As concluded by Lester *et al*. (2016), DMPP might have a greater scope to increase *AE* of urea in higher rainfall or irrigated production regions, or when high rates of N fertiliser 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 a 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 with conventional urea. Limited moisture availability during the study constrained the 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 *AE* of urea in summer seasons expected to have high rainfall rates, such as in *la Niña* phases of the El Niño Southern Oscillation 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 under which DMPP might have a substantial scope to increase grain yields in subtropical cereal cropping systems.

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