Research article

Effects of hotter, drier conditions on gaseous losses from nitrogen fertilisers

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ABSTRACT

Global warming is expected to cause hotter, drier summers and more extreme weather events including heat waves and droughts. A little understood aspect of this is its effects on the efficacy of fertilisers and related nutrient losses into the environment. We explored the effects of high soil temperature (>25 °C) and low soil moisture (<40% water filled pore space; WFPS) on emissions of ammonia (NH_3) and nitrous oxide (N_2O) following application of urea to soil and the efficacy of urease inhibitors (UI) in slowing N losses. We incubated soil columns at three temperatures (15, 25, 35 °C) and three soil moisture contents (20, 40, 60% WFPS) with urea applied on the soil surface with and without UIs, and measured NH_3 and N_2O emissions using chambers placed over the columns. Four fertiliser treatments were applied in triplicate in a randomised complete block design: (1) urea; (2) urea with a single UI (N-(n-butyl) thiophosphoric triamide (NBPT); (3) urea with two UI (NBPT and N-(n-propyl) thiophosphoric triamide; NPPT); and (4) a zero N control. Inclusion of UI with urea, relative to urea alone, delayed and reduced peak NH_3 emissions. However, the efficacy of UI was reduced with increasing temperature and decreasing soil moisture. Cumulative NH_3 emission did not differ between the two UI treatments for a given set of conditions and was reduced by 22–87% compared with urea alone. Maximum cumulative NH_3 emission occurred at 35 °C and 20% WFPS, accounting for 31% of the applied N for the urea treatment and 25%, on average for the UI treatments. Urease inhibitors did not influence N_2O emissions; however, there were interactive impacts of temperature and moisture, with higher cumulative emissions at 40% WFPS and 15 and 25 °C accounting for 1.85–2.62% of the applied N, whereas at 35 °C there was greater N_2O emission at 60% WFPS. Our results suggest that inclusion of UI with urea effectively reduces NH_3 losses at temperatures reaching 35 °C, although overall effectiveness decreases with increasing temperature, particularly under low soil moisture conditions.

1. Introduction

Ammonia (NH_3) emissions from agriculture contribute to air pollution (Erisman et al., 2008), threaten nitrogen (N) sensitive ecosystems, and can contribute to soil and water acidification (Guthrie et al., 2018). Agricultural sources account for 80–95% of global NH_3 emissions with c. 20% attributed to fertiliser use (Skorupka and Nosalewicz, 2021). Likewise, emissions of nitrous oxide (N_2O), which has a 100-year global warming potential 273 times that of carbon dioxide (IPCC et al., 2021) and also depletes tropospheric ozone (Sutton et al., 2013), are mainly from N fertilisers and manure applied to crops (IPCC et al., 2021).

Urea is the most used N fertiliser globally, and in 2020 it represented c. 50% of total synthetic N fertiliser use (IFASTAT, 2022). The dominance of urea is due to its high N content (46% N), low production and storage costs, and flexibility as a soil or foliar application (Cantarella et al., 2008; Matczuk and Siczek, 2021; Silva et al., 2017; Wang et al., 2020). However, it can be subject to high losses via NH_3 volatilisation following surface application (Matczuk and Siczek, 2021) with reported losses of up to 40% of the applied N (Cantarella et al., 2018; Folina et al., 2021). Urea hydrolysis results in a sharp increase in pH around the

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vicinity of urea granules, causing a shift from NH_4^+ towards volatile NH_3 (Harrison and Webb, 2001). The rate of hydrolysis and NH_3 loss depends on various factors including soil pH and soil pH and NH_4^+ buffering by reaction with the soil solid, as well as soil temperature and moisture (Cameron et al., 2013; Matczuk and Siczek, 2021). These factors affect urease enzyme activity (Matczuk and Siczek, 2021) and rates of movement of urea and ammoniacal-N and pH changes through the soil away from urea application zone (Rachhpal-Singh and Nye, 1986).

One strategy to reduce NH_3 emissions from urea is the co-application of urease inhibitors (Matczuk and Siczek, 2021). Urease inhibitors temporarily inhibit soil urease activity, retarding urea hydrolysis and minimising the pH increase around urea granules, thereby reducing subsequent NH_3 volatilisation from surface applied urea prior to its movement deeper into the soil by diffusion and mass flow. Globally, reductions in NH_3 emission from surface applied urea of >50% by UI have been reported across different soils and environmental conditions in both field and laboratory studies (Abalos et al., 2014; Li et al., 2018; Sha et al., 2020b). The effect of UI on N_2O emission from urea is uncertain. Several studies found decreased N_2O emission when UI was added with surface-applied urea (Saggar et al., 2013; Sanz-Cobena et al., 2016), whereas others observed an increase (Drury et al., 2017; Martins et al., 2017), or no significant change (Carswell et al., 2019; Wallace et al., 2018; Wang et al., 2020). Nitrous oxide emission is predominantly driven by the rate of N input (Qin et al., 2021) and may be non-linearly related to rates of nitrification and denitrification (Lin and Hernandez-Ramirez, 2021).

The stability and effectiveness of UI can be affected by soil properties (e.g., texture, microbial activity, pH) and temperature and moisture conditions (Folina et al., 2021). Watson et al. (1994) evaluated the UI NBPT (N-(n-butyl) thiophosphoric triamide) across 16 soil types and found it to be more effective in soils prone to NH_3 volatilisation, with high pH and low organic matter content. Similarly, Suter et al. (2011) reported that, under wheat or pasture, NBPT was more effective in alkaline than acidic soils, in soils with low urease activity, and at lower (5–15 °C) compared with higher (25 °C) soil temperatures. The half-life of NBPT is shorter at high temperatures, both in storage (Watson et al., 2008) and in soil (Cantarella et al., 2018).

Under current trajectories, mean global air temperatures may increase by up to 4 °C by 2100 as a result of human induced climate change (IPCC et al., 2021). Hotter and drier summers and more extreme weather events are predicted for Europe and the UK (Met office, 2023). To date, few studies have evaluated the effectiveness of UI in reducing NH_3 emission from surface applied urea at temperatures >25 °C and soil moisture below 40% water filled pore space (WFPS). There is insufficient evidence to make recommendations on the use of UI in regions experiencing temperatures up to 40 °C as well as under agricultural and ecological drought conditions. The use of UI under such conditions may be increasingly important, as agriculture intensifies around the globe to feed the growing world population (Global Food Security, 2023).

The objective of this study was, therefore, to assess the influence of higher temperatures across a range of soil moisture conditions on the effectiveness of UI in reducing NH_3 volatilisation from surface-applied urea, and the impact on N_2O emissions.

2. Materials and methods

2.1. Soil preparation and properties

Soil was obtained from a field under grass at Rothamsted Research – North Wyke in the southwest of England (45.294 N, 4.8096 W). The soil is Crediton series, a very stony, loamy, typical brown earth (Dystric Cambisol, FAO classification) derived from Permian and Carboniferous reddish breccia (National Soil Resources Institute, 2021). The field had received 145 kg ha^{-1} of NPK (25–5–5) fertiliser in the year it was sampled (2020). The average annual rainfall at North Wyke is 1042 mm and mean annual soil temperature is 12 °C. Representative soil samples

were collected from three separate locations within the field to a depth of 10 cm, with approximately 110 kg (dry weight basis) collected in total. The three soil samples formed the replicates used throughout the incubation experiment. After collection, the soil was sieved (<2 mm) and air dried to a constant weight. The main soil characteristics are given in Table 1.

Particle size distribution was measured using the method of Kettler et al. (2001). Soil pH at a soil:water ratio of 1:2.5 (w:v) was measured with a Jenway combination electrode and Model 3320 pH meter, cation exchange capacity by the cobalt hexamine method (ISO 23470, 2007), and total N and C by dry combustion (LECO TruMac Combustion analyser). Extractable soil ammonium and total oxidised N (nitrate plus nitrite) were determined by shaking 5 g soil in 50 cm^3 2 M KCl with 50 mg L^{-1} phenylmercuric acetate (KCl/PMA) on an orbital shaker (150 rev min^{-1}, 60 min), filtering (Sartorius grade 292 filter paper) and photometric analysis (Aquakem 250, Thermo Scientific, UK). Soil urea-N was analysed in the 2 M KCl extract as described by Greenan et al. (1995). Soil urease activity was measured after incubating 1 g of moist soil with 1.5 ml of 79.9 mM urea solution at 37 °C for 2 h, followed by extraction of NH_4–N in a mixture of 2 M KCl and 1 M HCl (KCl/HCl; Kandeler et al., 1999). Plant available P was measured by extraction with $NaHCO_3$ (Olsen et al., 1954) and colorimetry (Murphy and Riley, 1962).

2.2. Experimental design

The experiment consisted of four N fertiliser treatments: urea (U; Diamond Fertilisers, Lincolnshire, UK); urea with the urease inhibitor NBPT (treatment henceforth is US; Origin SUSTAIN®, Hertfordshire, UK); urea with two urease inhibitors (treatment henceforth is UL NBPT and N (n-propyl)-thiophosphoric triamide (NPPT); N-Shield® Diamond Fertilisers, Lincolnshire, UK); and a zero N control (C). The treatments were evaluated at three temperatures (15, 25 and 35 °C) and three soil moisture contents (20, 40 and 60% WFPS). Soil was packed into columns (10 cm depth, 10.3 cm diameter) at a bulk density of 1.1 g cm^{-3}. Air-dried soil was pre-wetted with deionized (DI) water to just below the desired WFPS before packing and compressing the soil in 2.5 cm layers, to a depth of 10 cm. After adding each layer of soil, sufficient DI water was added to bring that layer to the desired WFPS. The volume of DI water (V, cm^3) needed to achieve the desired WFPS ($WFPS_{desired}$, %) was calculated according to:

$$V = \frac{WFPS_{desired}}{100} \times V_{core} \left(1 - \frac{\rho_b}{\rho_p} \right) \qquad (1)$$

where V_{core} is the core volume (cm^3), ρ_b is bulk density (g cm^{-3}) and ρ_p is particle density (g cm^{-3}). To maintain soil WFPS over the incubation period, soil columns were watered to their specific weight every 48 h.

The experiment was conducted as a split plot design with a factorial treatment structure. There were several runs in a controlled

Table 1
Main soil properties.

Property	Value
Sand (%)	40.8 ± 1.35
Silt (%)	35.6 ± 0.82
Clay (%)	23.6 ± 0.59
pH (1:2.5 H_2O)	6.2 ± 0.02
Cation exchange capacity (meq kg^{-1} DW)	93.7 ± 3.19
Total C (g C kg^{-1} DW soil)	19.9 ± 0.5
Total N (g N kg^{-1} DW soil)	2.1 ± 0.04
Extractable nitrate + nitrite (mg N kg^{-1} DW soil)	11.4 ± 0.55
Extractable ammonium (mg N kg^{-1} DW soil)	7.8 ± 0.18
Extractable urea (mg N kg^{-1} DW soil)	0.4 ± 0.17
Urease activity (ug N g^{-1} h^{-1})	246.8 ± 34.15
Olsen P (mg P kg^{-1} DW soil)	2.4 ± 0.07

DW is dry weight, DI is deionized water and data are means ± standard error with ($n = 3$ except urease activity $n = 9$).

environment room to allow for different combinations of temperature and moisture and there were three blocks within each run. Temperature and moisture were applied blocks within runs and treatments were applied to chambers within each block. The soil incubation post fertilisation was conducted over thirty days after initially equilibrating the chambers at the designated temperature for seven days. After temperature equilibration, N fertiliser treatments were surface applied to the soil at a rate of 70 kg N ha^{-1} and gas sampling was initiated.

Additional soil columns (depth of 10 cm, and internal diameter of 4.3 cm) were prepared and equilibrated for 7 day at the experimental temperature and moisture settings to allow destructive soil sampling at t0 to be carried out. These cores were covered with Parafilm and punctured to allow gas exchange. At the end of the equilibration period, these cores were sub-sampled at 0–1.25, 1.25–2.5, 2.5–5 and 5–10 cm depth and extracted with KCl/PMA or KCl/HCl for determination of NH_4^+, total oxidised N and urea-N. Urease activity was also determined on a bulked depth sample. Total dissolved N was extracted from 10 g of the pre- and post-incubated soils using 50 ml 0.5 M K_2SO_4 solution and analysed with a TOC/TN analyser (Shimadzu UK Ltd, Milton Keynes, UK).

2.3. Gas flux measurements

Cumulative NH_3 emissions were determined from each chamber using an air throughflow system based on that of Misselbrook et al. (2005). Air was passed through 80 ml of 0.02 M H_3PO_4 prior to entering the soil chamber headspace (to remove any background NH_3 in the air) and through another 80 ml of 0.02 M H_3PO_4 after passing through the chamber headspace to capture volatilised NH_3. The air flow system for NH_3 measurement ran continuously through the incubation, except whilst acid traps were changed or when sampling for N_2O (which typically lasted 2.5 h). The inlet and outlet acid traps of each chamber were changed daily for the first 14 days of the experiment and 3 times weekly after that. The outlet acid trap solutions were transferred and made up to 100 ml volume in volumetric flasks, then subsampled and stored at 4 °C in the dark before analysis of NH_4–N using automated colorimetry (Aquakem 250 discrete photometric analyser; Thermo Scientific, UK).

Nitrous oxide fluxes were measured using a closed chamber approach, according to de Klein et al. (2012). Air (30 ml) was sampled from the chamber headspace after sealing the lid, at 0, 20, 40 and 60 min and transferred to 22 ml vials. To ensure equilibrium of pressure within the chambers, 30 ml of ambient air was added to the chamber head space following each sample removal through a side air entry point. This introduction of ambient air was accounted for in subsequent calculations. Gas sampling started one day prior to N fertiliser application. As for NH_3, N_2O sampling was conducted daily for the first 14 days following N fertiliser application and 3 times a week after that. The N_2O concentrations in the chamber headspace were measured using a PerkinElmer Clarus 580 Gas Chromatograph, fitted with an electron capture detector, and a flame ionisation detector housing a methanizer.

2.4. Data analyses

The rate of NH_3 emission (F, g N m^{-2} h^{-1}) was estimated according to (Misselbrook et al., 2005):

$$F = \frac{XV}{At} \tag{2}$$

where X is the ammoniacal-N concentration measured from the outlet acid trap solution (g l^{-1}), V is the volume of this solution (l), A is the soil surface area (m^2), and t is the duration of the sampling period (hours). The flux during periods when NH_3 sampling was paused was calculated as the average of the flux in the period immediately before and immediately after the air flow was switched off. Total NH_3 emission (g

NH_3–N) for the sampling period was determined as XV. The cumulative NH_3 emission throughout the incubation (following fertiliser application) was calculated by summing emissions for each sampling period. The percentage of the urea-N applied to each chamber lost as NH_3–N was calculated according:

$$\% \ NH_3 \ loss = \frac{NH_3 \ emitted_{net}}{applied \ N} \times 100 \tag{3}$$

where NH_3 emitted$_{net}$ (g N m^{-2}) is the emission value obtained after subtracting the control treatment (no urea-N applied) from the total emission for each sampling period, and applied N is the amount of N applied (g) as urea.

Nitrous oxide fluxes were calculated from the linear increase in N_2O concentrations between t = 0 and t = 60 min (de Klein et al., 2012), as follows:

$$F = H\frac{dC}{dt} \tag{4}$$

where F is N_2O flux (ug N_2O–N m^{-2} s^{-1}), H is the ratio of the internal chamber volume (m^3) to soil surface area (m^2), C is the N_2O concentration in the chamber (mg N l^{-1}), and t is time of sampling. The designation dC/dt is used to represent the time rate of change in C (slope of the linear regression). Cumulative N_2O emissions between two sampling events were calculated as the product of the mean flux rate and the time interval between the measurements. These were then summed to derive cumulative gas loss for the duration of the experiment.

Treatment effects on the cumulative NH_3 and N_2O emissions, as well as the temperature and moisture effects on the emission reduction potential of the urease inhibitors were evaluated using a linear mixed model (REML) with block ((experiment.replicate)/chamber/sampling number) as random effect and fixed term as (temperature*moisture*fertiliser treatment*day). Pairwise comparisons of the data were made using the least significant difference test, with differences between treatments considered significant where p < 0.05. All data required transformation (square root) to meet model assumptions of data normality. Statistical analyses were carried out using GenStat (21st edition).

3. Results

3.1. Temperature and soil moisture effects on daily ammonia flux

Daily NH_3 flux was significantly impacted by fertiliser treatment, temperature, soil moisture and their interaction (Tables 2 and 3). Flux from the control treatment was negligible at all temperatures and soil moisture conditions. Average daily flux (across the 30-d measurement) for U increased with increasing temperature and decreased with increasing soil moisture (Fig. 1). The average daily flux for U was generally greatest at 35 °C (0.10 g NH_3–N m^{-2} d^{-1}) followed by 25 °C and 15 °C under the same WFPS, except at 20% WFPS where the average daily flux at 15 and 25 °C was not statistically different (0.07 and 0.08 g NH_3–N m^{-2} d^{-1}, respectively). However, at 20% WFPS, the peak emissions at 25 and 35 °C were not significantly different, but were 32% greater, on average, than that at 15 °C. At 40% WFPS, average daily flux for U was 0.03, 0.05 and 0.07 g NH_3–N m^{-2} d^{-1} at 15, 25 and 35 °C, respectively, with peak emission being similar at 35 °C and 25 °C, 48% greater than that at 15 °C. At 60% WFPS, average daily flux was 0.01, 0.03 and 0.04 g NH_3–N m^{-2} d^{-1} at 15, 25 and 35 °C, respectively, with peak emissions at 25 and 35 °C greater by 75 and 65%, respectively, compared to 15 °C. Most emissions from U occurred during the first 14 days after N addition, with emission peaks occurring on day 1 at 25 and 35 °C and on day 2 at 15 °C (Fig. 1).

The inclusion of UI with urea significantly ($p < 0.001$) reduced the average daily NH_3 flux compared to untreated urea and peak emission was generally reduced and delayed (Fig. 1). The UI treatments, US and

Table 2
Daily and cumulative NH₃–N and N₂O–N emissions according to linear mixed effects model in response to temperature, moisture, and nitrogen source.

		NH3 flux (g N m−2 d−1)	Cumulative NH3 loss (g N m−2)	N2O flux (g N m−2 d−1)	Cumulative N2O loss (g N m−2)
Temperature (°C)					
		LSD (0.0035)	LSD (0.0564)	LSD (0.0034)	LSD (0.0655)
15		0.4733 ± 0.0011 [0.0158]	0.4497 ± 0.0190 [0.3271]	0.4676 ± 0.0011 [0.0088]	0.4287 ± 0.0220 [0.1701]
25		0.4786 ± 0.0011 [0.0219]	0.5987 ± 0.0190 [0.5028]	0.4684 ± 0.0011 [0.0095]	0.4540 ± 0.0223 [0.1901]
35		0.4933 ± 0.0012 [0.0359]	0.8476 ± 0.0190 [0.9253]	0.4682 ± 0.0012 [0.0094]	0.4153 ± 0.0219 [0.1604]
Moisture (% WFPS)					
		LSD (0.0034)	LSD (0.0564)	LSD (0.0034)	LSD (0.0655)
20		0.0439 ± 0.0034 [0.0439]	0.8544 ± 0.0190 [0.9776]	0.4675 ± 0.0012 [0.0087]	0.4156 ± 0.0223 [0.1531]
40		0.0221 ± 0.0018 [0.0221]	0.5787 ± 0.0190 [0.4793]	0.4706 ± 0.0011 [0.0116]	0.4693 ± 0.0220 [0.2041]
60		0.0121 ± 0.0011 [0.0121]	0.4629 ± 0.0190 [0.2983]	0.4665 ± 0.0011 [0.0077]	0.4131 ± 0.0219 [0.1634]
Fertiliser					
		LSD (0.0031)	LSD (0.0566)	LSD (0.0030)	LSD (0.0544)
C		0.4593 ± 0.0012 [0.0010]	0.1431 ± 0.0205 [0.0228]	0.4662 ± 0.0011 [0.0075]	0.3853 ± 0.0208 [0.1418]
US		0.4811 ± 0.0012 [0.0229]	0.7021 ± 0.0205 [0.6105]	0.4692 ± 0.0011 [0.0104]	0.4501 ± 0.0208 [0.1919]
UL		0.4820 ± 0.0012 [0.0240]	0.6482 ± 0.0205 [0.5566]	0.4681 ± 0.0012 [0.0092]	0.4404 ± 0.0213 [0.1742]
U		0.5017 ± 0.0012 [0.0474]	1.0347 ± 0.0205 [1.1504]	0.4687 ± 0.0011 [0.0098]	0.4549 ± 0.0208 [0.1862]
Significance of fixed effects					
Temperature		<0.001	<0.001	0.919	0.517
Moisture		<0.001	<0.001	0.058	0.148
Fertiliser		<0.001	<0.001	0.258	0.051
Significance of interaction effects					
Temperature × moisture		<0.001	0.007	0.055	0.003
Temperature × fertiliser		<0.001	<0.001	0.079	0.024
Moisture × fertiliser		<0.001	<0.001	0.173	0.071
Temperature × fertiliser × moisture		<0.001	0.187	0.983	0.911

Values are predicted mean values ± standard error ($n = 3$) from REML analysis, with real means shown within brackets. The least signicant difference value were determied at $p < 0.05$.

Table 3
Mean daily NH₃–N emissions under varying temperature, moisture, and nitrogen sources.

Fertiliser		Daily NH₃ Flux (g N m⁻² d⁻¹)		
	Moisture (% WFPS)	20	40	60
	Temperature (°C)			
C	15	0.4586 ± 0.0034 [0.0003]	0.4588 ± 0.0034 [0.0005]	0.4588 ± 0.0034 [0.0005]
	25	0.4596 ± 0.0034 [0.0013]	0.4594 ± 0.0034 [0.0011]	0.4596 ± 0.0033 [0.0013]
	35	0.4595 ± 0.0040 [0.0012]	0.4603 ± 0.0034 [0.0019]	0.4593 ± 0.0033 [0.0010]
US	15	0.4953 ± 0.0034 [0.0375]	0.4633 ± 0.0034 [0.0047]	0.4603 ± 0.0034 [0.0019]
	25	0.4983 ± 0.0034 [0.0407]	0.4688 ± 0.0034 [0.0099]	0.4691 ± 0.0033 [0.0104]
	35	0.5555 ± 0.0041 [0.1062]	0.4955 ± 0.0034 [0.0359]	0.4800 ± 0.0033 [0.0209]
UL	15	0.4929 ± 0.0034 [0.0345]	0.4627 ± 0.0034 [0.0042]	0.4600 ± 0.0034 [0.0017]
	25	0.4834 ± 0.0034 [0.0255]	0.4696 ± 0.0034 [0.0107]	0.4669 ± 0.0033 [0.0082]
	35	0.5726 ± 0.0038 [0.1260]	0.5057 ± 0.0034 [0.0472]	0.4771 ± 0.0033 [0.0179]
U	15	0.5233 ± 0.0034 [0.0747]	0.4889 ± 0.0034 [0.0314]	0.4690 ± 0.0034 [0.0104]
	25	0.5238 ± 0.0034 [0.0780]	0.5007 ± 0.0034 [0.0466]	0.4880 ± 0.0033 [0.0333]
	35	0.5328 ± 0.0039 [0.0767]	0.5205 ± 0.0034 [0.0645]	0.4942 ± 0.0033 [0.0363]

Values are predicted mean values ± standard error ($n = 3$) from REML analysis, with real means shown within brackets. The least signicant difference value was 0.0097 at $p < 0.05$.

emission peak relative to U at all temperatures and soil moistures, with the delay decreasing as temperature increased, being 4 days at 15 °C, 3 days at 25 °C, and 2 days at 35 °C. At 35 °C, across all soil moistures and for U and UI treatments, NH₃ emissions persisted for up to 20–25 days after treatment application, whereas at 15 and 25 °C NH₃ emissions returned to baseline (that of the C treatment) by 14 days. Prolonged emission up to 19 days was also noticeable at 15 °C and 20% WFPS for UI treatments.

3.2. Temperature and soil moisture impact on cumulative ammonia emissions

Cumulative NH₃ emissions were significantly affected by temperature, soil moisture and fertiliser treatment (Table 2), and all two-way interactions between these three factors were also significant. Cumulative NH₃ emission was negligible from the control treatment but increased with increasing temperature and decreasing soil WFPS for all fertiliser treatments (Fig. 2). The greatest cumulative NH₃ emissions were from U at 20% WFPS, at 1.42, 1.72 and 2.19 g NH₃–N m⁻² at 15, 25 and 35 °C, respectively, accounting for 20, 24 and 31%, respectively, of the applied urea-N. At 40% WFPS, cumulative NH₃ emissions were 0.60, 1.02 and 1.42 g NH₃–N m⁻² at 15, 25 and 35 °C, respectively, accounting for 8, 14 and 19%, respectively, of the applied urea-N. At 60%
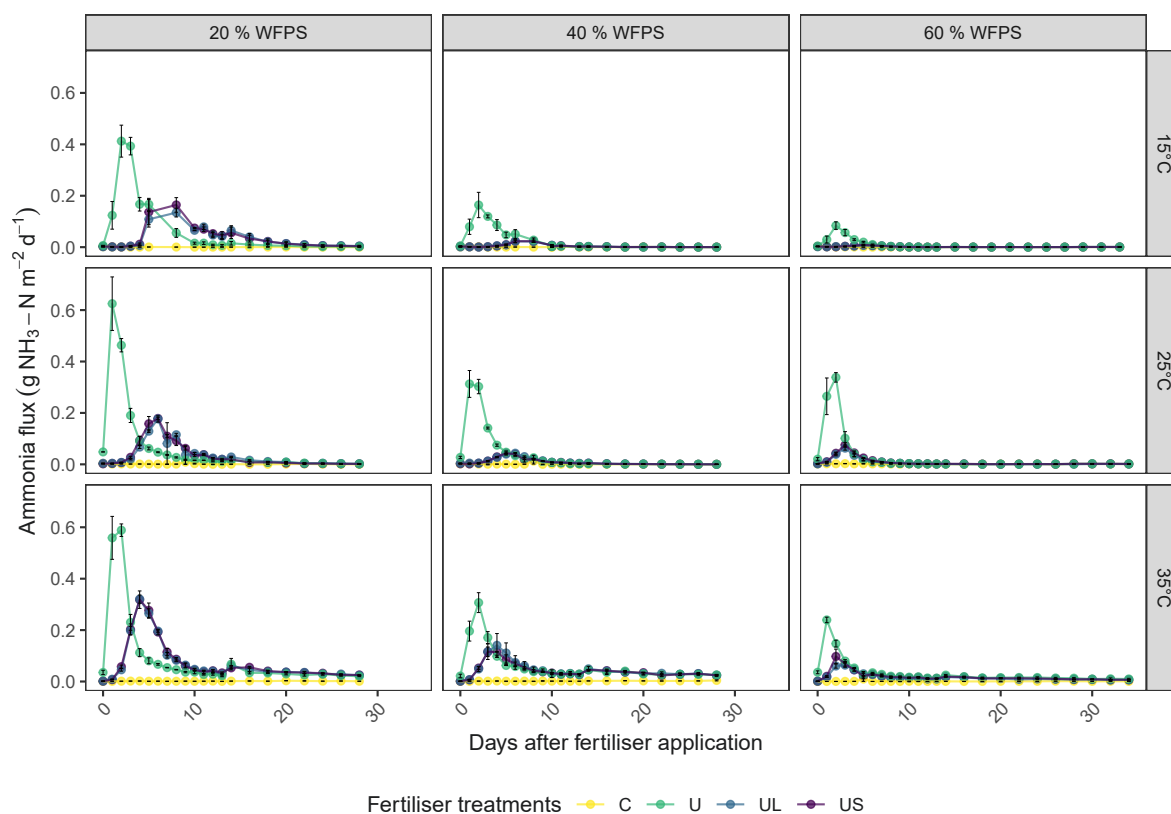
UL did not differ significantly at all temperatures and soil moistures. The reduction in peak emission for UI treatments, compared with U, typically decreased with increasing temperature and with decreasing soil moisture (Fig. 1). At 20% WFPS, UI reduced peak emission relative to U by 64, 72, and 46% at 15 °C, 25 °C and 35 °C, respectively; at 40% WFPS, respective reductions were 86, 86, and 58%, and at 60% WFPS, respective reductions were 91, 80 and 60%. The average daily NH₃ flux for the UI treatments (US and UL treatments were not significantly different) was 0.04, 0.04 and 0.08 g NH₃–N m⁻² d⁻¹ at 15, 25 and 35 °C, respectively at 20% WFPS, 0.004, 0.01 and 0.05 g NH₃–N m⁻² d⁻¹, respectively at 40% WFPS, and 0.002, 0.01 and 0.02 g NH₃–N m⁻² d⁻¹, respectively at 60% WFPS. Inclusion of UI with U delayed the NH₃

Fig. 1. Ammonia flux (g NH_3–N m^{-2} d^{-1}) over thirty days following treatment application, of the control (C), urea (U) and U with urease inhibitors (UL and US) at 15, 25 and 35 °C and at 20, 40 and 60% water filled pore space (WFPS). Datapoints represent mean values and vertical error bars depict standard error of mean (*n* = 3).

WFPS, cumulative NH_3 emissions were 0.25, 0.83 and 0.91 g NH_3–N m^{-2} at 15, 25 and 35 °C, respectively, accounting for 3, 11 and 13%, respectively, of the applied urea-N.

At all temperatures and soil moistures, cumulative NH_3 emissions were significantly greater from U relative to the UI treatments (Fig. 2), which were equally effective in reducing the emission. However, the efficacy of the UI in reducing emissions decreased with increasing temperature and with declining soil moisture. The inclusion of UI with urea (averaged across both UI treatments) reduced cumulative NH_3 losses relative to urea alone by 87, 86 and 52% at 15 °C, by 75, 79 and 50% at 25 °C, and by 48, 33, 22% at 35 °C for 20, 40 and 60% WFPS, respectively.

3.3. Temperature and moisture effect on nitrous oxide emission from N treatments

There was no significant effect of fertiliser treatment or temperature on average daily N_2O flux (Table 2). However, there was a significant effect of moisture and the interaction between temperature and moisture. Average daily N_2O–N flux at 40% WFPS was significantly greater than that at 20 or 60% WFPS, which were not significantly different from each other. At the lowest incubation temperature of 15 °C, average daily N_2O–N flux was significantly greater at 40% WFPS than at 20 and 60% WFPS, whereas at 25 °C, there was no significant difference in the average daily N_2O–N flux at 40 and 20% WFPS but both were greater than that at 60% WFPS (Fig. 3). At the highest incubation temperature of 35 °C, there was no significant effect of soil moisture.

Cumulative N_2O–N emission was significantly affected by fertiliser treatment and the interactions between temperature and fertiliser treatment and temperature and moisture (Table 2). The C treatment had significantly less cumulative N_2O–N losses than US, UL and U which were not significantly different from each other. Additionally, the

interaction between fertiliser treatment and temperature was predominantly related to the differences between the C treatment and the other fertiliser treatments (Fig. 4). Across all fertiliser N treatments, the cumulative N_2O emission at 15 °C was greater at 40% WFPS compared to 20% WFPS, however, both were not significantly different from cumulative N_2O emission at 60% WFPS. At 25 °C, cumulative N_2O–N emission was significantly greater at 40 and 20% WFPS relative to 60% WFPS. At 35 °C, cumulative emission at 60% WFPS was significantly greater than that at 40 and 20% WFPS. Averaged across the U, US and UL treatments, at 15 °C net cumulative N_2O emission accounted for 0.00, 2.38 and 1.89% of the applied N, at 20, 40 and 60% WFPS, respectively (Fig. 4). At 25 °C cumulative net emission accounted for 0.53, 1.76, and 1.80% of applied N, and 0.00, 0.32, and 0.41% of applied N at 35 °C, at 20, 40 and 60% WFPS, respectively.

3.4. Soil urease activity, ammonium, nitrate, and total N

Soil urease enzyme activity after 7 days preincubation was significantly affected by the interaction between temperature and soil moisture ($p < 0.030$). Urease activity was generally significantly higher at 35 °C (286 and 178 µg N g^{-1} h^{-1}) and 25 °C (201 and 102 µg N g^{-1} h^{-1}) under 20 and 40% WFPS, respectively, compared to 60% WFPS where there was no significant difference between temperature. Moisture effect on urease activity was not consistent and varied at each temperature.

Following incubation, soil total dissolved N content was greater for the N fertiliser treatments, which did not differ significantly, than the C treatment across all temperatures and soil moistures (Fig. 5; soil NH_4^+-N and NO_3^--N concentrations are presented in Supplementary Figs. S1 and S2). The N concentrations decreased with soil depth, and at 10 cm there were no significant differences between the C and other N treatments for any N form. Greatest retention of applied N was at 15 °C and 20% WFPS, and least retention of N at 15 °C and 60% WFPS and 35 °C and 40%
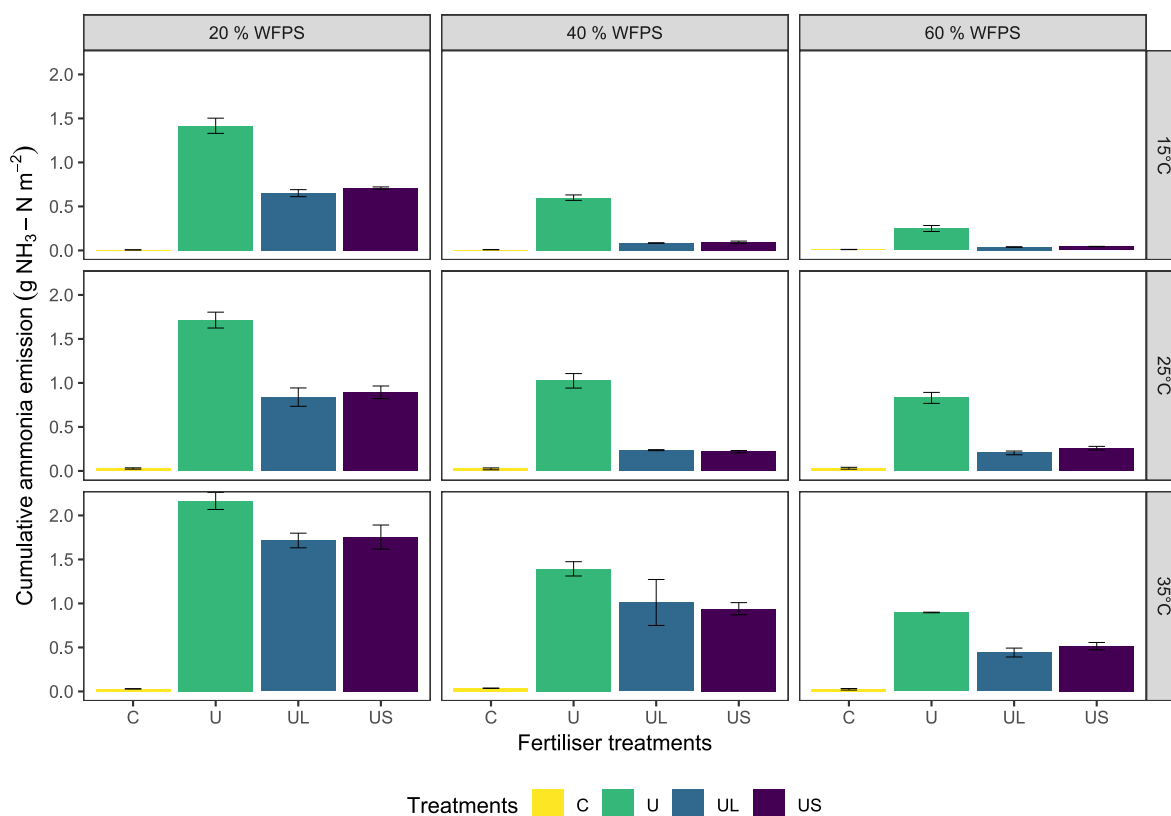
Fig. 2. Cumulative ammonia emissions (g NH_3–N m^{-2}) over the thirty-day incubation period, after application of the control (C), urea (U) and urea with urease inhibitor (UL and US) treatments at 15, 25, 35 °C and 20, 40 and 60% water filled pore space (WFPS). Datapoints represent mean values and vertical bars depict standard error of the mean ($n = 3$).

WFPS.

4. Discussion

4.1. Temperature and moisture effects on NH_3 loss from urea

The following processes need to be considered to understand the combined effects of temperature and moisture on NH_3 loss from urea applied to soil (for a mechanistic model, see Rachhpal-Singh and Nye, 1986). Urea dissolves rapidly in the soil solution and is then hydrolysed to ammonium (NH_4^+) and bicarbonate (HCO_3^-) ions in the following reaction catalysed by urease:

$$CO(NH_2)_2 + CO_2 + 3H_2O \rightarrow 2NH_4^+ + 2HCO_3^-$$
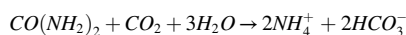
The HCO_3^- ions so formed tend to raise the soil pH, and this favours conversion of NH_4^+ to NH_3, which is volatile.

volatilization

↑

$- - - - - - - - - - - - - - -$ **atmosphere**

soil

$NH_{3(g)}$

⇅ ↑
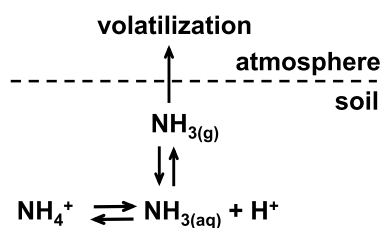
$NH_4^+ \rightleftarrows NH_{3(aq)} + H^+$

'Volatilisation' is the transfer of NH_3 gas from the soil surface to the atmosphere above. The reaction scheme above shows that during volatilisation, NH_4–N (i.e., $NH_4^+ + NH_3$) at the soil surface is depleted, and H^+ ions will accumulate tending to decrease the soil pH, but they will be neutralized by diffusion of HCO_3^- ions in. The overall rate of volatilisation therefore depends on the following linked rate processes, each of

which is to some extent influenced by temperature and moisture.

1. Movement of dissolved urea into the soil and its simultaneous hydrolysis;
2. Movement of NH_4–N away from the zone of urea hydrolysis and towards the depletion zone at the soil surface, with simultaneous diffusion of gaseous NH_3 in the soil air and its transfer across the soil-atmosphere boundary;
3. Movement of acids and bases (principally H_3O^+–H_2O and H_2CO_3–HCO_3^-) to and from the zones of urea hydrolysis and NH_4–N depletion.

A decrease in soil moisture will tend to decrease rates of diffusion of dissolved urea, NH_4–N and acids and bases through the soil, but it will also increase the soil air space, and therefore the gaseous diffusion of NH_3 to the soil surface. We have found increased volatilisation with deceased soil moisture content in our experiments, suggesting the latter effect is the more important. Likewise, Rachhpal-Singh and Nye (1986) found by modelling that volatilisation increased with decreases in soil moisture content below field capacity. In our experimental system the soil moisture content was constant. But under evaporating conditions, mass flow of dissolved reactants with water towards the soil surface will increase rates of volatilisation, and vice versa for infiltration (Freney et al., 1981; Kirk and Nye, 1991).

Up to some temperature optimum, urease activity and hence urea hydrolysis will increase with temperature (Suter et al., 2011). Rates of diffusion of NH_3 gas and the dissolved reactants will tend to increase with soil temperature, as will NH_3 transfer across the soil-atmosphere boundary (Kirk and Nye, 1991). The solubility of NH_3 gas decreases with increasing temperature, and the dissociation of NH_4^+ increases, both of which will favour increased volatilisation (Kirk and Nye, 1991).

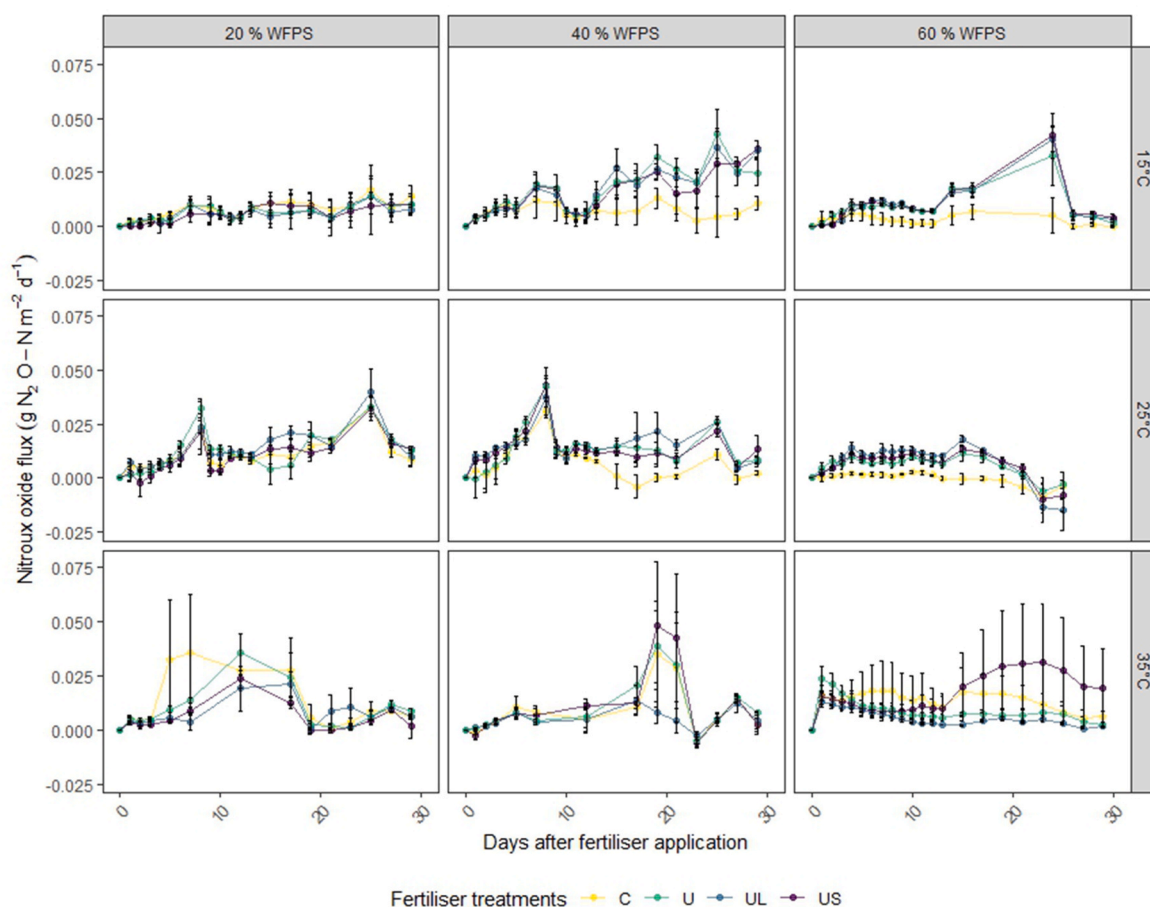In our incubation study, we observed the lowest emissions from the

Fig. 3. Nitrous oxide flux (g N_2O–N m^{-2} d^{-1}) over thirty days following treatment application, of the control (C), urea (U) and U with urease inhibitors (UL and US) at 15, 25 and 35 °C and at 20, 40 and 60% water filled pore space (WFPS). Datapoints represent mean values and vertical error bars depict standard error of mean (n = 3).

soils with the highest soil moisture (60% WFPS) and the highest emissions under the driest soil (20% WFPS). Similarly, Yerokun (1997) reported higher NH_3 volatilisation when soil moisture was maintained at 25% field capacity, compared to soil moisture adjusted to 100% field capacity. McGarry et al. (1987) also reported NH_3 losses to increase with decreasing soil moisture content. Because of the hygroscopic nature of urea, its granules readily dissolve on the soil surface, even where soil moisture is low, allowing hydrolysis of urea and therefore NH_3 volatilisation (Dari et al., 2019).

As observed by Li et al. (2017) in a sub-humid continental climate in China, initial conditions of light precipitation (2–4 mm) with high relative humidity (60–78%) were favourable for NH_3 volatilisation. Low rainfall and high air humidity can provide sufficient moisture for urea hydrolysis and the desorption of ammoniacal-N from the soil but not enough to move urea and NH_4^+/NH_3 into the soil profile, resulting in substantial NH_3 volatilisation (Craig and Wollum, 1982). However, conditions of low relative air humidity (35–50%) and heavy rainfall (60 mm) after N top dressing can limit NH_3 volatilisation (Li et al., 2017) because urea is displaced deeper into the soil. Under high soil moisture, there is greater solubilisation and diffusion of urea into the soil, thus reducing urea hydrolysis on the soil surface and susceptibility to volatilisation (Carswell et al., 2019; Holcomb et al., 2011). An incorporation of urea to a depth of 5 cm or more can help to minimize NH_3 volatilisation (Fenn and Miyamoto, 1981; Holcomb et al., 2011). Scenarios of wet and drying soil events can also greatly influence NH_3 emissions as reported by Engel et al. (2011), with substantial NH_3 losses (30–44% of the applied N) when urea was applied to a wet or damp soil surface followed by a drying soil due to low rainfall, but much lower losses

(<10% applied N) when the urea was applied to a dry soil surface followed by abundant rainfall in a winter wheat field. These findings illustrate the importance of wetting and drying soil events for NH_3 emissions from urea.

4.2. The efficacy of urease inhibitors in reducing ammonia losses as affected by temperature and moisture

The peaks in NH_3 emission were delayed and reduced where urea was treated with UI in this study, as reported elsewhere (e.g., Martins et al., 2017; Tian et al., 2015; Wang et al., 2020). In our study, the inclusion of UI (as US and UL) with urea delayed the emission peaks by 2–4 days after fertiliser addition. A delay in peak emission of 1 day through use of NBPT was observed by Wang et al. (2020) for a loamy loess soil (pH 7.2) at 55% WFPS and incubated at 25 °C for 30 days, whereas Soares et al. (2012) reported a longer delay of 7–9 days for a Red Latosol (pH 5.9) at 60% WFPS and incubated at 25 °C for 22 days. A metanalysis by Silva et al. (2017) showed that inclusion of NBPT delayed peak NH_3 loss by 3.5 days on average across a variety of climatic regions (temperate, cold, tropical), with peak NH_3 emission occurring on average at day 4.8 and 8.3 after surface application of urea and urea treated with NBPT, respectively. In a study by Abalos et al. (2012), UI did not delay the NH_3 peak emission, but the peak from the urea treated with NBPT was reduced by a factor of 2.4 compared with that from urea, and Wang et al. (2020) reported peak NH_3 emission of 0.27 g NH_3–N m^{-2} d^{-1} for NBPT treated urea, compared with 0.84 g NH_3–N m^{-2} d^{-1} for urea. Our study is consistent with these findings, as UI reduced peak NH_3 emission by >40% relative to urea alone, across all temperature
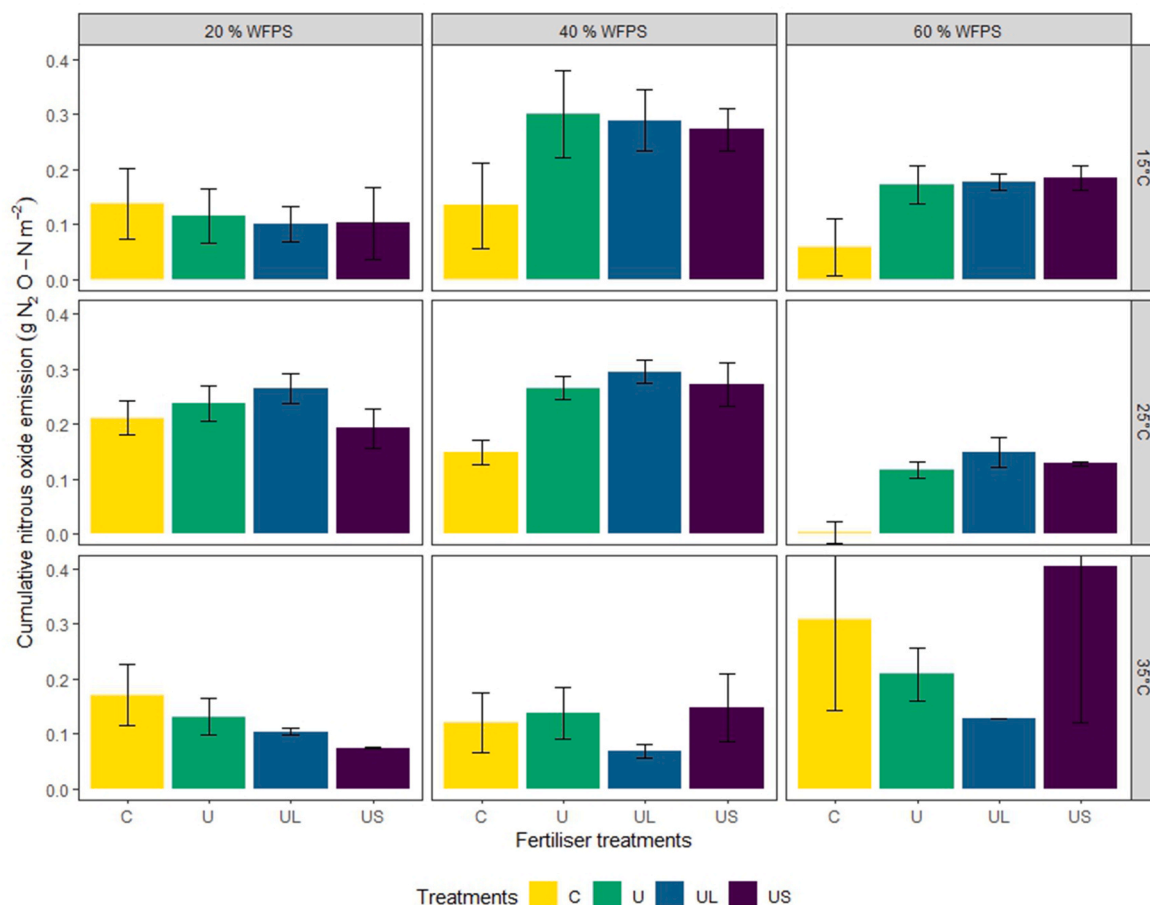
Fig. 4. Cumulative nitrous oxide emissions (g N_2O–N m^{-2}) over the thirty-day incubation period for the control (C), urea (U) and urea with urease inhibitor (UL and US) treatments at 15, 25, 35 °C and 20, 40 and 60% water filled pore space (WFPS). Datapoints represent mean values and vertical bars depict standard error of the mean ($n = 3$).

and moisture conditions.

Application of UI delays urea hydrolysis and slows NH_4^+ release and increase in soil pH, therefore delaying and reducing the peak NH_3 emission rate and enabling urea movement deeper into the soil (Suter et al., 2011; Tasca et al., 2011). The inclusion of NBPT and NBPT/NPPT with urea has been shown to greatly reduce urease activity for up to 15 days after urea application, depending on soil temperature and soil type (Li et al., 2017; Sanz-Cobena et al., 2011).

Most of the NH_3–N losses from our experiment happened within the first 14–15 days after N application. Nonetheless, at 35 °C, despite the evident delayed and reduced NH_3 emission by UI over U, NH_3–N emissions for both U and UI treatments continued for up to 20 days (particularly at 20 and 40% WFPS). Similar prolonged NH_3 emissions from both urea and urea plus UI was reported by Tian et al. (2015) in a subtropical cotton field, where major losses of NH_3 occurred within 30 days but persisted up to 40 days at high mean temperature of 31.8 °C and 14.4–15.1% moisture (w/w). The prolonged emissions in our study could be due in part to higher concentrations of NH_4^+ in the upper soil surface (0–1.25 cm depth) after urea hydrolysis at 35 °C and low WFPS (20 and 40%) as observed from soil analysis at the end of experiments. The combined effect of high temperature and low moisture will have favoured volatilisation by upward gaseous diffusion of NH_3 (Siman et al., 2020). Several authors have reported prolonged NH_3 emission from urea in dry soils at various temperatures (5–25 °C), suggesting low moisture was the driving factor and not temperature (Holcomb et al., 2011).

Similar to the effect on peak emission rate, cumulative NH_3 emission over 30 days was significantly lower (by 22–87%) from the UI

treatments relative to urea alone, consistent with reductions reported elsewhere (Carswell et al., 2019; Silva et al., 2017; Tian et al., 2015). However, it was evident from our study that the efficacy of the UI decreased with increasing temperature and with decreasing soil moisture. A similar temperature effect, across the range 5–25 °C was reported by Suter et al. (2011) for applications to wheat and pasture soils in south-eastern Australia. Siman et al. (2020) observed only limited efficacy of NBPT (c. 8% emission reduction) at high temperature (45 °C) and intermediate soil moisture (around 10% gravimetric water content). At elevated temperature, NBPT undergoes fast degradation, shortening the inhibition effect and leading to greater NH_3 volatilisation (Clay et al., 1990; Engel et al., 2011). In addition, at high temperatures, the lower UI efficacy can be due to the rate of urea hydrolysis exceeding the rate of NBPT conversion into its oxygen analogue NBPTO (N-(n-butyl) phosphoric triamide), which is the direct inhibitor of urease (Oliveira et al., 2014). Our findings show a clear difference in UI efficacy between 25 and 35 °C, in contrast to Siman et al. (2020), who suggested that the decomposition of NBPT to NBPTO in soil only occurs at temperatures above 35 °C. The increase in soil moisture enhanced UI efficacy and reduced NH_3 volatilisation, especially at low temperature in our study. However, NBPT efficacy can be limited at WFPS above 65% (Sanz-Cobena et al., 2012). For instance, in subtropical agroecosystems in Brazil, Ribeiro et al. (2020) found UI had little effect during winter because of significant rainfall after N application.
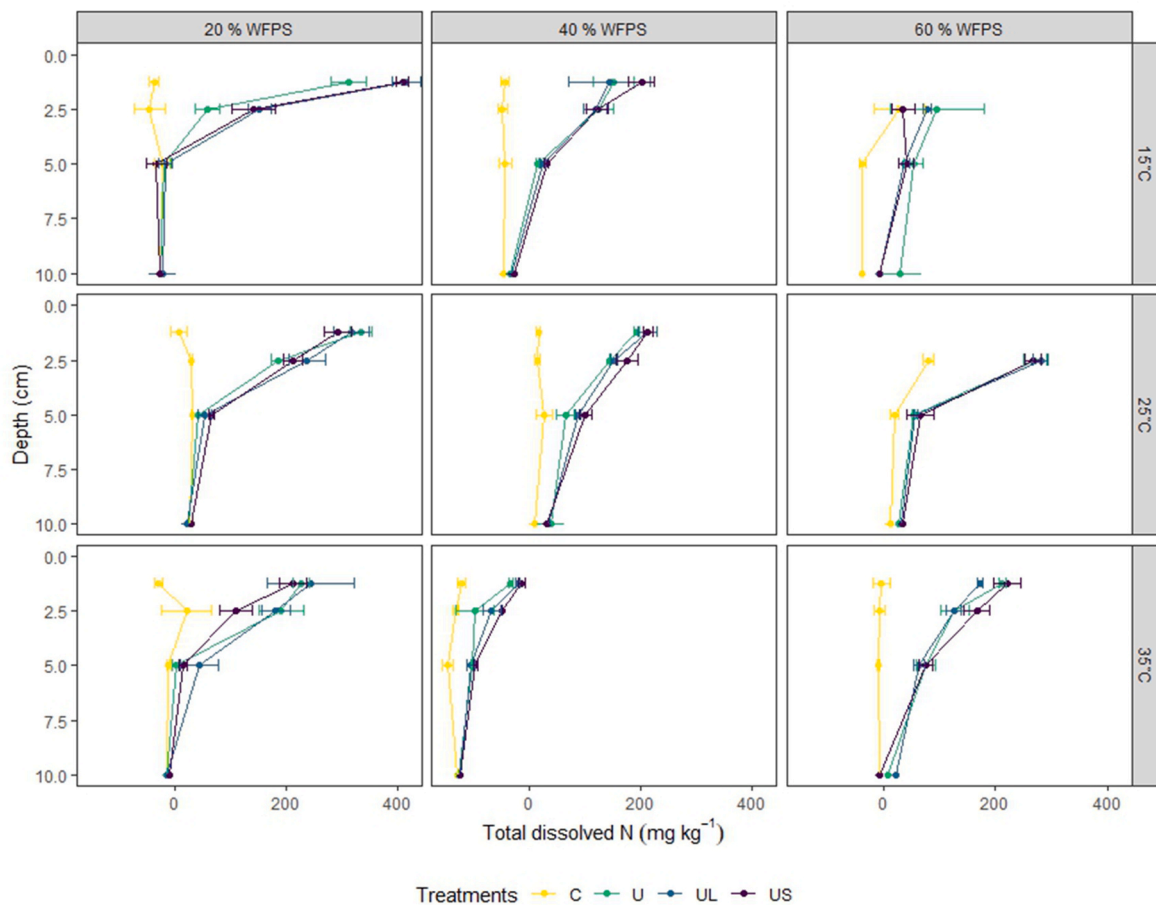
Fig. 5. Soil total dissolved N concentration following incubation for the control (C), urea (U) and urea with urease inhibitor (UL and US) treatments at 15, 25, 35 °C and 20, 40 and 60% water filled pore space (WFPS). Datapoints represent mean values and vertical bars depict standard error of the mean ($n = 3$).

4.3. Effect of soil conditions and urease inhibitors on nitrous oxide emission

In our study, N_2O emissions were affected by temperature and predominantly soil moisture, with greater emissions at 40% WFPS at 15 and 25 °C, although the highest N_2O emission at 35 °C was at 60% WFPS. Our findings align with those of Wallace et al. (2018) who observed a noticeable increase in N_2O emissions from a neutral-alkaline clay soil after N application when soil moisture was between 40 and 60% WFPS, suggesting nitrification was the main source. Our findings contrast with the observations of Sanz-Cobena et al. (2016), who reported negligible N_2O emission at 40% WFPS and greater emissions at 60 and 80% WFPS. They observed the greatest emission at 60% WFPS, considered as an optimum condition for nitrification, and a threshold for water and aeration controlling soil microbial processes (Menéndez et al., 2012). Sey et al. (2008) measured higher soil respiration from heterotrophic microorganisms at 40% and at 80% WFPS, both corresponding to N_2O peaks, however overall N_2O emissions were greatest at 80% WFPS. Nitrous oxide emissions are predominantly from autotrophic nitrification at lower soil moisture contents and denitrification at moisture contents above 60% WFPS (Bateman and Baggs, 2005). However, denitrification can occur at soil moisture <60% WFPS due to anaerobic microsites within soil aggregates (Martins et al., 2017; Sey et al., 2008). Overall, our findings suggest that soil moisture is the primary process affecting N_2O emissions associated with N fertiliser applications to soils.

The inclusion of UI did not influence either the average daily N_2O flux or the cumulative emission from surface applied urea in our study, similar to the findings of Carswell et al. (2019), Wallace et al. (2018). However, other studies have reported significantly lower cumulative

N_2O emissions from urea treated with NBPT, with mean reduction ranging between 35% and 86% (Abalos et al., 2012; Ribeiro et al., 2020; Sanz-Cobena et al., 2012; Tian et al., 2015). In Sanz-Cobena et al. (2016), the decrease in N_2O emission was linked to the reduction in soil NH_4^+ concentration as a result of NBPT inclusion, suggesting that nitrification was the main process of N_2O production in these soils. A positive correlation between soil NH_4^+ concentration and N_2O emission has been reported in studies where UI effectively mitigated N_2O emissions (Abalos et al., 2012; Sanz-Cobena et al., 2016). By reducing the NH_4^+ concentration, NBPT limits the NO_3^- supply for denitrification, and may also decrease the soil denitrification potential as observed by Abalos et al. (2012). In our study, soil NH_4^+ concentration was measured only at the end of incubation, but the lack of a significant difference between the NH_4^+ concentration under urea alone and urea treated with UI (US and UL) could explain why UI did not influence N_2O emission. Although, UI effect on N_2O emissions following fertilisation with urea was not observed in this study, indirect N_2O emissions from NH_3 emissions would be reduced by inclusion of UI, due to the reductions in NH_3 emissions as reported elsewhere (Martins et al., 2017; Hu et al., 2020).

Losses of the applied urea-N were significantly greater as NH_3 than N_2O under all temperature and soil moisture conditions in our incubation study. In addition, our results suggest that both UI (US and UL) can significantly abate NH_3 emissions and may offer a potential mitigation option for NH_3 volatilisation from urea-fertilised soils under high temperatures, although the longevity and efficacy of the UI may be lower than under more temperate conditions. Suter et al. (2011) suggested that a higher concentration of NBPT may be required under conditions >25 °C in irrigated pasture in Australia. NBPT concentrations up to 1000 ppm have been shown to enhance UI efficacy under tropical

climatic conditions in Brazil (Mira et al., 2017), although other studies have shown no benefit in reducing emission or increasing crop yield of increasing the NBPT concentration above the commercially recommended concentration of c. 500 mg kg^{-1} (Antisari et al., 1996; Silva et al., 2017; Watson et al., 2008). However, these studies were conducted under more temperate conditions, and an assessment of higher NBPT concentration under relevant agroecosystems experiencing high temperature and low moisture conditions is warranted. Furthermore, as nitrification was likely the dominant pathway for N_2O emissions from our soil at WFPS below 60%, an assessment of nitrification inhibitors under these conditions may also be relevant in a warmer and drier climate.

5. Conclusions

Soil temperature and moisture influenced NH_3 emissions from all urea fertiliser treatments, with highest emission occurring at the highest soil temperature (35 °C) and lowest soil moisture (20% WFPS). Inclusion of either UI (US and UL) with urea significantly and equally decreased average daily NH_3 flux and cumulative emission under all temperature and moisture conditions. However, the effectiveness of the UI to reduce NH_3 emissions declined as temperature increased and as soil moisture decreased. Ammonia emission continued for longer following urea application at 35 °C (up to 25 days) than at 15 or 25 °C (up to 14 days). Nitrous oxide emission was not affected by either UI. However, the combined effect of soil moisture and temperature influenced N_2O–N emissions with higher cumulative emissions measured under low moisture (40% WFPS, favourable for nitrification) at 15 and 25 °C, but higher at 60% WFPS at 35 °C. The results suggest treatment of urea with UI is a promising mitigation strategy for reducing NH_3 emissions in warmer and drier climates, however the reduction in its efficacy may be an area for further refinement in a smart fertiliser.

Credit statement

Marieme Drame: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Visualization, Writing-Original Draft, **Alison Carswell**: Conceptualization, Methodology, Visualization, Writing-Reviewing and Editing, Supervision, **William Roberts**: Investigation, **Jess Hood**: Formal analysis, **Martin Jemo**: Writing-Review & Editing, **Sigrid Heuer**: Writing-Review & Editing, **Mark Pawlett**: Writing-Review & Editing, **Guy Kirk**: Writing-Review & Editing, Supervision, **Tom Misselbrook**: Validation, Data curation, Writing-Reviewing and Editing, Supervision.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Alison Carswell reports financial support and statistical analysis were provided by Rothamsted at North Wyke.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.118671.

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