



Mitigate N₂O emissions while maintaining sugarcane yield using enhanced efficiency fertilisers and reduced nitrogen rates

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Abstract Conventional fertiliser nitrogen (N) inputs to sugarcane farming promote gaseous losses of the greenhouse gas nitrous oxide (N₂O). This study investigated the effects of a nitrification inhibitor coated urea (NICU) and a 50:50 blend (N wt%) of polymer coated urea and conventional urea (PCU + U), both at a sub-recommended rate (112 kg N ha⁻¹), on N₂O emissions and productivity in a sugarcane crop. Three rates of conventional urea (70%, 100% and 130% of the recommended rate at 160 kg N ha⁻¹) were also assessed.

Nitrous oxide emissions were measured over a 7.5-month sugarcane crop using automatic chambers. High N₂O emissions (> 50 g N₂O–N ha⁻¹ d⁻¹) occurred in the first 2 months after fertiliser application, and the variability in daily emissions was best described by a combination of pH, soil nitrate concentration, soil temperature, water filled pore space and soil ammonium concentration. The blended PCU + U resulted in 62% higher, but non-significant, net fertiliser-induced N₂O emissions, while NICU significantly reduced net emissions by 81%, compared to conventional urea at the same rate (112 kg N ha⁻¹). Net emissions from conventional urea increased linearly with increasing rate, with a mean emission factor of 2.6%. Thus, applying NICU at 70% of the recommended rate achieved the greatest N₂O emission reduction compared to a PCU + U blend or conventional urea at the same N rate. There was no significant reduction in yield when the fertiliser N rate was reduced to 70%. Further field trials are required to ascertain whether the use of reduced N rates and/or enhanced efficiency fertilisers can mitigate N₂O emissions while maintaining or increasing productivity in the long term.

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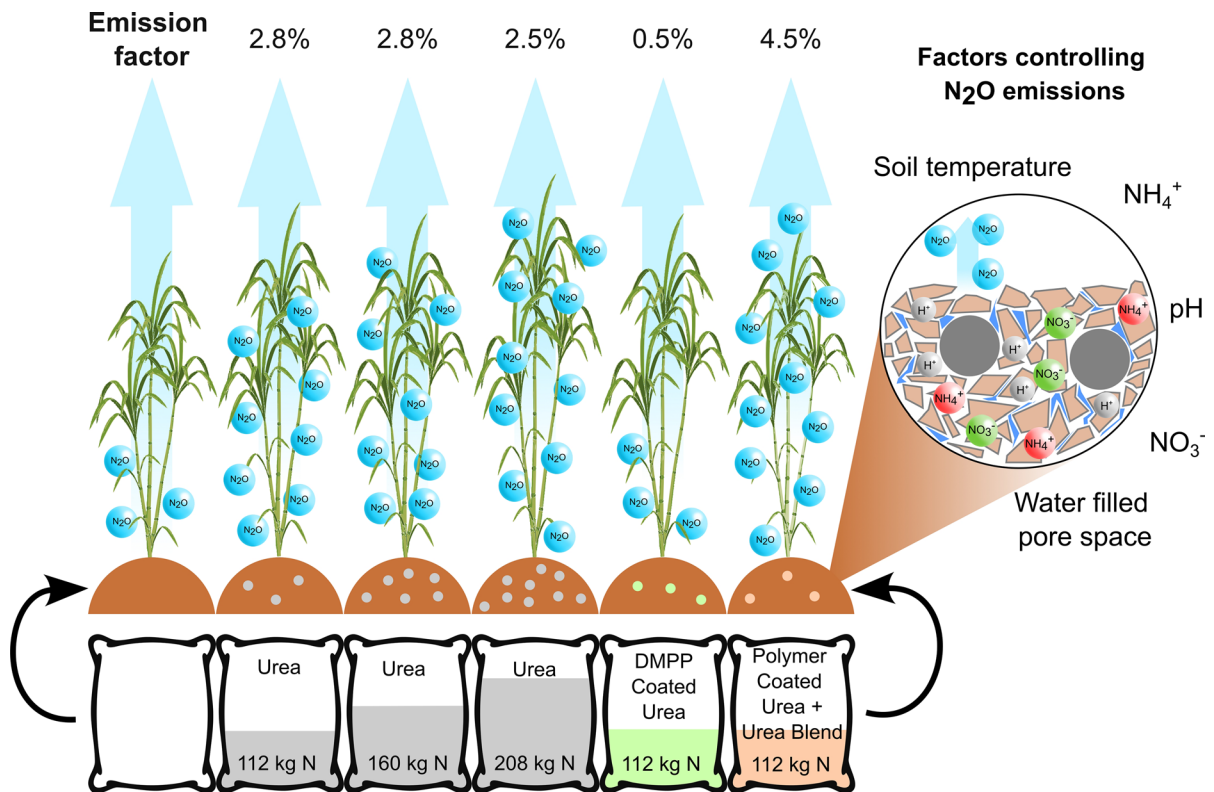
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Graphical abstract



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Introduction

Nitrogen (N) additions to croplands have resulted in increases in emissions of the greenhouse gas nitrous oxide (N₂O) since the industrial revolution (Tian et al. 2020). Considering that N₂O is 265 times more potent as a greenhouse gas compared to carbon dioxide (CO₂), practices which may mitigate N₂O emissions in agriculture with high N₂O emissions deserve more extensive investigation.

Sugarcane is a crop which generally receive large quantities of N fertiliser in pursuit of higher yields. A meta-analysis of 67 studies found that average N₂O emissions from sugarcane soil were 2.26 kg N₂O–N ha⁻¹ yr⁻¹, with an emission factor (EF) of 1.21% (Yang et al. 2021). However, studies reporting large EFs and

large emissions (Wang et al. 2016a, b), which serve to demonstrate the variability in emissions in different cropping systems, were excluded from the meta-analysis as outliers. Nonetheless, the reported global sugarcane EF is still higher than reported EFs for cereals (1.04%) (Walter et al. 2015), rice (0.68%) (Linquist et al. 2012), maize (0.65%) (Zhang et al. 2019) and all agriculture sectors (1.0%) (IPCC 2019). The Australian Government's National Inventory Report uses an EF of 1.99% for sugarcane, which is the highest EF for inorganic fertiliser N applied to agriculture production systems in Australia (Department of Industry Science Energy and Resources 2021). Higher EFs can be a symptom of an inefficient cropping system with respect to N usage. Nitrogen use efficiencies (NUE; percentage of fertiliser N assimilated by plants) in sugarcane of between 7 and 40% were reported from Brazil (Otto et al. 2016) and Australia (Bell et al. 2015). The aspirational goals for management practices are to simultaneously increase

NUE and maintain or increase yields, while reducing offsite impacts such as N_2O emissions.

Main practices that hold promise in achieving the aforementioned goals include N rate reductions from overuse of fertiliser N and the application of enhanced efficiency fertilisers (EEF) such as nitrification inhibitor-coated urea (NICU) or controlled release polymer-coated urea (PCU). Reducing the rate of applied N fertiliser decreases the quantity of N_2O emissions by lowering substrate availability. However, there is growing evidence that the proportion of applied N emitted as N_2O also decreases with a reduction in N rate (Kim et al. 2013; Shcherbak et al. 2014). Exponential increases in EFs were observed in 141 collated EF data points from sugarcane studies applying between 0 and 290 kg N ha⁻¹ yr⁻¹ (Yang et al. 2021) and, more recently, at an Australian sugarcane site between 0 and 250 kg N ha⁻¹ yr⁻¹ (Takeda et al. 2021). Therefore, smaller proportions of applied N can be lost from the system at lower rates, compared to at higher rates. This is in contrast to the current IPCC tier 1 method which assumes a linear response of N_2O emissions to increasing quantities of applied N.

EEFs broadly aim to alter the usual release of N from conventional urea or alter N transformations in soil to achieve a crop or environmental benefit (Timilsena et al. 2015). The use of NICU aims to reduce potential leaching and N_2O emission pathways by inhibiting the microbially mediated process of nitrification. Consequently, there is a smaller soil pool of NO_3^- available to be denitrified to N_2O or leached out if conducive soil conditions occur. A meta-analysis of crops applied with N fertilisers in conjunction with nitrification inhibitors reported yield and NUE increases of 7.5% and 12.9% from 27 and 21 studies, respectively (Abalos et al. 2014). Average N_2O emission reductions of 38% across cropping systems have been reported when NICUs were applied compared to conventional urea (Akiyama et al. 2010). In sugarcane specifically, most studies observed significant reductions in N_2O emissions with NICU (Gonzaga et al. 2018; Soares et al. 2015; Wang et al. 2016b, c; Wang and Moody 2015), while two studies in Australia showed similar overall emissions between NICU and urea treatments (Wang et al. 2016a, b).

Commercial use of PCU in broadscale cropping has gained interest in the past 10 years, as the environmental concerns over N inputs have increased. The polymer coating of PCU regulates the release of N in a predictable pattern (e.g. sigmoidal or exponential) to better

match crop N demand, therefore reducing the amount of N in soil available to be lost from the system. In a meta-analysis of a variety of crops the application of PCU increased crop yield and N uptake, and decreased leaching and N_2O emissions (Yang et al. 2020). However, there is a dearth of information regarding the effects of PCU on sugarcane cropping systems, which are arguably very different to grains systems in terms of management practices and climatic conditions. From the limited data to date, PCU applied to sugarcane cropping was found to increase N_2O emissions at some sites (Soares et al. 2015; Wang et al. 2016b, c), and decrease emissions at other sites (Wang et al. 2016b), possibly due to differing release characteristics of the PCU used at each site and/or different environmental and soil conditions (Wang et al. 2016b). The lack of consistency of the efficacy of these mitigation practices in sugarcane systems requires further in-field data and improved understanding of the driving factors.

The objectives of this study were to determine the effects of different fertiliser types (PCU+U blend, NICU or urea) and rates on N_2O emissions and productivity in sugarcane cropping in Australia. It was hypothesised that the use of PCU blend and NICU would increase NUE, and consequently decrease N_2O emissions and increase yield compared to conventional urea.

Methods

Site and treatments

The experimental site was located at Bundaberg, Queensland, Australia (24°54'52.86" S, 152°24'52.63" E). The site had been cropped with sugarcane for over 20 years with green cane trash blanketing practiced. The crop was planted in 2016 and canes were harvested annually with the crop residues left on the ground surface. Long term (1990–2020) average annual rainfall for the region is 926 mm with the majority received between December and March. The site received supplemental irrigation via a travelling water winch irrigator when required. The long term mean daily maximum and minimum air temperatures were 27.1 °C and 16.7 °C, respectively. Highest air temperatures occur in January and the lowest in July. The soil was classified as a Kandosol under the Australian Soil Classification (Isbell 2016). The soil physicochemical properties are shown in Table 1.

Table 1 Soil physicochemical properties (mean \pm standard error; $n=4$)

Depth (mm)	pH	EC ($\mu\text{S cm}^{-1}$)	TC (mg g^{-1})	TN (mg g^{-1})	Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)	ECEC (cmol kg^{-1})	Bulk density (g cm^{-3})
0–200	5.2 \pm 0.1	116 \pm 15	19.1 \pm 0.5	1.1 \pm 0.1	12 \pm 0.2	40 \pm 0.5	15 \pm 0.4	32 \pm 0.8	4.7 \pm 0.1	1.61 \pm 0.03 (1.25 \pm 0.03)*
200–400	4.7 \pm 0.1	120 \pm 16	11.0 \pm 0.7	0.7 \pm 0.1	10 \pm 0.4	36 \pm 0.4	15 \pm 0.8	39 \pm 0.5	3.4 \pm 0.1	
400–600	5.1 \pm 0.1	126 \pm 19	5.2 \pm 0.2	0.5 \pm 0.1	8 \pm 0.4	29 \pm 0.9	10 \pm 1.1	53 \pm 1.1	3.8 \pm 0.1	
600–1000	5.3 \pm 0.1	113 \pm 13	3.4 \pm 0.1	0.4 \pm 0.0	8 \pm 0.5	24 \pm 0.8	10 \pm 0.8	58 \pm 0.6	4.2 \pm 0.1	

EC, electrical conductivity; TC, total carbon; TN, total nitrogen; ECEC, effective cation exchange capacity. *Bulk density from the Inter-row/row

The study commenced at the start of the third ratoon (regrown crop) in November 2019. Six treatments with four replicates were established in a randomised block design (Supplementary Figure S1). The treatments were: (1) Nil fertiliser N applied (0 N); (2) Conventional urea applied at 112 kg N ha⁻¹, equivalent to 70% of the recommended rate (112N_U); (3) Conventional urea applied at 160 kg N ha⁻¹, the recommended rate based on the Six Easy Steps (6ES) industry guideline (160N_U); (4) Conventional urea applied at 208 kg N ha⁻¹, equivalent to 130% of the recommended rate (208N_U), to simulate some farmers' practices; (5) Nitrification inhibitor (DMPP) coated urea (Entec®) applied at 112 kg N ha⁻¹ (112N_NICU); and (6) 50:50 blend (N wt %) of PCU (Agromaster Tropical®) and conventional urea applied at 112 kg N ha⁻¹ (112N_PCU+U). Entec® contains 46% N while Agromaster Tropical® contains 44% N with a stated release period of 3 months.

Each plot was 20 m long and 7.3 m wide, with a row spacing of 1.83 m. Each plot included 4 rows of cane on raised beds. The site was subsurface fertilised on 11 November 2019, by applying fertiliser in a slit ~100 mm deep and ~200 mm on each side of and parallel to the cane row. Slits were sealed using press wheels. Each sealed fertiliser slit hereafter is referred to as a fertiliser band. The first irrigation at the site occurred two days after fertiliser application on 13 November 2019. Harvest was completed on 1 July 2020.

Nitrous oxide emission measurements

Twenty-one automatic chambers were installed at the site on 12 November 2019 (one day after fertiliser application) and removed on 30 June 2020 (one day prior to harvest). Eighteen of the chambers were installed over one fertiliser band (or a similar position for the 0 N treatment) to one side of the crop row in each plot in replicates 1–3, while three chambers were installed in the centre of the inter-row of the 0 N plots to allow the upscaling of emissions to a hectare basis (Supplementary Figure S1). Sugarcane plants were not present in the chambers, so only emissions from soil were measured. Only three replicates were used for measurement of N₂O, due to the number of automatic chambers available. The chamber over the fertiliser band represented two thirds of the area between

adjacent rows, and the inter-row chamber represented one-third. The twenty-one chambers were connected to two independent sampling systems, with nine chambers on one system and twelve on the other. Chambers for one treatment were split across both systems, to minimise data loss if one system malfunctioned. Over the 231 days when the systems were installed, 4872 daily mean fluxes were obtained across all chambers with 10.9% of them being linearly interpolated from near measurements due to instrument breakdown or power outages.

A detailed description of the 9-chamber system, from which the design and manufacture of the 12-chamber system was based, was reported by Wang et al. (2011) and given in Supplementary Methods S2. N_2O fluxes were calculated from the linear increase in N_2O concentration from four headspace samples over the closure period, accounting for air temperature, air pressure, headspace volume and soil surface area. Equations for flux calculations have previously been reported by Barton et al. (2008). Samples were discarded when the correlation coefficient (r^2) was <0.80 for N_2O . The daily flux rate was calculated as the mean of all flux rates on one day. Ten and eight flux measurements were calculated for every 24-h period for the 9- and 12-chamber systems, respectively. For days where individual chambers or systems malfunctioned, the chamber flux rates were interpolated linearly between the preceding and following days where measurements had occurred. Cumulative emissions were calculated as the sum of all daily flux rates over the trial period.

Soil measurements

Soil sampling for the determination of soil mineral N (ammonium [NH_4^+] and NO_3^-) was undertaken to a depth of 200 mm on the fertiliser band in fertilised treatments and from an equivalent location on the row in the 0 N treatment. The inter-row position was also sampled in the control and the 160N_U treatments, to assess whether there was lateral movement of fertiliser N into the inter-row space. The first post-fertilisation sampling occurred approximately 3 weeks after fertilisation, followed by approximately monthly samplings for 3 months and a final sampling prior to harvest. The field moist soil samples were stored at 4°C for <1 week before 20 g of moist soil was extracted with 75 ml of 2 M KCl. NH_4^+

and NO_3^- concentrations in the resulting supernatants were determined using colourmetric techniques (Rayment and Lyons 2011). pH of soil samples was determined on 1:5 soil water extracts after samples were dried at 40°C and sieved to <2 mm (Rayment and Lyons 2011). Gravimetric soil water content was determined by oven drying at 105°C for >48 h. NH_4^+ and NO_3^- contents in soil were expressed on an oven dry basis.

An initial sampling to 1000 mm depth (divided into 0–200, 200–400, 400–600 and 600–1000 mm) was undertaken prior to fertilisation to determine soil physicochemical properties (Table 1). Samples were dried at 40°C for >48 h and then sieved to <2 mm diameter. Particle size distribution was determined using the hydrometer method (Thorburn and Shaw 1987). pH and EC were determined in a 1:5 soil water suspension. Total carbon and N were determined after further grinding the <2 mm sample to <0.1 mm before analysis by combustion (CN928 Series, LECO, Michigan, USA). Effective cation exchange capacity (ECEC) was determined by summing exchangeable bases (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and exchangeable acidity (Al^{3+} and H^+) which were determined from extractions with 1 M NH_4Cl and 1 M KCl, respectively (Rayment and Lyons 2011). Bulk densities from the row and inter-row were determined at harvest from 0 to 100 mm and 100–200 mm depths using steel rings approximately 100 mm in diameter, before drying at 105°C for >48 h.

Yield and aboveground biomass N determination

Yield and aboveground plant N uptake were determined at harvest on 01 July 2020, by manually harvesting two 5 m sections from the middle two rows of each plot, which together were equivalent to 18.3 m². The number of stalks within the harvested sections were counted. The total aboveground biomass from the cut section was weighed, before a ratio of stalk to total aboveground biomass was determined on a subsample of biomass by recording the total weight of the subsample and then the weight of the stalks without leaves and cabbages (i.e. millable stalk). The ratio was applied to the total cut biomass weight to determine cane yield. Stalks were cut between the 5th and 6th dewlap, or the 8th and 9th dewlap on flowering stalks, before all leaves were stripped from the stalk to leave a clean millable stalk. Six clean millable

stalks were used to determine commercial cane sugar content (CCS). A further six complete aboveground plants were used for determination of total N uptake by separating the plant samples into stalk and leaves (green and dead) plus cabbage. Each plant part was mulched, then dried at 60°C to determine moisture content, followed by grinding to < 1 mm before total N determination by combustion (CN928 Series, LECO, Michigan, USA). Aboveground fertiliser N recovery was calculated as:

$$\text{Aboveground fertiliser N recovery(\%)} = \frac{\text{treatment N uptake} - \text{control N uptake}}{\text{N rate}} \times 100 \quad (1)$$

Auxiliary measurements

An onsite weather station recorded rainfall and soil temperature on the row and inter-row at depth of 50 mm (RX300, ONSET, MA, USA). Soil moisture was measured on the row and inter-row using Environscan probes (Sentek, SA, AUS) at a depth of 70–130 mm. Soil moisture measurements were recorded on a volumetric basis and converted to water filled pore space (WFPS) as outlined by Wang et al. (2011). Due to instrument techni-

cal difficulties and delayed installation of soil moisture probes, onsite data were not available in the month following fertilisation. Missing weather data was backfilled

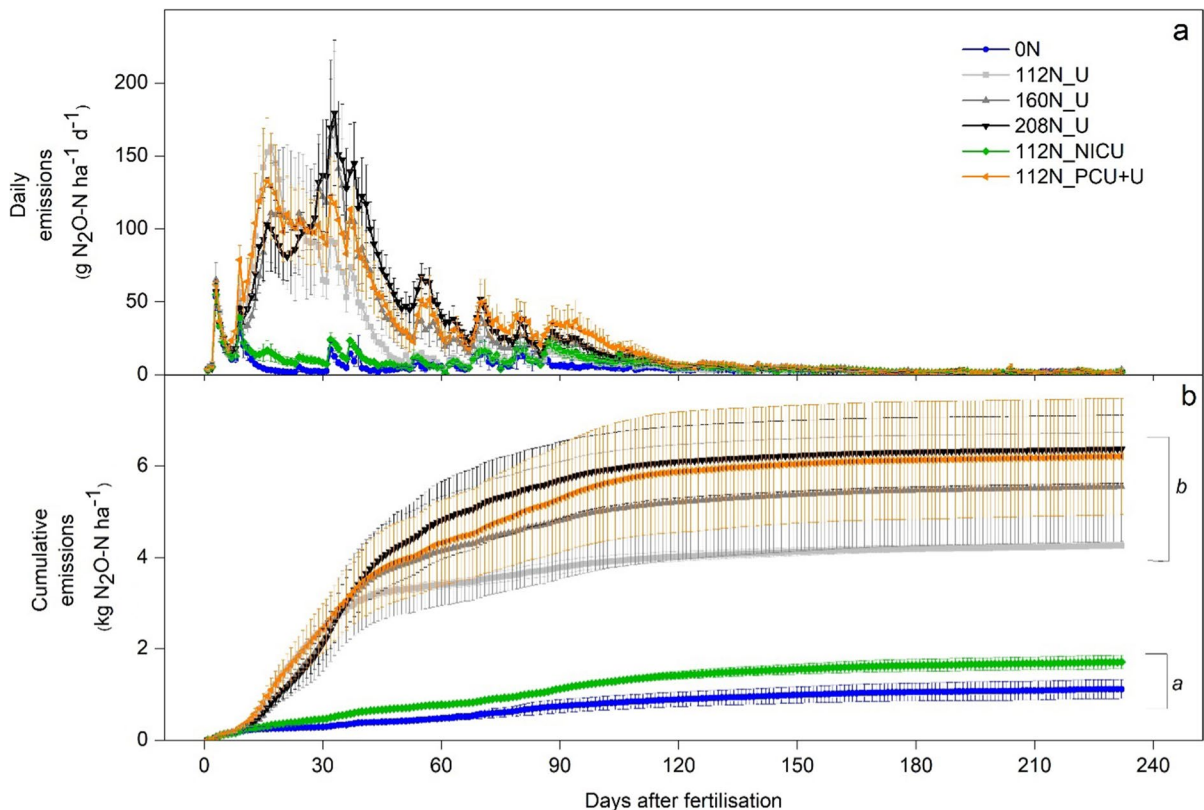


Fig. 1 Dynamics of **a** daily and **b** cumulative nitrous oxide emissions at the site during the 2019–2020 season. Different italicized letters in **b** indicate significant differences in whole-season cumulative emissions at $P < 0.05$. U, urea; NICU, nitrifi-

cation inhibitor coated urea; PCU+U, Polymer coated urea in a 50:50 ratio (N wt%) with urea; 0 N, nil applied N; 112 N, 112 kg N ha⁻¹; 160 N, 160 kg N ha⁻¹; 208 N, 208 kg N ha⁻¹. Values are mean \pm standard error (n=3 plots)

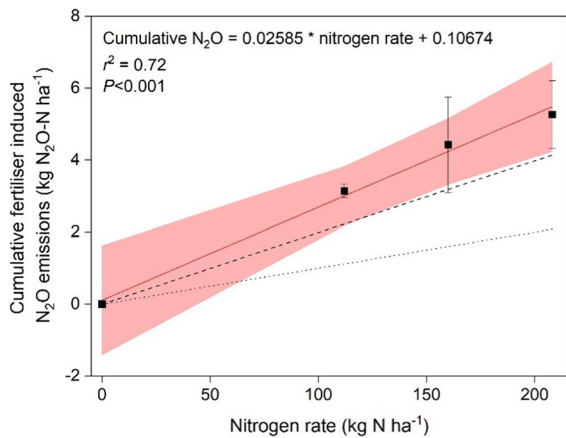


Fig. 2 Cumulative fertiliser-induced N_2O emissions (treatment emissions minus control emissions) at different applied N rates of conventional urea. Dotted line is prediction using the IPCC default emission factor (1.0%). Dashed line is prediction based on the Australian government's emission factor for sugarcane (1.99%). Solid red line is the fitted linear regression of the measured data. Shaded area is the 95% confidence interval of the linear regression. Values are mean \pm standard error ($n=3$ plots)

with data from the SILO database (<https://www.longpaddock.qld.gov.au/silo/>).

Statistics and data analysis

Statistics were completed in R (R Core Team 2021) using the packages agricolae V1.3-5, rstatix V0.7.0 and MASS v7.3-53.1. Analysis of variance (ANOVA) was used to test for significant differences between treatments for total cumulative N_2O emissions, cane yield, sugar yield, emissions intensity, aboveground plant N uptake and aboveground fertiliser N recovery. Significance of differences was determined at the $P < 0.05$ level using LSD. Emissions intensity (i.e. the N_2O emissions produced from the production of 1 t of product) was determined by dividing N_2O emissions ($\text{kg N}_2\text{O-N ha}^{-1}$) by the cane or sugar yield (t ha^{-1}). Where data were not normally distributed, a log transformation was applied, except for NH_4^+ proportion data which was logit transformed. Two-way repeated measures ANOVA was used to compare soil NH_4^+ or NO_3^- concentrations between the inter-row of the 0 N and 160N_U treatments, as well as to compare concentrations between positions within the 0 N or 160N_U treatments. Pairwise T tests were used to compare WFPS and soil temperature between row and inter-row positions. Exponential and linear

models were fit to the fertiliser-induced emissions (differences in N_2O emissions between fertilised and unfertilised treatments) at different rates. Models were compared using adjusted r^2 , Akaike Information Criteria (AIC) and Bayesian Information Criteria (BIC). Stepwise multiple linear regression was used to determine which measured variables [soil NO_3^- -N concentration, soil NH_4^+ -N concentration, soil mineral N concentration (NO_3^- -N + NH_4^+ -N), pH, soil temperature and WFPS] best explained the variability in daily chamber N_2O emissions. Data for days between two consecutive soil sampling activities were interpolated by linear regression for soil NO_3^- -N, NH_4^+ -N, mineral N concentrations and pH, except that those for the period between fertiliser application and the first soil sampling were not estimated because of the potentially abrupt and non-linear changes following fertilisation. Graphing was completed in OriginPro (OriginLab Corporation 2021).

Results

Cumulative emissions

Cumulative emissions from the Urea treatments increased with increasing application rate (112N_U: $4.3 \text{ kg N}_2\text{O-N ha}^{-1}$ < 160N_U: $5.5 \text{ kg N}_2\text{O-N ha}^{-1}$ < 208N_U: $6.4 \text{ kg N}_2\text{O-N ha}^{-1}$) although the differences were not significant ($P > 0.05$; Fig. 1b). The whole-season fertiliser-induced emissions also linearly increased with the increasing rates of fertiliser N applied (Fig. 2).

The majority of emissions occurred within the first 3 months after fertilisation over the entire 231 days (Fig. 1b). 90% of total emissions from all Urea and PCU+U treatments occurred by between 91 and 99 days after fertilisation. While 90% of total emissions in the control and NICU treatments occurred by between 144 and 155 days after fertilisation.

The lowest cumulative emissions were recorded from the 0 N treatment ($1.1 \text{ kg N}_2\text{O-N ha}^{-1}$). The 112N_PCU+U treatment emitted $6.2 \text{ kg N}_2\text{O-N ha}^{-1}$, which was 62% higher than the 112N_U treatment, although the difference was not significant ($P > 0.05$). In contrast, the application of NICU significantly reduced net N_2O emissions by 81% compared to urea at the same N rate.

The EF for Urea treatments varied slightly in the order 112N_U = 160N_U (2.8%) > 208N_U (2.5%).

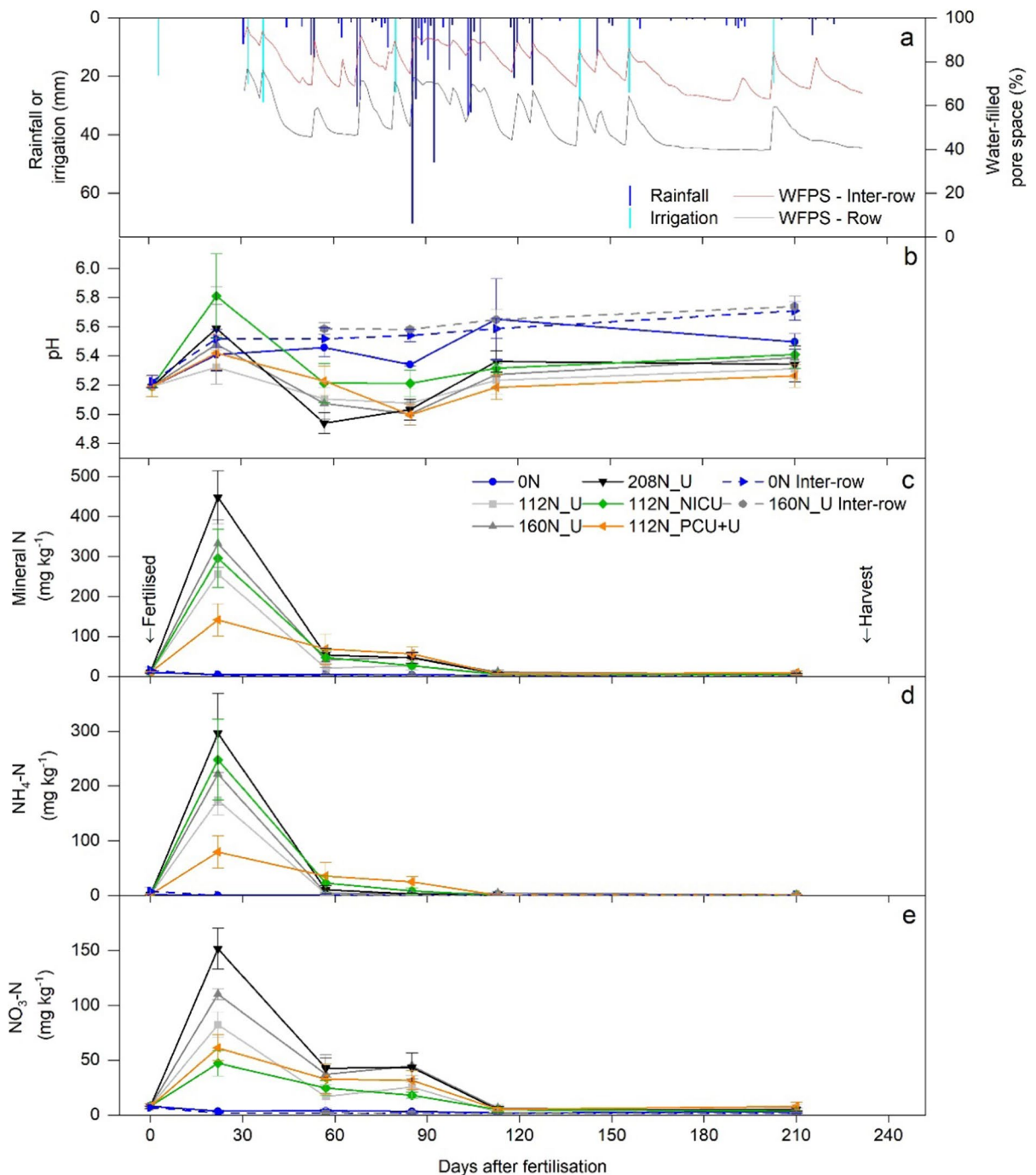


Fig. 3 Dynamics of **a** rainfall, irrigation, water-filled pore space (WFPS) at 100 mm depth, **b** soil pH, **c** soil mineral N, **d** ammonium (NH₄⁺) and **e** nitrate (NO₃⁻) content in 0–200 mm depth at the site during the 2019–2020 season. U, urea; NICU, nitrification inhibitor coated urea; PCU+U, Polymer coated

urea in a 50:50 ratio (N wt %) with urea; 0 N, nil applied N; 112 N, 112 kg N ha⁻¹; 160 N, 160 kg N ha⁻¹; 208 N, 208 kg N ha⁻¹. Values are mean ± standard error in **b**, **c**, **d** and **e** (n=4 plots)

Table 2 Productivity, aboveground N uptake, fertiliser N recovery (mean \pm standard error; $n=4$ plots) and emissions intensity (mean \pm standard error; $n=3$ plots)

Treatment	Cane yield (t ha ⁻¹)	Sugar yield (t ha ⁻¹)	Aboveground N uptake (kg N ha ⁻¹)	Aboveground fertiliser N recovery (%)	Emissions intensity	
					(kg N ₂ O–N t ⁻¹ cane)	(kg N ₂ O–N t ⁻¹ sugar)
Control	87.2 \pm 4.9 ^b	13.3 \pm 0.8 ^a	105.6 \pm 7.6 ^b		0.013 \pm 0.003 ^c	0.089 \pm 0.022 ^c
112N_U	100.7 \pm 2.1 ^a	15.5 \pm 0.4 ^a	126.7 \pm 5.5 ^{ab}	18.9 \pm 11.1 ^a	0.042 \pm 0.001 ^b	0.279 \pm 0.007 ^b
160N_U	98.1 \pm 6.2 ^{ab}	15.2 \pm 0.8 ^a	149.6 \pm 10.1 ^a	27.5 \pm 4.5 ^a	0.055 \pm 0.009 ^{ab}	0.360 \pm 0.058 ^{ab}
208N_U	109.0 \pm 8.7 ^a	16.2 \pm 1.0 ^a	140.3 \pm 14.4 ^a	16.7 \pm 3.5 ^a	0.060 \pm 0.003 ^{ab}	0.409 \pm 0.022 ^{ab}
112N_NICU	97.5 \pm 3.8 ^{ab}	15.1 \pm 0.4 ^a	133.7 \pm 9.7 ^a	25.1 \pm 6.6 ^a	0.017 \pm 0.002 ^c	0.111 \pm 0.012 ^c
112N_PCU+U	96.6 \pm 1.0 ^{ab}	14.9 \pm 0.3 ^a	127.7 \pm 6.5 ^{ab}	19.7 \pm 7.7 ^a	0.064 \pm 0.013 ^a	0.416 \pm 0.080 ^a

U, urea; NICU, nitrification inhibitor coated urea; PCU+U, Polymer coated urea in a 50:50 ratio (N wt %) with urea; 0 N, nil applied N; 112 N, 112 kg N ha⁻¹; 160 N, 160 kg N ha⁻¹; 208 N, 208 kg N ha⁻¹. Different lettering in the same column indicates significant differences between treatments at $P < 0.05$

A linear regression between the cumulative fertiliser N-induced N₂O emissions and N rate gave an overall EF of 2.6% for urea (Fig. 2). The blended PCU+U had the highest EF of 4.5% and the NICU had the lowest of 0.5% at 112 N.

Dynamics and controlling factors of daily N₂O emissions

Daily N₂O emissions reached their highest level approximately 1 month after fertilisation (Fig. 1a), which coincided with the highest measured soil mineral N contents, irrigation events and higher soil temperatures (Fig. 3a–e). During this time most treatments had periods of emissions of > 100 g N₂O–N ha⁻¹ day⁻¹, except for the 0 N and NICU treatments, which maintained daily emissions of < 30 g N₂O–N ha⁻¹ day⁻¹. Emissions from all treatments reduced to low levels by 4 months after fertiliser application and remained low (< 5 g N₂O–N ha⁻¹ day⁻¹) for the remainder of the trial, regardless of rainfall or irrigation events.

Stepwise linear regression showed that among the explanatory variables measured, the daily N₂O emissions were best explained by:

$$\begin{aligned} \text{Log}(\text{daily N}_2\text{O-N emission}) = & 0.027 * \text{NO}_3^- \text{-N} \\ & + 0.174 * \text{Temp} + 0.008 * \text{WFPS} + 0.004 \\ & * \text{NH}_4^+ \text{-N} - 1.979 * \text{pH} \\ & + 7.419 (r^2 = 0.83, P < 0.001, n = 1252) \end{aligned} \quad (1)$$

where NO₃⁻-N is the soil NO₃⁻-N concentration (mg kg⁻¹) in the top 0–200 mm; Temp is the soil temperature at 50 mm depth; WFPS is the waterfilled pore space at 100 mm depth; NH₄⁺-N is the soil NH₄⁺-N concentration (mg kg⁻¹) in the top 0–200 mm; and pH is the soil pH in the top 0–200 mm. The main influencing variables were soil pH, soil temperature and soil NO₃⁻-N concentration.

Cane yield, sugar yield and nitrogen uptake

There were no significant differences between cane yields from the fertilised treatments, with yields ranging from 97 to 109 t ha⁻¹ (Table 2). The 0 N treatment produced 87 t ha⁻¹ and was marginally significantly ($P=0.055$) lower than urea treatments applied at 112 and 160 kg N ha⁻¹. Although there were no significant differences between sugar yields from different treatments, the 0 N treatment produced 11–17% less sugar than the fertilised treatments. Aboveground N uptake in the fertilised treatments ranged from 126.7 to 149.6 kg N ha⁻¹. All fertilised treatments had higher N uptakes than the 0 N treatment, but the effect of N application was only significant in the two highest Urea N rates and the 112N_NICU treatment. An increase in urea application rate to 130% of the recommended rate did not increase crop N uptake, while a reduction to 70% exhibited a decreasing trend in N uptake of 11–15% ($P > 0.05$) across different fertiliser formulations. The apparent aboveground fertiliser N recovery ranged from 16.7% for 208N_U

to 27.5% for 160N_U, with no significant differences between treatments. The emissions intensity of the NICU treatment, whether calculated on cane or sugar yield, was not significantly different to the control treatment (Table 2). The 112N_NICU treatment reduced emissions intensity by 60% whether calculated on cane or sugar yield compared to urea at the same rate (Table 2).

Dynamics of environmental variables and soil mineral N

Water filled pore space was significantly ($P < 0.05$) higher in the inter-row than the row (Fig. 3a), with an average daily WFPS of 77% (range: 62–96%) and 52% (range: 40–77%) in the inter-row and row, respectively. The soil temperature at 50 mm depth was not significantly ($P > 0.05$) different between row and inter-row positions (data not shown), with the average daily temperature being 23.1 °C (range: 15.0–27.9 °C) and 23.2 °C (range: 15.8–27.8 °C) respectively.

With the absence of soil sampling in the first 21 days after fertilisation, highest soil pH on the fertilised rows (range: 5.32–5.81) was observed 22 days after fertilisation, while the pH in the control rows peaked at 5.65 after 113 days (Fig. 3b). At 22 days after fertilisation, the NICU treatment had the highest pH while at all other sampling dates the rows in the control had the highest pH compared to fertilised treatments; however, the differences were only significant at 85 days after fertilisation.

Soil NH_4^+ and NO_3^- concentrations were not significantly different between the inter-rows of the 0 N and the 160N_U treatments ($P > 0.05$) (Fig. 3d, e), indicating there was no significant lateral movement of NH_4^+ or NO_3^- from the fertiliser band to the inter-row position. The NH_4^+ and NO_3^- concentrations in the row and inter-row of the control and the inter-row of 160N_U treatment were similar, with no significant ($P > 0.05$) differences between these positions.

Measured mineral N ($\text{NH}_4^+ + \text{NO}_3^-$) content in soil peaked in the first month after fertiliser application and declined to low levels ($< 11 \text{ mg kg}^{-1}$) over the following 3 months (Fig. 3c,d,e). Soil NH_4^+ and NO_3^- concentrations on the fertiliser band 22 days after application increased linearly with increasing N rate in the urea treatments. PCU blended with urea (112N_PCU+U) produced the lowest soil mineral N content 22 days after application but had the highest mineral N

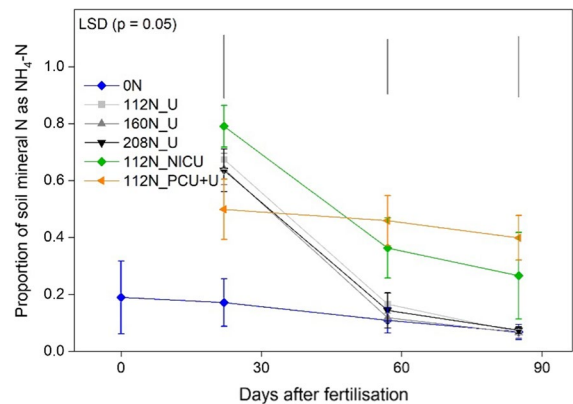


Fig. 4 The proportion of soil mineral N as NH_4^+ -N in the top 0–200 mm of fertiliser bands at different N rates and fertiliser forms in the first 3 months after fertilizer application. U, urea; NICU, nitrification inhibitor coated urea; PCU+U, Polymer coated urea in a 50:50 (N wt %) with urea; 0 N, nil applied N; 112 N, 112 kg N ha⁻¹; 160 N, 160 kg N ha⁻¹; 208 N, 208 kg N ha⁻¹. Values are mean \pm standard error (n=4 plots)

content 57 and 85 days after application compared to all other fertilised treatments. The 112N_NICU treatment produced similar soil mineral N contents to the 112N_U treatment 22 days after application and similar mineral N contents to the 112N_PCU+U treatment at 57 and 85 days after application.

The NICU maintained a higher proportion of mineral N as NH_4^+ -N than urea at the same rate, for approximately 3 months after fertilisation (Fig. 4). At each sampling time during this period the NICU had a significantly ($P < 0.05$) higher proportion of mineral N as NH_4^+ -N than at least one urea treatment. Although NICU initially had the highest proportion of mineral N as NH_4^+ -N compared to all fertilised treatments at 22 days after application, the PCU+U treatment had the highest proportion of mineral N as NH_4^+ -N at 57 and 85 days after application compared to all other fertilised treatments ($P < 0.05$), including the NICU treatment ($P > 0.05$).

Discussion

Effectiveness of enhanced efficiency fertilisers

The two EEFs used in this study resulted in divergent effects on N_2O emissions, with NICU significantly

reducing emissions and PCU+U increasing emissions compared to urea at the same rate. The resulting EF for NICU (0.5%) was below the IPCC EF (1%) for agriculture and the Australian EF (1.99%) for sugarcane, while the PCU+U EF (4.5%) was much higher. The values recorded in our study for NICU are within the range (mean: 0.419%; confidence interval: 0.171–0.734%) of EF values collated in a meta-analysis of EEFs from sugarcane (Yang et al. 2021), while the PCU+U EF falls outside the 95th percentile. Our observations here are similar to results reported from a sugarcane crop in Brazil where a PCU increased EF by 41% and NICU (DMPP) reduced EF by 97% averaged over two seasons, compared to urea (Soares et al. 2015). In the third year in the same area, NICU (DMPP) also reduced EF by 97%, but PCU+U non-significantly decreased EF by 7% compared to urea (Soares et al. 2016). In another study in Brazil, the nitrification inhibitor dicyandiamide reduced EF by 75% compared to urea when averaged across treatments and seasons (Gonzaga et al. 2018).

The decreased and increased EF from NICU and PCU+U blend, respectively, were due to the resultant mineral N dynamics created by each EEF and their interactions with the prevailing environment. In the case of NICU, higher proportions of the soil mineral N as NH_4^+ were recorded for about 3 months in comparison to other fertilised treatments, which reduced availability of NO_3^- for denitrification over the high emission summer period, resulting in lower N_2O emissions (Figs. 3c, d and e and 4). In contrast, the PCU+U blend was effective at maintaining higher soil mineral N after the first month from application compared to traditional urea (Figs. 3c and 112N_PCU+U vs. 112N_U). This was caused by the PCU+U blend having 56 kg N ha^{-1} as conventional urea available upfront for nitrification resulting in an initial increase in N_2O emissions, similar to other conventional urea treatments (Fig. 1a). A further 56 kg N ha^{-1} of PCU+U was partly available to be released over the following 3 months. This prolonged the release of N from the PCU+U blend, providing more NO_3^- for denitrification and thus higher N_2O emissions, compared to the 112N_U treatment (Fig. 4).

These observed changes to soil mineral N dynamics did not translate into significant productivity or

N efficiency benefits. The limited number of studies to date have reported a variety of effects of EEFs on sugarcane productivity. Wang et al. (2016a) found that urea formulation (NICU, PCU+U or urea) did not significantly affect sugarcane or sugar yield at the same N application rate. Di Bella et al. (2013) found 100% PCU increased cane yield compared to urea at the same rate on two soil types in North Queensland, Australia. Increased yields were also achieved with three different blend ratios of PCU and urea when applied at 200 kg N ha^{-1} compared to 100% urea at the same rate in the dry tropical Burdekin region, however no yield increase was observed when fertiliser was applied at lower rates or at other sites (120, 160 kg N ha^{-1}) (Di Bella et al. 2014). The presence of conditions which exacerbate N losses through leaching, runoff and/or denitrification often accompany observed yield increases from PCU application (Di Bella et al. 2013; Dowie et al. 2019; Wang and Reeves 2020).

Simulation studies provide an opportunity to assess the effectiveness of EEF at different sites and under different weather conditions in a cost-effective manner. Simulations run using 100 years of climate data from the Tully region of Queensland, Australia on two contrasting soils found that soil type was a critical factor affecting productivity benefits of PCU (Verborg et al. 2018). Although benefits may be observed with respect to reduced N losses and prolonged N supply in wet soil conditions (Wang et al. 2016c), productivity benefits will be negated if extended wet soil conditions also reduce crop yield potential, as the crop will not be able to make use of the additional N supply. The effect of EEF on sugarcane productivity is the result of a number of factors including soil conditions, rainfall, fertiliser timing and rate, and other management practices.

The pre-existing reported data coupled with our current study indicate that there is more certainty in achieving N_2O emission reductions when using NICU compared to PCU. Achieving certainty with N_2O reductions from PCU may be more difficult due to the wide array of N release patterns from different products coupled with either applying PCU alone or in blends with conventional urea at different ratios, in addition to high variability of soil properties (e.g., drainage) and weather conditions (e.g., rainfall amount and distribution).

Effectiveness of reducing N rate

Any reductions in the rate of applied fertiliser N to mitigate N_2O emissions need to be balanced against potential productivity and/or environmental impacts. Indeed a 30% reduction in N rate from the recommended 160 kg N ha^{-1} resulted in a 22% reduction in N_2O emissions (Fig. 1b) with little change in yield parameters (Table 2). These results support previous findings from modelled and observed data from Australian sugarcane regions. For instance, modelled reductions in N rate by 29% from the average farmers' rate at Mackay, Australia resulted in a 40% reduction in emissions with little effect on yield (Thorburn et al. 2010). Decreases in emissions from 8 to 59% have been measured in Australian sugarcane with reductions in fertiliser application from the recommended rates between 25 and 50% (Allen et al. 2010; Takeda et al. 2021; Wang et al. 2016b). Several previous studies reported no significant reductions in yield associated with sub-optimal N rates (Kingston et al. 2008; Takeda et al. 2021). Thus, the recommended fertiliser N application rates for at least some Australian sugarcane production systems may be decreased for mitigating N_2O emissions without the cost of yield loss. However, how much and where the recommended N rate can be decreased and whether yield can be maintained longer term with lower N inputs require further investigation.

In this study, EFs of fertiliser N changed little with N rate, which contrasts with recent studies in sugarcane that reported N_2O emissions increasing exponentially with N rate (Takeda et al. 2021; Yang et al. 2021). However inter-annual variability in the relationships of N_2O emissions to N rate was reported in a study across multiple cropping years in Brazil, where one out of three years did not exhibit increasing EFs with N rate (Degaspari et al. 2020). The inter-annual variabilities in EF trends are influenced by the extent of N_2O -conductive conditions each year. Specifically, in the current study, rainfall/irrigation rarely increased WFPS > 70% and averaged 52% overall on the rows where fertiliser was located, which might have limited N_2O production. Indeed, if soil and environmental conditions are restrictive (i.e. N is not the limiting factor in N_2O production) either temporally or spatially, then having additional N available at higher rates will not lead to increasing EFs. Also, in another study in Brazil at two sites, where urea was

applied at 4–5 rates ($60\text{--}180 \text{ kg N ha}^{-1}$) including a nil fertiliser N rate, it was found that N_2O emission plateaued or decreased at the highest rate at each site (Signor et al. 2013). The authors hypothesised that this was due to a negative effect of N on microbial activity (Signor et al. 2013). Indeed the lack of increased EFs at higher N rates may be explained by constraining conditions in the fertosphere of banded fertiliser. Soil NO_3^- concentration in the fertiliser band in our study increased linearly with N rate but at a slower rate than NH_4^+ , suggesting that nitrification per unit of fertiliser N was slower at higher applied N rates. Wetselaar et al. (1972) reported complete nitrification inhibition at $\text{pH} > 8$ or when the NH_4^+ -N concentration in soil solution was above 3000 ppm. These conditions have been observed in the fertosphere of band applied fertilisers, including soils with similarly low pH (5.2) to this study (Janke et al. 2019, 2021). Although the soil pH of the fertilised treatments in our study were lower than that reported in fertosphere studies, this does not preclude this theory from applying in this instance since high soil pH usually occurs in the first few weeks after urea application when no soil sampling was undertaken in the current study and only bulk soil (not just the fertosphere) was sampled for pH later. Constrained nitrification at higher N rates would proportionally decrease nitrate availability for denitrification and therefore N_2O emissions from both nitrification and denitrification. Therefore, studies measuring EFs at different rates over multiple years are required to gain a better understanding of the inter-annual variability in EF trends and its influencing factors.

Linear increases in N_2O emissions with increasing fertiliser N was observed over a N input range up to 208 kg N ha^{-1} in our study, while higher rates of N were applied in other studies reporting exponential increases in N_2O emission with increasing fertiliser N in sugarcane (Takeda et al. 2021; Yang et al. 2021). Kim et al. (2013) conceptualised increases in N_2O emissions with N rate and posited three phases of increase: (1) linear increase (2) exponential increase and (3) steady state, related to the interaction between plant N uptake and microbial N use. If all N application rates occur within phase 1, linearity will be observed. Measurements which span across phase 1 and 2 would elicit an exponential response. The boundaries of these phases can change based on factors (e.g. weather, soil conditions etc.) which

affect N loss and plant and microbial use of N, consequently they can change spatially and temporally. Even though exponential increases may occur at rates far above the recommended rate for a site or region, in this case 160 kg N ha⁻¹, there is little practical benefit gained from assessing and determining N₂O emissions at such high N rates that are rarely used in a region.

Controlling factors of N₂O emissions

Soil NO₃⁻-N concentration, soil temperature and pH had the largest influence on the variability in daily N₂O emissions, with soil NH₄⁺-N concentration and WFPS having a lesser influence (Eq. 2). Nitrate is a substrate in the denitrification process that produces N₂O and/or N₂ under anaerobic conditions, while soil temperature can increase the rate of microbial processes when other factors are not limiting (Dalal et al. 2003). Soil pH had a negative relationship with N₂O, i.e., N₂O emissions decreased with increasing pH. This is because the ratio of N₂O/N₂ produced from denitrification increases as pH decreases (Rochester 2003; Šimek and Cooper 2002). The lesser influence of WFPS on daily N₂O emissions in Eq. 2 could be because high WFPS coincided with high NO₃⁻-N and temperature during the first 4 months of the trial period (Figs. 1a and 3a and d). It is widely accepted that a WFPS > 60% is conducive to various degrees of anaerobic conditions, making denitrification dominant over aerobic nitrification (Davidson 1993). During the 4-month high emission period following fertilisation, at least 44 days exceeded 60% WFPS on the row where the fertiliser was located, while WFPS was above 60% on all days in the inter-row. Even on days exhibiting < 60% WFPS, there could be anaerobic microsites within the soil creating localised denitrification hotspots. This coupled with the fact that soil NO₃⁻ explained more variability in emissions than soil NH₄⁺, suggests that denitrification was the dominant pathway of N₂O production in this system.

The simultaneous presence of multiple N₂O promoting factors in Australian sugarcane systems provide ideal conditions for N₂O emissions to occur. In the case of our study, urea fertiliser was applied in late spring, leading to high mineral N contents coming into summer when soil temperatures and WFPS were high and retention of residues from the previous crop (i.e., green cane trash blanketing) provided

large carbon inputs. Indeed, the large emission events (> 10 g N₂O-N ha⁻¹ d⁻¹) from conventional urea occurred over summer up to 4 months after fertilisation, when the above conditions were present together (Fig. 1). This presents a challenge to reducing N₂O emissions in these systems.

Considering that soil temperature is uncontrollable by management actions in this system, altering pH or NO₃⁻ availability are the main methods to reduce N₂O emissions. Increasing soil pH through the application of soil ameliorants (e.g. lime) has been shown in both laboratory (Das et al. 2022) and field studies (Barton et al. 2013) to be an effective management practice to reduce N₂O emissions. Modifying NO₃⁻ availability through split applications of N to reduce the over-supply of N have been trialled in sugarcane with varying results (Allen et al. 2010) and may not always be possible due to site accessibility in wet conditions or due to the height of the crops. Based on the results from this study and our previous studies (Wang et al. 2016b, c), reducing fertiliser N rates and applying NICU instead of conventional urea provide effective management strategies to reduce N₂O emissions from Australian sugarcane farms.

Conclusion

This study demonstrated that reducing N application to 70% of the recommended rate for conventional urea maintained sugarcane yield, sugar productivity and crop N uptake, regardless of the fertiliser formulations used. However, the reduction in the N rate with conventional urea did not result in significant decreases in N₂O emissions over the crop growing season. In contrast, using nitrification inhibitor-coated urea at 70% of the recommended rate substantially decreased the seasonal N₂O emissions. The use of a blend (50:50 N wt %) of polymer coated urea and urea at the sub-recommended rate resulted in higher but non-significant emissions, compared to the conventional urea at the recommended or sub-recommended rate. Thus, the type of enhanced efficiency fertiliser selected, with the intention to reduce N₂O emissions, needs to be carefully considered to avoid perverse outcomes. These results suggest that nitrification inhibitor coated urea may be more reliable in achieving N₂O reductions in subtropical sugarcane production than the blended polymer coated urea and

urea. However, potential exists to modify blending ratios of polymer coated urea and urea, to alter the N availability to crops and soil and this may provide a solution to reduce emissions from blended products. Therefore, other polymer-coated urea formulations with various release dynamics and different blending ratios with urea should be studied to assess their potential benefits over various soil and seasonal conditions. Although productivity was maintained at the sub-recommended rate with both enhanced efficiency fertilisers and urea, whether this can be sustained in the long term or achieved at other sites requires further investigation.

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Author contributions SR: Investigation, Data Curation, Formal analysis, Writing-Original Draft, Visualization. WW: Conceptualization, Methodology, Writing-Review & Editing, Supervision, Project administration, Funding acquisition. SG: Investigation, Resources.

Declarations

Competing interests The authors declare no competing interests.

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