Three-dimensional dynamics of nitrogen from banded enhanced efficiency fertilizers

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Abstract A range of enhanced efficiency fertilizers (EEFs) have been developed in response to widespread recognition of poor nitrogen (N) use efficiency (NUE) in agriculture; however, their effective utilization is not properly understood when applied in sub-surface bands. This study quantified soil chemical changes and the distribution of N species that arose from sub-surface banding of urea, a controlled release polymer-coated urea (PCU) and urea coated with either nitrification inhibitors (NIs) or a urease inhibitor (UI), over 71 days in a field trial. Banding NIs extended the duration of nitrification inhibition for up to 50 days longer than banded urea, although the duration of NI-conferred inhibition was dependant on the rate of NI-urea application. The UI preserved urea-

N at a concentration which was 16-fold higher *cf.* standard urea over 7 days, but no urea-N was detected after 21 days. This suggests that the NUE benefits of UIs are transient when applied in sub-surface bands. Slow release of urea-N from banded PCU resulted in lower concentrations of N in the soil solution. This reduced N dispersal by *ca.* 50 mm *cf.* urea, resulting in a N-enriched zone which was considerably smaller. Relatively benign chemical conditions around PCU bands enabled rates of nitrification ($\text{NH}_4\text{-N}:\text{NO}_3\text{-N}$ ratio of 46%) which were similar to urea. Collectively, these results demonstrate the relative efficacy and risks of the different EEF technologies, when applied in fertilizer bands. This knowledge supports the effective utilization of band-applied EEFs for improved NUE in agricultural systems.

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Introduction

Nitrogen (N) is frequently one of the most limiting nutrients to agricultural production, so crop responses to fertilizer-N application are often recorded. However, inappropriate fertilizer use can lead to a leakage of N from agricultural systems through leaching, over-

land flow and gaseous emission. This N loss may disrupt the nutrient balance and dynamics of natural ecosystems, adversely impacting inhabitants and diminishing the ability of the ecosystem to provide services (Galloway et al. 2003; Hatfield and Follett 2008). With a growing world population driving increasing demand for agricultural products, there is a very real need to address N use efficiency (NUE) in a manner that enables sustainable intensification of agriculture without detrimental impacts on the surrounding environment.

The emergence of enhanced efficiency fertilizers (EEFs) on the N-fertilizer market indicates recognition by industry that new fertilizer technology may provide a key tool for improving NUE in agriculture. Enhanced efficiency fertilizers utilise technologies such as nitrification inhibitors (NIs), urease inhibitors (UI), and controlled release products [e.g., polymer-coated urea (PCU)]. Detailed descriptions of the mode-of-action for these technologies can be found in McCarty (1999), Shaviv (2001) and Engel et al. (2015). Briefly, NIs inhibit the oxidation of ammonia (NH_3) to nitrite (NO_2^-); UIs function by restricting the conversion of urea to ammonium (NH_4^+); and PCU slows the release of urea into the soil solution. These technologies aim to improve the synchrony of fertilizer-N availability with plant demand by minimizing the time when N is in a form, such as nitrate (NO_3^- -N), which is susceptible to loss from agricultural systems.

However, while EEFs have been widely investigated (Alonso-Ayuso et al. 2016; Barker and Sawyer 2017; Engel et al. 2015; Rowlings et al. 2016), there has been little research into the interaction between EEFs and fertilizer application method. Specifically, much of the research into EEFs has employed broadcast and/or incorporated placement of N-fertilizer, with few studies utilizing banded fertilizer application. Those that do (Lester et al. 2016; Scheer et al. 2016; Wang et al. 2016) typically focus analysis on agronomic responses or gaseous N emissions. This is not a comprehensive assessment of EEF behaviour in soils and consequently, the extrapolation of effective EEF utilization to other environments and scenarios is limited. Banding fertilizers in or near the root zone is a method of enhancing the opportunity for nutrient uptake by plants and minimising the risk of nutrient losses (Sanchez et al. 1990; Sandral et al. 2017); it is also an increasingly common practice in crop production for minimising soil disturbance

associated with tillage. However, banding N-fertilizers creates a vastly different biochemical environment in which N transformations will occur, compared to when the same product is broadcast or mixed into soil (Bezdicsek et al. 1971; Hauck and Stephenson 1965; Janke et al. 2019; Passioura and Wetselaar 1972; Wetselaar et al. 1972). This alteration in soil biochemistry is likely to impact EEF efficacy and will have implications for the effective utilization of EEF products when applied in sub-surface fertilizer bands.

The main objective of the current study was therefore to assess the performance of a range of band-applied EEFs in the field, by measuring the vertical and lateral distribution and transformations of fertilizer-N. The performance of different urea-based EEF products were contrasted to that of a standard urea band to identify any NUE benefits that may be realised from the adoption of different EEF technologies (i.e., NIs, UIs, or polymer coating). In addition, several rates of a NI treatment were included to give a preliminary indication of the potential for rate manipulation and the effect of in-band N concentration on NI efficacy. The direct measurement of N transformations and the associated soil biochemistry complements the wide body of literature reporting symptomatic effects (viz., yield, growth indicators, N_2O emissions, etc.) of EEFs in the field (Kawakami et al. 2012; Li et al. 2015; Nash et al. 2013; Thapa et al. 2016). The results provide a mechanistic understanding of how EEFs impact soil N transformations when applied in sub-surface bands.

Materials and methods

Site description

The field experiment was undertaken in a black Vertosol (Isbell 2016) at the University of Queensland research station (27° 34' 06" S, 152° 19' 55" E), Gatton Campus, Queensland, Australia. The key soil characteristics are presented in Table 1. The site has been regularly used for forage production.

Preparation of field site

In mid-September 2017, the site was disced and then rotary hoed to prepare for a cover crop. Forage sorghum (*Sorghum* spp. var. Super Sweet Sudan) was

Table 1 Chemical and physical characteristics of the field soil (0.10 m depth)

Order ^a	Location	Colour	Coarse sand	Fine sand	Silt	Clay	pH (1:5 water)	EC (1:5) (dS m ⁻¹)	eCEC (mmol _c kg ⁻¹ soil)	Mineral N (mg kg ⁻¹)	NO ₃ -N (mg kg ⁻¹)	TOC (%)
PSA (%)												
Vertosol	Gatton	Grey	3	16	21	62	7.8	0.07	493	2	< 1	1.13

^aIsbell (2016)

Where PSA refers to particle size analysis; pH (1:5 soil:water); EC (1:5 soil:water), electrical conductivity; eCEC, effective cation exchange capacity; N, nitrogen; TOC, total organic carbon

drilled at a rate of 33 kg ha⁻¹ to a depth of *ca.* 0.05 m in rows 0.50 m apart. The crop was cut and removed as hay *ca.* one month after planting to deplete background mineral N reserves. This was followed by an application of natural gypsum at a rate of 1 T ha⁻¹, which was broadcast onto the ratooning forage sorghum crop. In mid-January, the forage sorghum was cut and removed again, with plant growth indicating little residual N remaining in the soil. The field was then ripped to a depth of *ca.* 0.30 m, and subsequently rotary hoed. One day prior to the application of fertilizer treatments, the site was sprayed with S-Metolachlor (1.92 kg ha⁻¹) and Atrazine (1.25 kg ha⁻¹) to control weeds.

Treatment application

Fertilizer treatments were applied at in-band concentrations equivalent to those when 50 to 150 kg N ha⁻¹ are applied at band spacings of 1.8 m (*viz.* 9–27 g N m⁻¹), with the high in-band concentration typical of that used in the sugarcane and cotton industries (Bell et al. 2014; Rochester and Bange 2016). The treatments were placed in 10 m plot lengths with 0.75 m between individual bands and a buffer of 2.5 m separating treatments. Four replications of each treatment were arranged in a randomized complete block design. Fine white sand was mixed with the N-fertilizer to allow for subsequent identification of the band location in the soil profile.

Treatments were: (i) Control (no N applied); (ii) urea low (9 g N m⁻¹ of row); (iii) urea medium (18 g N m⁻¹ of row); (iv) urea high (27 g N m⁻¹ of row); (v) ENTEC® low (9 g N m⁻¹ of row); (vi) ENTEC® medium (18 g N m⁻¹ of row); (vii) ENTEC® high (27 g N m⁻¹ of row); (viii) 3,4 dimethylpyrazol

succinic acid (DMPSA)-urea high (27 g N m⁻¹ of row); (ix) Green Urea NV® high (27 g N m⁻¹ of row); and (x) Agromaster Tropical® high (27 g N m⁻¹ of row). Urea was standard granular urea, which is commonly used as a N source in many agricultural industries. ENTEC® is granular urea coated with the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) at a rate of 1.84 g DMPP kg⁻¹ urea. The DMPSA treatment is a urea product coated with a blend of DMPP and succinic acid, also aiming to deliver inhibitory properties to nitrification (Pacholski et al. 2016). Green Urea NV® is a granular urea coated with the urease inhibitor (N-(n-butyl) thiophosphoric triamide) (NBPT) at a rate of 0.48 g NBPT kg⁻¹ urea. Agromaster Tropical® is a polymer coated urea with a reported 90-day release profile (Impact Fertilizers 2019). Hereafter, the treatments are referred to by their active ingredient/coating and/or base ingredient and rate as: (i) control; (ii) urea low; (iii) urea medium; (iv) urea high; (v) DMPP-urea low; (vi) DMPP-urea medium; (vii) DMPP-urea high; (viii) DMPSA-urea high; (ix) NBPT-urea high; and (x) PCU high.

Soil environment and rainfall/irrigation

Following N-fertilizer application, electronic data loggers were set up at three points across the experimental site to record soil temperature (°C) at 0.10 m using 5TM Sensor probes (Decagon, 5TM Soil Moisture and Temperature). A rainfall sensor (ECRN-100) was set up in the middle of the site to record irrigation and rainfall events (mm). ECH2O software was used to download and interpret data from the data loggers. Soil moisture data were collected at 30-min intervals using two frequency domain reflectance probes (Sentek EnviroSCAN) at depths of 0.10 and

0.30 m below the soil surface. Raw data were converted to volumetric water content using soil water characteristics defined by pressure plate methods.

Soil sample collection

During sampling events, a small trench was dug perpendicular to the fertilizer band. When white sand (identifying the N band) was located on the two opposing faces of the trench, a string line was aligned over the band on the soil surface, and extended a small distance from the trench. A $350 \times 200 \times 70$ mm ($l \times b \times d$) metal open-face profile sampler, with a small notch at the bottom to allow for centre-of-band alignment with the string line, was inserted to a depth of 0.25 m. A 350×200 mm ($l \times b$) piece of sheet metal was inserted vertically down the open front of the profile sampler to a depth of *ca.* 0.25 m. The sheet metal and profile sampler were clamped together and the entire unit was removed from the soil by excavation. The clamps were detached and a clay cutting wire was run between the sheet metal and profile sampler to remove the front face (sheet metal) without disturbing the soil profile. The intact soil blocks were wrapped in plastic packing wrap and transported to cold room storage (3–5 °C) prior to sectioning and sampling.

In the laboratory, the soil blocks for each treatment were sectioned using a 50 mm grid (measuring from the bottom left corner), with 9 individual zones collected for analysis at varying height, depth, and lateral distances from the band zone. The analysed zones included (distances as mm from centre of band zone): (1) 75–125 mm directly above; (2) 25–75 mm at 45° above; (3) 25–75 mm directly above; (4) 75–125 mm lateral distance; (5) 25–75 mm lateral distance; (6) band zone (designated the ‘fertosphere’): 0–25 mm horizontal and vertical; (7) 25–75 mm at 45° below; (8) 25–75 mm directly below; and (9) 75–125 mm directly below (see Supplementary Fig. S2). At 49 and 71 days after fertilization (DAF), the sampling method varied slightly, with only three soil samples taken directly from the exposed soil profile using horizontally inserted 50 mm diameter sample tubes. These samples pertained to zones 3 (25–75 mm directly above band), 6 (centre of band to 25 mm horizontally and vertically), and 8 (25–75 mm directly below band). At all sampling times, soil within each individual zone was mixed to homogenize, and two representative samples of 10 g soil were

taken. One sample (10 g) was used for analysis of $\text{pH}_{1:5\text{w}}$ and $\text{EC}_{1:5}$, the other sample (10 g) was used to determine KCl-extractable N. Where urea-N measurements were undertaken, a separate 2 g soil sample was taken and immediately frozen prior to extraction and analysis.

Soil $\text{pH}_{1:5\text{w}}$ and $\text{EC}_{1:5}$

The $\text{pH}_{1:5\text{w}}$ and $\text{EC}_{1:5}$ of soil samples were measured in a 1:5 (w/v) soil-water solution by adding 50 mL deionized water to 10 g soil. Both $\text{pH}_{1:5\text{w}}$ and $\text{EC}_{1:5}$ were measured using a pH/EC Robot (Labfit AS-3020, Australia) with 60 s of stirring prior to measurement. The $\text{pH}_{1:5\text{w}}$ was recorded when multiple (5) values within a range of 0.02 units were recorded, and likewise $\text{EC}_{1:5}$ values were taken when variation between 5 readings was within 0.02 dS m^{-1} . A maximum reading time length of 60 s was set for the $\text{pH}_{1:5\text{w}}$ and $\text{EC}_{1:5}$ of each sample. Values for $\text{pH}_{1:5\text{w}}$ were arithmetically averaged from four replicate samples, and this was checked against the geometrical mean of H^+ concentrations to ensure correct interpretation (Boutilier and Shelton 1980). Electrical conductivity values (dS m^{-1}) were similarly averaged from four replicate samples.

Soil N extraction

Urea-N analysis was carried out by high performance liquid chromatography (HPLC) of 1:5 soil-water (w/v) extracts, using a Thermo Fisher Ultimate 3000 U-HPLC system (Germany) with a Thermo Fisher DAD 3000 diode array detector and following modified versions of the methods detailed for urea (MicroSolv 2010). Data were processed using Chromeleon 7.4 acquisition software and results are reported as mg L^{-1} . Urea-N values from HPLC analysis were expressed as the solution concentration (mg urea-N L^{-1}) of extractions. Extraction of mineral N followed standard methods (Method 7C2a: Rayment and Lyons 2010), using a 1:5 (w/v) ratio with 2M KCl (i.e., 10 g soil with 50 mL 2M KCl). Following centrifuging, extracts were analysed by segmented flow analysis for $\text{NH}_4\text{-N}$ (Searle 1974), and $\text{NO}_2\text{-N}$ and $\text{NO}_x\text{-N}$ (Best 1976; Bremner 1965). Concentrations of $\text{NO}_3\text{-N}$ were determined by calculating the difference between $\text{NO}_x\text{-N}$ and $\text{NO}_2\text{-N}$ (Best 1976; Bremner 1965). Mineral N values are reported as mg N kg soil^{-1} (1:5

w/v 2M KCl). Ammonia (aqueous NH_3) concentrations were calculated by applying the pK_a value of the $\text{NH}_4^+ \leftrightarrow \text{NH}_3$ reaction at 25 °C (Emerson et al. 1975), then determining the NH_3 (molarity) from known K_a , H^+ (molarity), and NH_4^+ (molarity) values in soil solution, as per Eq. 1 (Erickson 1985). Quantities of ammonia were calculated by determining the moles in solution, multiplying by the molecular weight of NH_3 and expressing as $\text{mg NH}_3 \text{ L}^{-1}$.

$$\text{NH}_3 = \frac{K_a \times \text{NH}_4^+}{\text{H}^+} \quad (1)$$

Statistical analysis

Statistical significance was determined by multiple ANOVAs to test the effects of (i) time; (ii) position (zones 6 and 8 only, as these were consistently measured over the 71-day experiment and were most impacted by the fertilizer band); (iii) N-fertilizer treatment; and the interactions of each of these factors. Statistical output for $\text{NH}_4\text{-N}$ is presented in Supplementary Material (Tables S1, S2); output for other measurements (urea-N, $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, aqueous NH_3 , pH, and EC), post-hoc analysis and mean + standard error tables are available on request.

Results and discussion

Environmental conditions during the study

Changes in soil moisture and temperature over the duration of the trial period will have potentially large impacts on the rate of N transformations and the possible movement of fertilizer-N out of the monitoring zone (i.e., the top 0.25 m of the soil profile). The soil temperature at a depth of 0.10 m averaged $26 \text{ °C} \pm 4 \text{ °C}$, with the highest temperatures occurring in the first month after fertilizer application and slowly declining thereafter (Fig. 1). The trial site received 450 mm of rainfall and irrigation during the 71-day monitoring period (Fig. 1), which primarily fell in three discrete wet periods. The first 150 mm fell within the first 7 DAF, a further 190 mm fell over a 10-day period between 18 and 28 DAF and 70 mm fell over a 3-day period from 53 to 55 DAF. The first two events in particular were large enough to cause short term waterlogging and trigger either leaching of $\text{NO}_3\text{-N}$

N into deeper profile layers or denitrification losses to the atmosphere [D. Rowlings (2019)—unpublished data]. In the absence of crop transpiration, the soil remained relatively moist for most of the incubation period despite the evaporative losses that occurred between rainfall events.

Unfertilized soil reactions over time

The distribution of N species (see Supplementary Material, Fig. S3) and the fluxes of $\text{pH}_{1:5\text{w}}$ and $\text{EC}_{1:5}$ (see Supplementary Material, Fig. S4) in the unfertilized soil profile (Control) are a result of variation in physico-chemical processes (i.e., solubilisation, precipitation, etc.), biological processes (decomposition, mineralization, etc.) (Carmo et al. 2016; Gerla 2013), and the effects of environmental conditions (i.e., wet-dry cycles, moisture content, water movement through soil, temperature, etc.) over time. Changes in these processes were used to benchmark the impact of fertilizer application.

In general, $\text{pH}_{1:5\text{w}}$ increased slightly with depth, although $\text{pH}_{1:5\text{w}}$ tended to be lowest in the 0.10–0.15 m depth (ca. 7.38) over the first 21 DAF (Fig. S4). From 49 DAF, $\text{pH}_{1:5\text{w}}$ values throughout the measured profile demonstrated a substantial decline of ca. 0.34 pH units and continued to exhibit acidification up to 71 DAF. This is consistent with increased nitrifying activity (Carmo et al. 2016) as indicated by increasing $\text{NO}_3\text{-N}$ and decreasing $\text{NH}_4\text{-N}$ concentrations at 49 and 71 DAF in untreated soil (Fig. S3). This also coincides with moderate increases in $\text{EC}_{1:5}$ (ca. 0.10 dS m^{-1} , Fig. S4) at 49 DAF whereby higher concentrations of soluble $\text{NO}_3\text{-N}$ likely contributed to the higher dissolved salt concentration. The initial flush of mineralization at 21 DAF (Fig. S3) was most pronounced in the disturbed soil in and around the position of the fertilizer tine (i.e., zones 1, 3, 6, 8 and 9—Fig. S2), and occurred in response to the increased soil moisture from irrigation and rainfall in the week following fertilizer application (Fig. 1). The relative proportions of mineral N present as $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ fluctuated during the monitoring period (Fig. S3), with $\text{NH}_4\text{-N}$ concentrations tending to dominate the mineral N species for the first 30 days of the experiment. After that, $\text{NO}_3\text{-N}$ was the principal mineral N species present as nitrification became the dominant N transformation process.

Fig. 1 Time scale of rainfall and irrigation (mm), temperature fluxes (°C, 0.10 m depth) and the average soil moisture ($\text{m}^3 \text{ water m}^3 \text{ soil}^{-1}$) at 0.10 and 0.30 m depths, where the dotted line indicates predicted values in the absence of direct measurement

While the absence of plants in this experiment prevented the determination of N dynamics in response to an actively growing crop, it facilitated the understanding of N fluxes in the soil without the confounding effects of crop water and N uptake. This enabled a comprehensive investigation of banded EEF behaviour and efficacy under field conditions that can be broadly applied to a range of agricultural systems.

Biochemical reactions and N dynamics of banded urea and EEFs

The impact of banded EEFs on biochemical reactions in the soil were investigated by comparing the 3-dimensional distribution and persistence of N species over time. From this, EEF effects on major

processes [urea hydrolysis, the equilibria of NH_4^+ and NH_3 , and nitrification (see Supplementary Material, Fig. S1)] were compared to a granular urea standard. Accordingly, the following discussion describes these processes in detail for standard urea and then focuses on the impact of each of the EEF technologies and implications for NUE. The influence of both the physico-chemical properties of the Vertosol and the mass flow of soil water on the efficacy of EEFs were also considered in this analysis (Nye 1979).

Banding standard urea induces inhibition of ureolytic activity and nitrification

Typically, the hydrolysis of applied urea in soils completes within 2–4 days (Antil et al. 2009;

Christianson et al. 1993). However, some urea-N (viz. 45 mg N kg^{-1} soil) was still present at 7 DAF in soil within the fertosphere and directly below the band (to

75 mm, Fig. 2). Rainfall from 2 to 5 DAF (Fig. 1) likely contributed to the vertical distribution of urea-N down the profile. This zone of incomplete urea

Fig. 2 Distribution of N species (mg N kg^{-1} soil) over time in soil treated with the high in-band concentration (27 g N m^{-1}) of banded urea. No measurement of urea-N was taken after 7 days. The grid indicates the zones (Fig. S2) that were sampled at each time point

hydrolysis suggests there was moderate inhibition of urease activity over the first week following application, where the initially high urea-N concentrations may have been sufficient to induce substrate (urea-N) saturation of urease (Bhat et al. 2011; Singh and Nye 1984). Alternatively, the high $\text{pH}_{1.5\text{w}}$ (ca. 8.20–8.30, Fig. 3) in the fertosphere may have reduced the affinity of urease for urea-N molecules, which has been observed even at low urea-N concentrations (Singh and Nye 1984).

Regardless of the apparent inhibition of some ureolytic activity, $\text{NH}_4\text{-N}$ persisted at concentrations of ca. 700–830 mg N kg soil⁻¹ in the same zones until at least 21 DAF (Fig. 2). Significantly elevated

concentrations of $\text{NH}_4\text{-N}$ were also recorded at 125 mm below the band and at 75 mm laterally and diagonally below the band at that time. The detection of $\text{NH}_4\text{-N}$ at these depths, which are further from the fertosphere than was recorded for urea-N (Fig. 2), suggests there may have been some leaching of urea-N which was followed by rapid hydrolysis to $\text{NH}_4\text{-N}$ at these depths. Alternatively, the deeper distribution of $\text{NH}_4\text{-N}$ may have been due to leaching of aqueous NH_3 . Elevated concentrations of aqueous NH_3 were observed within the fertosphere and below at 7 DAF (Fig. 4), as a consequence of the high $\text{NH}_4\text{-N}$ concentrations and elevated pH (Fig. 3) in those zones (Emerson et al. 1975; Erickson 1985). The $\text{NH}_4\text{-N}$ at

Fig. 3 Heat maps of pH fluxes over time in response to banded N-fertilizer treatments. The pH indicated outside the sample zone (marked with grid) is representative of the average pH throughout the profile in control soil at that time

Fig. 4 The distribution of calculated aqueous NH_3 concentrations (mg L^{-1}) over time in response to banded N-fertilizer treatments. Concentrations of aqueous NH_3 were always $< 0.1 \text{ mg L}^{-1}$ in unfertilized soil and for all treatments after 49 days

the lower depths in the profile may therefore have also been a result of N re-distribution as aqueous NH_3 that was subsequently converted back to $\text{NH}_4\text{-N}$ in the less alkaline and lower $\text{NH}_4\text{-N}$ environment at depth. By 34 DAF, $\text{NH}_4\text{-N}$ concentrations outside the fertosphere and the zone below had moderated to $< 60 \text{ mg N kg soil}^{-1}$ (Fig. 2), with concentrations of $\text{NH}_4\text{-N}$ immediately below the band being the last to decline below $100 \text{ mg N kg soil}^{-1}$.

The decrease in $\text{NH}_4\text{-N}$ concentration with time (Fig. 2) was consistent with nitrification processes, although the time required for nitrification of the applied fertilizer was much longer than expected. There was little evidence of nitrification by 7 DAF, with high concentrations of $\text{NH}_4\text{-N}$ (*ca.* $700\text{--}900 \text{ mg N kg soil}^{-1}$) in the fertosphere and immediately below (i.e., zones 6 and 8, Fig. S2). At this time, concentrations of $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ represented $< 2\%$ of the total mineral N (Fig. 2), although these low concentrations may also be partly due to

leaching or denitrification loss during the heavy rain that fell between fertilizer application and 7 DAF (Fig. 1). Nonetheless, the high concentrations of $\text{NH}_4\text{-N}$ persisted in these regions during the drier period from 7 to 21 DAF and $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations remained relatively low. In contrast, 40–60% of the measured mineral N in zones outside of the fertosphere and soil immediately below (zones 6 and 8) was present as $\text{NO}_3\text{-N}$ by 21 DAF (Fig. 2). This indicates a strong and persisting inhibitory effect on nitrifying activity within the fertosphere and up to 75 mm below for up to 21 DAF.

Three key chemical changes associated with urea hydrolysis are known to contribute to nitrification inhibition, including (i) a shift to a more alkaline pH; (ii) an increase in local salinity; and (iii) elevated aqueous NH_3 concentrations. While the functional pH limits of nitrifiers vary considerably across a range of soil types (Guo et al. 2017; Nicol et al. 2008; Silva et al. 2012; Ying et al. 2017) increases of nearly 1 pH

unit were observed in the fertosphere and immediately below the urea band (Fig. 3) in this study. This created a nearly 10-fold change in the H^+ concentration relative to what the indigenous nitrifying population were adapted to (Nicol et al. 2008; Ying et al. 2017) and is likely to have disrupted nitrifying activity. Previous studies have also identified substantial increases in EC as inhibitory to nitrification due to the osmotic effect that high salt concentrations have on nitrifying organisms (Claros et al. 2010; McClung and Frankenberger 1985, 1987; McCormick and Wolf 1980). However, in the urea-treated soil in this field experiment, the measured EC was best correlated (data not shown) with fluctuations in the concentration of NO_2-N and NO_3-N , reflecting changes in the soluble salt concentration, rather than indicating zones of nitrification inhibition. The conditions of this field experiment (viz. large soil volume and movement of water through fertilizer bands) meant that inhibitory effects of raised EC on nitrification were unlikely to have occurred. However, it is noted that under dry field conditions the inhibitory effect of elevated EC on nitrification may have been greater, as soluble salts would not have moved out of the fertosphere and dispersed through a larger soil volume. Elevated aqueous NH_3 may also have influenced the nitrification process, with known toxicities to *Nitrosomonas* at a minimum NH_3 concentration of $10\text{--}150\text{ mg L}^{-1}$ and $0.1\text{--}4.0\text{ mg L}^{-1}$ for *Nitrobacter* (Anthonisen et al. 1976; Bae et al. 2001; Suthersan and Ganczarczyk 1986). According to these toxicity thresholds, only the second step of nitrification would have been inhibited in response to NH_3 toxicity in this field study (Fig. 4). However, the aforementioned aqueous NH_3 toxicity ranges were identified primarily from pure culture studies of specific bacteria (i.e., *Nitrosomonas* and *Nitrobacter*), and may not be representative of the NH_3 sensitivity of a nitrifying community in soil. There are limited reports on NH_3 sensitivity of nitrification in soils, although initial inhibitory effects on nitrification within the zone of fertilizer application have been observed in some field studies following the application of anhydrous NH_3 fertilizer (Kyveryga et al. 2004; McIntosh and Frederick 1958). Given the strength of the inhibition observed at 7 DAF (i.e., very limited NO_2-N and NO_3-N production), it is suggested that substantial increases in both alkalinity and aqueous NH_3 concentrations may have contributed to the inhibition of nitrification.

Although limited NO_3-N was recovered at 34 DAF, a significant decline in NH_4-N concentrations between 21 and 34 DAF (Fig. 2) was indicative of substantial nitrification over this time period. The general decline in NO_3-N observed throughout the entire urea-treated soil profile between 21 and 34 DAF (Fig. 2) was likely the result of leaching into deeper soil layers or denitrification following ca. 140 mm of rainfall from 24 to 28 DAF (Fig. 1). By 49 DAF substantial concentrations of NO_3-N had re-appeared in and below the fertosphere, indicating continuing net nitrification of the residual NH_4-N . At this time, NO_3-N represented ca. 60% of the mineral N in each zone (i.e., zones 3, 6, 8, Fig. S2) of the $150 \times 150\text{ mm}$ soil column, with the balance of measured mineral N primarily found as NH_4-N .

Nitrification inhibitors prolong the inhibitory effects of urea bands

In comparison to standard urea, the inhibitory effects on nitrification were greater and persisted for longer in soil treated with high rates of DMPP-urea (Fig. 5) and DMPSA-urea (see Supplementary Material, Fig. S5). Concentrations of NH_4-N were consistently higher and more widely distributed in profiles of the NI-urea treatments (cf. Fig. 2), indicating reduced oxidation and greater movement of N as aqueous NH_3 (Fig. 3).

In the DMPP-urea treatment, substantially higher NH_4-N concentrations up to 71 DAF (Fig. 5) provide evidence for an extension of inhibitory effects of up to ca. 50 days longer than that observed for standard urea (ca. 21 days of inhibition observed in standard urea bands), with this persistence primarily observed within the fertosphere and immediately below. At 49 DAF, concentrations of NO_3-N had started to increase considerably in DMPP-urea treated soil, but were still less than 50% of those recorded for standard urea. This extended period of inhibition contrasts to other studies that utilized mixed application and/or did not include a urea-based fertilizer (Chen et al. 2010; Guardia et al. 2018a, b; Irigoyen et al. 2003), in which inhibitory effects of DMPP were seen for only 14–30 days. Janke (2020) hypothesized that as DMPP primarily remains within the fertosphere (characterized by high pH, raised salinity, and elevated aqueous NH_3 concentrations), a large proportion of microbial activity and associated inhibitor degradation may be prevented, effectively inhibiting nitrification whilst preserving

Fig. 5 Distribution of N species (mg N kg⁻¹ soil) over time in soil treated with the high in-band concentration (27 g N m⁻¹) of banded DMPP-urea. No measurement of urea-N was taken after 7 days

the inhibitor. The prolonged nitrification inhibition at an equivalent in-band concentration (i.e., 27 g N m⁻¹) of DMPP-urea in this field experiment, and also

that of another field study under similar conditions (Scheer et al. 2016), supports this hypothesis.

Over the trial period, DMPSA-urea did not demonstrate a greater or more prolonged inhibitory effect on nitrification compared to DMPP-urea (Figs. 5, S5), as had been claimed (Pacholski et al. 2016). While $\text{NH}_4\text{-N}$ concentrations were similar to that of DMPP-urea throughout the trial period, concentrations of $\text{NO}_3\text{-N}$ were generally higher over the first 49 DAF, and significantly so at 21 DAF. It is postulated that the dependence on microbial degradation of succinic acid for DMPP release (Pacholski et al. 2016) may impair the initial effectiveness of DMPSA-urea in banded applications. The hostile conditions of a urea-based band may have a general inhibitory effect (Park et al. 2016; Rietz and Haynes 2003) on a range of microorganisms that are required for the ‘release’ of this inhibitor. Further investigation is required to determine whether this product is effective in banded applications.

The duration of NI-conferred inhibition is dependent on the rate of application

Increasing the rate of fertilizer application (i.e., in-band concentrations) of urea and DMPP-urea progressively prolonged both net (Figs. 2, S6) and DMPP-induced (Figs. 5, S7) nitrification inhibition. Despite a three-fold increase of in-band fertilizer concentrations and consequent variations in $\text{NH}_4\text{-N}$ concentrations, $\text{NO}_3\text{-N}$ concentrations were similar at all application rates at 7 DAF. This was most likely indicative of inhibitory effects on nitrification due to the elevated pH and aqueous NH_3 concentrations observed in and around the fertosphere (Figs. 3 and 4, S8, S9), but could also be partly due to loss of nitrification products in response to the rainfall which occurred between fertilizer application and 7 DAF (Fig. 1). Nonetheless, similar $\text{NH}_4\text{-N}$ concentrations between fertilizer treatments applied at the same rate (Fig. 6) suggest that at 7 DAF, chemical changes associated with urea hydrolysis (Figs. 3, 4 and 7, S8, S9) created conditions inhibitory to nitrification irrespective of NI addition or fertilizer application rate. However, by 21 DAF declining $\text{NH}_4\text{-N}$ concentrations in the low and medium urea treatments contrasted to those of DMPP-urea, indicating the initiation of DMPP-conferred inhibition in the lower application rates (Fig. 6). For the lowest fertilizer rate, the greatest effect from DMPP was seen at this time, with the average $\text{NH}_4\text{-N}$ concentration in the fertosphere and soil immediately

below (i.e., zones 6 and 8) *ca.* 10-fold higher in the DMPP-urea treatment *cf.* standard urea. By 49 DAF, $\text{NH}_4\text{-N}$ concentrations were similar between fertilizer products at the low fertilizer application rate (Fig. 6), indicating that the inhibitor effects had fully dissipated by this time.

Soil treated with the medium and high rates of urea demonstrated sharp declines in $\text{NH}_4\text{-N}$ concentrations between 21 and 34 DAF, which was not observed in the DMPP-urea treatments at the same rates (Fig. 6), indicating an inhibitory effect of DMPP on nitrification. For the medium fertilizer treatment, this was the period of greatest benefit from DMPP-addition, with the concentration of $\text{NH}_4\text{-N}$ 14-fold higher *cf.* standard urea. While nitrification inhibition was still evident at 71 DAF in the medium fertilizer application rate, there was a much greater inhibitor-conferred effect at the highest fertilizer application rate at this time. This effect was manifest as much greater differences in $\text{NH}_4\text{-N}$ concentration between urea and DMPP-urea treatments (i.e., 20-fold higher for DMPP-urea). The trend of increasing nitrification inhibition with fertilizer application rate suggests an even longer inhibitory period was possible at the high in-band concentration than was observed over this 71-day experiment.

While net nitrification observed in urea bands is attributed to large and persistent changes in soil chemistry (Figs. 3, 4 and 7, S8, S9), increasing nitrification inhibition at higher in-band concentrations of DMPP-urea suggests that DMPP may also have a ‘saturating’ effect on soil microbes within the fertosphere. Increasing the rate of DMPP-urea to achieve higher in-band N concentrations also increased the in-band concentration of DMPP (6–17 mg DMPP m^{-1} band). Despite the ratio of DMPP:N remaining constant at all fertilizer application rates, a similar volume of soil (i.e., the fertosphere) received up to three-fold more inhibitor at the high in-band concentration compared to the lowest fertilizer application rate. In addition, the presence of DMPP with banded urea appeared to exacerbate conditions hostile to microbes (i.e., raised pH and aqueous NH_3), with such conditions dissipating later in DMPP-urea bands applied at the same in-band concentrations as standard urea (Figs. 3, 4 and 7, S8, S9). This is likely an effect of DMPP-induced $\text{NH}_4\text{-N}$ preservation limiting nitrification-driven pH decreases

Fig. 6 The average $\text{NH}_4\text{-N}$ concentration (mg N kg^{-1} soil) of the fertosphere and soil immediately below (zones 6 and 8, Fig. S2) over time in urea and DMPP-urea treatments

and the maintenance of high aqueous NH_3 concentrations.

NI fertilizers may allow N rate reductions

Similar indicators of plant-available N (i.e., concentrations of $\text{NO}_3\text{-N}$ and total mineral N) were observed in the soil profile from the medium in-band concentrations of DMPP-urea (Fig. S7B) and the high in-band concentrations of urea (Fig. 2) from *ca.* 34 DAF. This observation suggests that application rates of N may be able to be reduced when using DMPP-urea (*cf.* standard urea) without adversely affecting N availability for crops. However, this may only apply to crops that do not require substantial N uptake immediately following fertilizer application, as N availability was considerably lower for the moderate DMPP-urea rate over the initial 34 DAF. Further, phytotoxic conditions in and around the fertosphere (Figs. 3, 4 and 7) may restrict early access of crop roots to fertilizer-N (Court et al. 1964a, b; Passioura and Wetselaar 1972). This suggestion is circumstantially supported by some studies in crops with long growing seasons (i.e., sugarcane) which reported a similar quantum of crop N uptake from reduced N application rates of DMPP-urea compared to urea (Dowie et al.

2019; Wang et al. 2016). In contrast, studies of short-season crops (i.e., cereals and grains), which have a much shorter and more intense periods of N demand, were unable to demonstrate additional crop N uptake from DMPP-urea (*cf.* standard urea) despite reduced losses and increased mineral N availability in the soil profile (Lester et al. 2016; Schwenke and Haigh 2019).

Urease inhibitors have limited impact in banded applications

Banding NBPT-urea resulted in substantial inhibition of ureolytic activity up to 7 DAF within, laterally to 75 mm, and below, the fertosphere (Fig. 8). Compared to standard urea, concentrations of urea-N were *ca.* 16-fold higher within the fertosphere of the NBPT-urea treatment. Higher concentrations were also detected vertically to 125 mm and laterally to 75 mm from the band with the lateral and vertical displacement consistent with movement of urea-N from the fertosphere by mass flow (in response to the 150 mm of rain that had fallen after fertilization—Fig. 1) and diffusion. However, by 34 DAF, the mineral N in soil profiles treated with NBPT-urea (Fig. 8) was similar to that of standard urea (Fig. 2). The lack of continued presence of elevated urea-N

Fig. 7 Heat maps of changes in electrical conductivity (dS m^{-1}) over time in response to banded N-fertilizer treatments

concentrations at 21 DAF (< 5% of the urea-N detected at 7 DAF) suggests that either the inhibitory effects of NBPT were short-lived, or that leaching prior to the 7 DAF sampling had caused a large amount of urea-N to move either below the measurement zone or simply away from the NBPT. While rapid leaching was unlikely in this low permeability soil, it is clear that at least some urea-N had moved into layers below the fertilizer band by 21 DAF. The relative immobility of banded NBPT in soils of high-clay and OM content has been recently identified by Janke (2020) and is likely a dominant factor in the rapid ‘loss-of-function’ observed in this and other studies (Watson et al. 1994; Adhikari et al. 2019). Soluble urea-N may diffuse and/or move with mass flow, creating an asynchrony of inhibitor and substrate location that reduces the effectiveness of NBPT. Even limited leaching, as

likely occurred in this study, may distribute urea-N beyond the zone of NBPT influence, which was measured at *ca.* 10 mm (i.e., within the fertosphere) in diffusion studies (Janke 2020). The transient effectiveness of NBPT once applied to soil is well known, and a range of soil factors may contribute to this. Rapid degradation has been found to occur under acidic conditions (Engel et al. 2015) and elevated temperatures (Watson et al. 2008), and loss-of-function is reported at high soil moisture content (Cantarella et al. 2018; Sanz-Cobena et al. 2016). While soil acidity is unlikely to have contributed to the degradation of NBPT in this trial (Table 1; Fig. 3), elevation of both soil moisture and temperature at various times between 7 and 21 DAF (Fig. 1) may have had an effect on NBPT performance. Anaerobic soil conditions can prevent the oxidation of NBPT to

Fig. 8 Distribution of N species (mg N kg^{-1} soil) over time in soil treated with the high in-band concentration (27 g N m^{-1}) of banded NBPT-urea. No measurement of urea-N was taken after 34 days

NBPTO, which is the molecule that is ‘active’ in inhibiting urease (Manunza et al. 1999). However, despite the heavy early rainfall (Fig. 1) and resulting high soil moisture content, the presence of considerably higher concentrations of urea-N in the profile

treated with NBPT-urea (*cf.* urea) at 7 DAF indicates that conditions were not sufficiently oxygen-limited to prevent the formation of NBPTO. An increase in soil temperatures to *ca.* 28°C may have increased the rate of chemical degradation of NBPT (Watson et al. 2008)

between 7 and 21 DAF, contributing to the gradual decrease in urea-N over this period. Increased soil temperatures may also enhance enzymatic activity which can outpace the conversion of NBPT to NBPTO (Carmona et al. 1990), further contributing to reduced inhibitor efficacy.

The transient effectiveness of this inhibitor in concentrated bands is consistent with other studies that utilized broadcast and/or incorporated UI (Cantarella et al. 2018; Sanz-Cobena et al. 2012; Singh et al. 2013) in that inhibitory effects were only observed for *ca.* 21 days. Banding therefore does not appear to influence the efficacy of the UI when compared to broadcast and/or incorporated applications. However, the potential for banded UI to reduce N losses (*cf.* standard urea) and improve crop recovery of fertilizer-N appears limited. The mechanism of regulating urea hydrolysis is primarily targeting reducing gaseous NH_3 losses, which is not a major N loss pathway in sub-surface bands (Rochette et al. 2013a, b). Further, significantly lower increases in pH (Fig. 3) and formation of aqueous NH_3 (Fig. 4) in and around NBPT-urea bands (*cf.* standard urea) enabled formation of similar concentrations of $\text{NO}_3\text{-N}$ to that of standard urea, despite lower concentrations of $\text{NH}_4\text{-N}$ (Figs. 2 and 8). This, combined with the preservation of N in the moderately soluble form of urea, may result in increased leaching as urea-N or $\text{NO}_3\text{-N}$ (Dawar et al. 2011; Ma et al. 1995) and/or denitrification ($\text{NO}_3\text{-N}$) loss of N in conditions where soil moisture content is high.

Controlled-release urea delivers a low basal supply of rapidly nitrified N

In contrast to the soluble N-fertilizers, banded PCU resulted in a persistent supply of urea-N to the soil solution until at least 34 DAF, with concentrations of urea-N primarily located in the fertosphere and directly below (Fig. 9). Over the measurement period to 34 DAF, peak urea-N recovery in soil solution occurred at 21 DAF in the same zones, and while urea-N concentrations in soil had decreased significantly by 34 DAF, this decrease may simply have been a response to the intense rainfall that occurred from 25 to 28 DAF (Fig. 1). Indeed, the persistently high $\text{NH}_4\text{-N}$ concentrations (Fig. 9) suggest release of urea-N to soil solution continued for much longer. However, the slow release of N from PCU granules resulted in the

formation of N concentration gradients in soil solution that were considerably lower than that of standard urea, with N distribution reduced by *ca.* 50 mm in soil profiles (*cf.* standard urea, Figs. 2 and 9). In dry conditions, the dispersal of N from the fertilizer band would likely be much lower, resulting in a smaller volume of soil N enrichment in and around the fertilizer band. Consequently, effective crop N uptake from PCU-N bands would rely on close seed placement to the fertilizer band and/or the development of a prolific root system in order to access the considerably reduced N-rich zone of soil.

In response to lower ureolytic rates (i.e., less urea available for hydrolysis at a given time), the changes in soil chemistry (Figs. 3 and 7) and aqueous NH_3 concentration (Fig. 4) were of lesser magnitude in and around the PCU fertosphere, resulting in rapid nitrification (Fig. 9). While $\text{NO}_3\text{-N}$ concentrations were comparatively lower than for other N-fertilizer treatments up to 21 DAF, the average ratio of $\text{NO}_3\text{-N}$ to $\text{NH}_4\text{-N}$ throughout the profile of soil treated with PCU (*ca.* 46%, Fig. 9) was similar to that of standard urea (*ca.* 45%, Fig. 2). Further, from 49 DAF, concentrations of $\text{NO}_3\text{-N}$ were higher in soil profiles of PCU-treated soil compared to other N-fertilizer treatments. This indicates a potentially longer window of risk for N loss via leaching or denitrification with this EEF if the later-released N is not captured by an actively growing crop. The frequent assessment of PCU performance at set time points, which typically do not extend to a timeframe whereby N release from PCU products is considered ‘complete’, potentially underestimates the risks of N losses from these products. Further, studies which investigate the efficacy of PCU products by assessing performance based on gaseous emission and crop yield indicators (Li et al. 2015; Rahman et al. 2018) may overlook N lost via leaching, which has been reported in several studies (LeMonte et al. 2016; Nelson et al. 2009) (Fig. 9).

Conclusions

The inhibition of nitrification in response to rapid hydrolysis of concentrated urea bands indicates that the benefit of NIs will not be realised until the conditions in and around the band became more favourable for nitrification. Increasing the rate of DMPP-urea application increases the extent and

Fig. 9 Distribution of N species (mg N kg^{-1} soil) over time in soil treated with the high in-band concentration (27 g N m^{-1}) of banded polymer-coated urea. No measurement of urea-N was taken after 34 days

duration of inhibitory effects, which has important implications for synchronising the availability of N from concentrated DMPP-urea bands with crop requirements.

Whilst some urea-N was preserved for *ca.* 7 days, banding UIs did not appear to offer any significant NUE benefits. Further, the preservation of N as urea-N and the relatively rapid nitrification of available $\text{NH}_4\text{-N}$

N may increase the risk of leaching and denitrification losses in environments and soil types which facilitate these loss pathways.

Compared to soluble forms of urea, PCU delivered lower daily $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations which may protect N from leaching and denitrification losses in isolated instances of high rainfall/irrigation soon after fertilizer application. However, distribution of N from the band is also reduced, resulting in a smaller N-enriched zone of soil. Banded PCU appears best suited for delivering a low, basal supply of N to plants that have root zones in close proximity to the fertsphere.

This study provides a comprehensive understanding of the supply, availability and distribution of N from a range of EEF technologies when applied in concentrated bands. This knowledge may be incorporated into agronomic advice for the effective utilization of banded EEFs, with the aim of improving NUE in agricultural systems.

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