Impact of contrasting fertilizer technologies on N dynamics from sub-surface bands of ‘pure’ or blended fertilizer applications

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Abstract. Enhanced efficiency fertilizer (EEF) technologies that employ product coatings to delay nitrogen (N) release or are chemically stabilized to inhibit key steps of N transformations in soil, offer potential for improving N use efficiency (NUE) in agricultural systems. However, the dynamics of N release and transformation from single technologies may result in a spatial or temporal mismatch of N supply and demand during a growing season. This may be overcome by use of blends of different technologies, provided the reduction in the concentration of stabilizing products does not reduce effectiveness. Laboratory incubations quantified the N dynamics around bands of controlled release fertilizer (CRF) and nitrification inhibited (NI) urea and varying blends of these technologies, and referenced this against conventional urea and biodegradable, plant oil-coated urea (POCU) applied at the same rates in two contrasting soils over 60 days. Blends of NI-urea (3,4–dimethylpyrazole phosphate; DMPP-urea) and a CRF (polymer coated urea; PCU) typically resulted in N concentrations and distribution that were intermediate to that of the constituent products in unblended applications. Changes in the proportions of each product were mirrored by urea-N concentrations around the bands in both soils, while the proportions of DMPP-urea in each blend were only related to the extent of nitrification inhibition in the Vertisol. A proportion of the POCU granules burst during the early stages of incubation, resulting in initially higher mineral N concentrations *cf*. PCU. However, both CRFs delayed N release and formation of NO_3-N relative to granular urea, and mineral N distribution was similar within each soil. Soil type had a significant impact on banded N dynamics. Where there was little effect of N-fertilizer treatment on NO_3-N production in the Ferralsol, the higher impedance to solute transport in the Vertisol contributed to a significant inhibitory effect of NI-urea on nitrification in both pure and blended DMPP-urea treatments. Using NO_3-N production as a benchmark for the risk of environmental loss, the efficacy of fertilizer treatments in this soil was of: DMPP-urea-PCU blends (higher ratio of PCU may offer small but insignificant benefit) > DMPP-urea = PCU > urea. These findings highlight the importance of soil properties in determining the N dynamics from different banded EEF products. Insights into the efficacy of biodegradable alternatives to polymer coatings and the efficacy of blended EEF products can improve the reliability of N supply while reducing environmental impacts, therefore offering greater opportunities to sustainably improve fertilizer NUE in cropping systems.

1 Introduction

Enhanced efficiency nitrogen (N) fertilizers (EEFs) are widely proposed as a key tool for meeting the competing demands of (i) improving agricultural productivity and (ii) reducing the impacts of agricultural activity on nearby environments. Broadly, these challenges involve improving N use efficiency (NUE) in agricultural systems. Current EEF technologies are deployed in fertilizer products which utilize controlled-release or nutrient stabilizing mechanisms which regulate fertilizer N transformations in soil to enhance crop N uptake and reduce potential losses to natural environments (Association of American Food and Plant Control Officials, 2013).

Controlled-release mechanisms aim to regulate the duration, rate and pattern of N release (Shaviv, 2001), providing a predictable supply of labile N under a given set of environmental conditions. The coating material of controlled-release fertilizers (CRFs) has evolved over time, with polymer-coated products currently being the most widely utilized form of this technology in agriculture. Recently, concerns of polymer "shell" persistence and the potential for these to carry unreleased N into natural ecosystems (Azeem et al., 2014; Trenkel, 2010) has led to investigation of a range of biodegradable coatings (Araujo et al., 2017; Li et al., 2016; Rotondo et al., 2018; Vadjung and Saengsuwan, 2018). Environmental concerns will continue to drive the development of biodegradable coatings in future CRF products, but the efficacy of these coatings for delivering a controlled release of N has only been explored in a very limited number of studies (e.g., Martinez et al., 2021).

Stabilized fertilizers function by reducing the rate of microbial activity at specific steps of N transformation, thereby regulating the formation of N products with greater risks of loss (Trenkel, 2010). Commercial stabilizing products currently target either of two key processes, viz. the hydrolysis of urea to ammonium carbonate ($[NH_4]CO_3$) with urease inhibitors (UIs), and the oxidisation of ammonia (NH_3) to nitrite (NO_2^-) with nitrification inhibitors (NIs). A wide range of compounds inhibit urease (Byrnes and Freney, 1995; Medina and Radel, 1988) and nitrification (Juliette et al., 1993; McCarty, 1999; McCarty and Bremmer, 1986; 1989) activities, with N-(n-butyl) thiophosphoric triamide (NBPT) and 3, 4-dimethylpyrazole phosphate (DMPP) being the most widely used compounds in urease and nitrification inhibitor formulations, respectively.

While the function and efficacy of EEFs is relatively well-defined under controlled-conditions (Azam et al., 2001; Benckiser et al., 2013; Creason et al., 1990; Du et al., 2006; Guardia et al., 2018; Shaviv et al., 2003), field performance of these technologies have not demonstrated consistent outcomes for yield improvement, N uptake and reductions in N losses (Dang et al., 2021; LeMonte et al., 2016; Lester et al., 2016; Li et al., 2015; Martinez et al., 2021; Nauer et al., 2018; Rowlings et al., 2016; Schwenke and Haigh, 2019; Wang et al., 2016b). This inconsistency has eroded confidence in EEFs to deliver improved NUE. In particular, concerns have been raised that the delivery of N from CRFs may be too slow to effectively meet early crop demand (Halvorson and Grosso, 2013; Nelson et al., 2009; Quemada et al., 2013; Thapa et al., 2016). Conversely, questions of inhibitor effectiveness have been raised where inhibition appears to be relatively transient (Chen et al., 2015; Fu et al., 2018; Shi et al., 2016). These concerns, combined with the higher fertilizer costs (per kg N) associated with EEF technology, raise real concerns about the effectiveness and the economic returns that can be derived from the use of products reliant on individual EEF technologies. In response, attempts have been made to blend the cheaper, readily soluble N products with variable proportions of EEF products to mitigate at least some of the potential N loss while minimising the financial risk.

Multiple field experiments have investigated the potential for blends and varying the ratios of urea and CRFs (typically, polymer coated urea [PCU]) to deliver improved NUE (Dhakal and Nelson, 2019; Guo et al., 2017; McKenzie et al., 2010; Nash et al., 2012; Noellsch et al., 2009; Patil et al., 2010; Payne et al., 2015; Wang et al., 2015). Whilst most of these experiments have found that blends of PCU and urea may reduce N losses (*cf.* urea alone), not all have reported positive outcomes for improved crop uptake and / or yield gains (McKenzie et al., 2010; Nash et al., 2012; Patil et al., 2010). Where benefits have not been recorded, 'failures' have been attributed to a disparity in N supply relative to crop demand (i.e., inadequate N available early in the season due to the delay in N supply from PCU) or conditions where N loss has been negligible and the addition of PCU has not provided any advantages (*cf.* urea). Where the supply of N from PCU-urea blends has not met initial crop demand, it is hypothesized that the uncoated urea component of the applied fertilizer blend may have been lost. Under high loss conditions, the substitution of N-stabilized products for the more 'vulnerable' urea in blends with PCU may provide additional protection against immediate leaching and / or denitrification losses. The combination of NI-urea and PCU in fertilizer bands may therefore create a more 'stable' and sustained supply of N *cf.* PCU-urea blends or urea alone. The concept of blending NI-urea and PCU products within fertilizer bands as a way of improving crop NUE has been recently tested in the Australian sugarcane industry (Bell et al., 2021; Connellan et al. 2021), where environmental conditions and soil characteristics are known factors for high N loss conditions. Sugarcane crops using these blends were consistently able to achieve similar crop N uptake to urea applications at 20 - 25% higher application rates, although yield responses were variable in some situations and rarely exceeded those achieved from using either NI alone, or a blend of urea and PCU (Connellan et al. 2021). Other evaluations of blended EEF products are limited, and the extent to which these reports of improved fertilizer-blend efficacy in sugarcane can be extrapolated to other soils, climates and cropping systems is limited by a lack of mechanistic studies. This study seeks to address this knowledge gap by determining the release, transformation rates and distribution of N from bands of granular urea, CRFs, stabilized urea and blends of these products in contrasting soils under controlled-environment conditions. A plant-oil coated CRF (Kingenta, 2018) is also included in this investigation for preliminary examination of N release dynamics from an example of a biodegradable fertilizer coating. This study aims to provide a mechanistic understanding of fertilizer-blend dynamics which may be used to predict the potential efficacy of different EEF blends in contrasting soils that underpin a variety of crop industries.

2 Methods

2.1 Soil collection, characterization, and preparation

Soil from the top 10 cm of the profile of a yellow Ferralsol and black Vertisol (IUSS Working Group, 2015) were collected from sugarcane farms in the Bundaberg district. The soils were chosen on the basis of their contrasting texture and physico-chemical properties (Table 1). Briefly, the Ferralsol was slightly acidic and had a low clay content, cation exchange capacity

(CEC), and pH buffering capacity (pHBC). The Vertisol had a high clay content, CEC and pHBC, and a neutral pH. Prior to incubation, soil was prepared by air-drying and sieving to < 2 mm. The moisture content at field capacity for both soils was determined using the column method described in Asher et al. (2002).

2.2 Incubation experiment

Prepared soil (air dry, sieved to < 2 mm) was added to a depth of 50 mm in round incubation pots (225 mm diameter PVC endcaps). Bulk density was adjusted to *ca*. 1.2 g cm^{-3} by tapping the pot base ten times on the bench, which settled the soil to a depth slightly below 5 cm. Deionized water was added to each pot to bring the soil mass to the pre-calculated field capacity moisture content (0.32 g g^{-1} and 0.12 g g^{-1} for the Vertisol and Ferralsol, respectively), taking into account the initial moisture content of air-dry soil. Pots were sealed with plastic cling wrap and the moisture was allowed to equilibrate overnight. Following moisture application, the Vertisol swelled approximately 0.5 cm in height, reducing the bulk density of this soil to *ca*. 1.1 g cm^{3}. Treatments of N-fertilizer were then applied by removing a 10 mm diameter core of soil, inserting the various fertilizer treatments to a depth of 50 mm, and then covering the fertilizer column with some of the previously removed soil to limit volatilization losses. All treatments were applied at a rate equivalent to the weight of fertilizer in a 50 mm section of a N-fertilizer band applied at 150 kg N ha^{-1} at 1.8 m row spacing (1350 mg N pot^{-1}). This rate and concentration was chosen to reflect typical application rates and band spacings in the Australian sugarcane industry (i.e., Six Easy Steps approach; SRA, 2018). The N-fertilizer treatments described in this paper include: (i) granular urea; (ii) granular urea coated with the NI, DMPP and marketed as ENTEC® (DMPP-urea); (iii) polymer coated urea granules with a 90-day release duration and marketed as Agromaster Tropical® (PCU); (iv) urea granules with a biodegradable coating and an 80-day release duration supplied by Kingenta Australia Ag PTY LTD as Plant Oil Coated Urea (POCU); (v) a 1:2 fertilizer blend of DMPP-urea and PCU (1:2 DMPP-PCU); and (vi) 2:1 fertilizer blend of DMPP-urea and PCU (2:1 DMPP-PCU). A moist glass fibre filter paper (125 mm diameter) was placed centrally on top of the soil to maintain humidity within the pot and allow for moisture adjustment without disturbing soil. Incubation pots were weighed to allow for on-going moisture adjustment, with moisture maintained at field capacity ± 0.5 % (moisture adjustment every 7 days). Incubation pots were sealed with plastic wrap and three pinholes were inserted to prevent the development of anaerobic conditions. The incubation was maintained at 23±1°C and duplicate pots were placed in a completely randomised design across two benches.

2.3 Sample collection

Destructive sampling occurred at 10, 35 and 60 days after incubation initiation (DAI). Soil in each pot was collected concentrically beginning with a 20 mm diameter central core (designated the '0-10 mm' position), and then in increments moving outwards from that central core designated as the 10-30 mm, 30-50 mm, 50-70 mm, 70-90 mm and 90-110 mm zones. These samples were collected using stainless steel sampling rings (diameters of 20, 40, 60, 80, and 100 mm) that were pushed down through the soil to isolate and progressively remove each ring of soil, beginning from the central 20 mm core, which contained the fertosphere (the volume of soil within '0-10 mm' of the fertilizer band, and inclusive of the band). Soil in each increment was completely removed from incubation pots and mixed to homogenize, with 2 × 10 g samples subsequently taken for analysis. One of the two soil sub-samples was used for pH and EC measurement (1:5 soil:water) and subsequently extracted with 2M KCl for analysis of mineral N species. The other sub-sample was extracted with deionized water for analysis of urea-N concentration. In fertilizer treatments containing controlled release products, intact granules were recovered prior to removal of soil samples from incubation pots. The granule samples were kept frozen until analysis for total N.

2.4 pH and electrical conductivity measurements

The pH and EC of soil samples were measured in a 1:5 (*w/v*) soil-water solution by adding 50 mL DI water to 10 g soil. Measurements for pH and EC were recorded after 1 minute of stirring. Values for pH and EC were arithmetically averaged from duplicate samples.

2.5 Soil extraction

Extraction of mineral N followed standard methods (Method: 7C2a, Rayment and Lyons, 2010), using a 1:5 (w/v) soil-solution extraction with 2M KCl (i.e., 10 g soil with 50 mL 2M KCl). Samples were shaken end-over-end for 1 hour and then removed and allowed to settle for approximately 15 minutes. A 10 mL aliquot of the extraction solutions was taken and centrifuged at 3700 rpm (RCF: 1760 × g) for 9 minutes, followed by pouring off and re-centrifuging of the supernatant. All solutions were frozen at until analysis. The solutions were analysed for NH_4^+-N (Searle, 1974), NO_2^--N and NO_x-N (Best, 1976; Bremner, 1965) by segmented flow analysis (SFA). Urea-N was extracted in 1:5 soil-water (w/v) solutions with the addition of 100 µL of 0.02 M Ag_2SO_4 (urease inhibitor, equiv. 62.4 µg g^{-1} soil) added immediately after water addition to soil samples (Douglas and Bremner, 1970). Samples were shaken end-over-end for 1 hour and then removed and allowed to settle for approximately 15 minutes. A 10 mL aliquot of the extraction solutions was taken and centrifuged at 3700 rpm (RCF: 1760 × g) for 9 minutes, followed by pouring off and re-centrifuging of the supernatant. All solutions were frozen until analysis. The urea extracts were analysed on a Thermo Fisher Ultimate 3000 U-HPLC system using a Thermo Fisher DAD 3000 diode array detector following modified versions of the methods detailed for urea-N (MicroSolv, 2010). In each batch, urea spikes were added to an aliquot of sample extract to monitor and quantify any urea loss during the analysis process, which was minimal. Previous experiments indicated that the high concentrations of urea-N generated in this study resulted in solubility issues such that recoveries were incomplete when extracted from soil with 2M KCl solution. Consequently, water extractions from soil were considered appropriate for determination of this N species.

2.6 Granule analysis

The organic N content of a sub-sample (*ca*. 0.1 g) of intact fertilizer granules was determined by digestion in concentrated sulphuric acid followed by the semi-micro Kjeldahl procedures outlined in Brech (1976), Searle (1974), and Youden and Steiner (1975). A second sub-sample (*ca*. 1.7 g) was analysed for mineral N content using segmented flow analysis (Best, 1976; Bremner, 1965; Searle, 1974) of solution containing crushed and dissolved granules (1:5 *w/v*). A separate incubation experiment, in which the conditions of the diffusion experiment were replicated on smaller scale, was conducted to determine the moisture uptake in controlled release products over time. At 10, 35 and 60 DAI, PCU and POCU granules were removed and gravimetric moisture was determined using oven drying methods at 40°C (Topp et al., 2007). The moisture content was incorporated into calculations to accurately determine the remaining organic and inorganic N (identified in Kjeldahl digestions of wet samples and SFA analysis of granule solution extractions), which is expressed as a percentage of CRF-N applied.

2.7 Data transformation

Urea-N values from HPLC analysis were expressed as the solution concentration (mg urea-N L^{-1}) of extractions. Mineral N values are reported as mg N kg $soil^{-1}$ as these data were obtained from soil extracts (1:5 w/v 2M KCl) and the mg N kg $soil^{-1}$ unit is comparable to that used in other studies. Concentrations of NO_3^--N were determined by calculating the difference between NO_x-N and NO_2^--N (Best, 1976; Bremner, 1965). Quantities of net NO_3-N were calculated by dividing the reported concentration (mg/L) for each sampled zone by the extractant volume and multiplying by the volume of soil in that zone. All zones were summed to calculate the net NO_3-N production in each pot (mg). The proportion of total N recovered was determined by summing the total N (mg) in soil solution with that remaining in granules in CRF and CRF-blend N-fertilizer treatments. It was assumed that any N immobilisation was minimal and / or consistent across treatments. This value was divided by either the soil solution or granule N content (mg) to calculate the respective proportion of total N (%). Ammonia (aqueous NH_3) concentrations were calculated by applying the pK_a value of the $NH_4^+ \leftrightarrow NH_3$ 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 Equation 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 mg NH_3 L^{-1}.

$$NH_3 = \frac{K_a \times NH_4^+}{H^+} \qquad Eq. 1$$

2.8 Statistical analyses

Analysis of chemical data ($pH_{1:5w}$ and $EC_{1:5w}$) and N (urea-N, mineral N and aqueous NH_3) concentrations was conducted by a three-way analysis of variance (ANOVA) for each soil with time, treatment, and distance from the fertosphere as factors. Granule N retention data was analysed by two-way ANOVA for each soil with time and fertilizer treatment as factors. Tukey's HSD method ($P<0.05$) was used to test means for significant interaction effects identified in ANOVAs. For CRF granule N, urea-N, mineral N and aqueous NH_3 datasets, statistical variation is represented in figures by standard error bars fitted to mean values at each point. Statistical differences for pH and EC are not presented within the manuscript as the number of interactions makes graphical presentation difficult to interpret. Where appropriate, significant effects are noted in the text, with the full statistical results available in Supplementary Material Part B.

3 Results and Discussion

3.1 Soil chemical changes vary with fertilizer form and soil type

Rapid hydrolysis of concentrated urea bands results in significant increases in soil pH, EC and aqueous NH_3 concentrations (Janke et al., 2021). This effect was observed in both soils treated with uncoated N-fertilizers (urea and DMPP-urea) and to a lesser extent in blended DMPP-urea and PCU treatments (Figs. 1 – 3). The slow release of small amounts of urea-N to soil solution from the single product CRF treatments (PCU, POCU) meant that these treatments demonstrated a much smaller zone of impact for ureolytic-induced increases in pH, EC and aqueous NH_3, although peak changes within the fertosphere (0-10 mm zone) did not appear to be any less severe than that of granular urea (Figs. 1 – 3). Further, the longer duration of release of urea-N from CRFs (Fig. 4), and thus the extended period of urea hydrolysis, meant that the pH remained high within the fertosphere over the 60-day incubation in treatments containing CRFs (Fig. 1). In the Ferralsol, the effects of the chemically 'hostile' zone extended as far as *ca*. 8 - 9 cm from the fertosphere in the granular urea and DMPP-urea treatment, with this zone reduced by 1 – 2 cm for the DMPP-urea/PCU blends and 3 – 4 cm for the two CRFs (Fig. 1, 2). The higher pHBC and CEC of the Vertisol (Table 1) buffered these chemical changes more effectively, and combined with the reduced permeability of this soil, resulted in a reduced zone of impact and less severe and more rapidly reversable pH and EC increases. For the Vertisol, the effects of rapid urea hydrolysis extended as far as *ca*. 6 cm for urea, DMPP-urea, and the 2:1 DMPP-urea/PCU blend. The impacted zone decreased by *ca*. 1 and 2 cm for the 1:2 DMPP-urea/PCU and CRF treatments, respectively.

Acidification of soil solution occurred outside the boundaries of the hydrolysing zone for each combination of soil and N-fertilizer treatment (Fig. 1). There was a clear trend for higher NO_3-N production in pots in which greater proportions of soil were at lower pH, suggesting nitrification was a causal factor for this acidification. However, correlation of specific zones of reduced pH and higher NO_3-N concentrations was poor (data not shown), likely due to the diffusive mobility of NO_3-N down high concentration gradients from the zones in which it was formed.

3.2 N dynamics in the Ferralsol

The high and widely distributed NH_4-N concentrations arising from bands of uncoated fertilizers in the Ferralsol (i.e., urea and DMPP-urea; Fig. 5) were somewhat preserved by the broad zone and persistence of modified chemical conditions which were inhibitory to nitrification (Figs. 1 – 3). Since DMPP distribution from fertilizer bands is limited to approximately 1 – 3 cm (Janke et al., 2021) and significant concentrations of NH_4-N were more widely distributed (up to 7 cm from fertosphere in both urea and DMPP-urea treatments), there was little effect of this inhibitor on nitrification *cf.* standard urea in this soil. Compared to the pure CRFs, the greater availability of substrate-N (i.e., NH_4-N in solution) combined with wider zones of modified soil chemistry meant that peak NO_3-N concentrations were higher (*ca*. 50 mg N kg^{-1} soil) but occurred further from the fertosphere in the 1:2 DMPP-urea/PCU blend (3 – 5 cm), 2:1 DMPP-urea/PCU blend (5 – 7 cm), and the urea and DMPP-urea treatments (7 – 9 cm). In contrast, narrower zones of soil impacted by urea hydrolysis meant that early and more rapid nitrification of released N was observed around bands of PCU (0-3 cm zone) and to a lesser extent POCU (0-5 cm zone) by 10 DAI in the Ferralsol (Fig. 5).

Despite the observed variation in NO_3-N distribution between N-fertilizer treatments (Fig. 5), the differences in total NO_3-N production were not large in the Ferralsol (*ca.* 30 – 70 mg N, Figs. 5, S2). Compared to standard urea, total NO_3-N production was most reduced in the PCU treatment (21%) over 35 DAI, where the 1:2 and 2:1 DMPP-urea/PCU blends produced total quantities of NO_3-N that were 9 and 14% lower, respectively (Fig. S2). While the controlled release mechanism appears to be more effective for regulating NO_3-N production when compared to bands of uncoated product (i.e., urea, DMPP-urea) over the short-term (10 – 35 DAI) in the Ferralsol, this is likely an outcome of simply less N being available for nitrification. When PCU and DMPP-urea are blended, greater proportions of PCU do not appear to confer greater regulation of NO_3-N formation. Rather, in the blended treatments, having a greater proportion of N as uncoated DMPP-urea reduced NO_3-N production (*cf*. greater proportions of PCU in the blend) by 5% at 35 DAI, with this trend becoming stronger over time (9% difference at 60 DAI). It is unclear if the inhibitory effect of a greater proportion of DMPP-urea in blends was due to (i) a better synchrony of N and DMPP in and around bands (having a portion of the N derived from the coated component of this blend meant that N did not disperse as far as N from pure applications of uncoated products) or (ii) greater ureolytic-induced chemical changes (Figs. 1-3) in response to a greater proportion of N being rapidly hydrolysed (i.e., from the uncoated DMPP-urea, where N from the coated urea would usually be exposed to ‘benign’ chemical conditions under pure PCU applications). Over time, the inhibitory effect of DMPP weakened as greater amounts of N were released from fertilizer bands containing blends with higher proportions of PCU and where the inhibitor to N ratio declined with time (i.e., progressively less of the applied N is “protected” in blends with greater proportions of PCU). By 60 DAI, treatments containing a CRF (pure or blended) demonstrated higher net NO_3-N production (Figs. 5, S2) as more slowly released N became available and was nitrified.

In this study, N that could not be found in the urea or mineral N pools (Table 2) was highest for urea (39% by 60 DAI) and DMPP-urea (37% by 60 DAI) treatments in the Ferralsol, with the majority (*ca*. 69%) of this being lost within 10 DAI (Table 2). Since most of the N in these treatments remained as NH_4^+ and the pH was significantly increased (Fig. 1), volatilization was likely the dominant loss pathway for this unaccounted N. These losses may have been an artefact of the incubation design, where only a small amount of soil covered the end (or top) of the fertilizer band. In field conditions, properly covered bands are typically not vulnerable to large volatilization losses (Rochette et al., 2013). The delayed delivery of N from the CRF N-fertilizers (Fig. 5, Table 2) combined with smaller increases in the soil pH (Fig. 1) meant that the risk of volatilization was smaller in these treatments and the proportion of unaccounted N was correspondingly lower (Table 2).

3.3 N dynamics in the Vertisol

In the Vertisol, very little nitrification was observed in any N-fertilizer treatment at 10 DAI (Figs. 6, S2). This is likely an outcome of (i) minimal NH_4-N diffusion to zones outside the chemically hostile conditions that formed around bands of uncoated fertilizers (i.e., urea, DMPP-urea) in this high CEC soil; and (ii) limited release of N from coated products. By 35 DAI, the production of NO_3-N from urea and CRF bands was significantly greater than that of the other fertilizer treatments

(Figs. 6, 7). In pure CRF bands, the phenomenon was similar to that in the Ferralsol where the benign chemical conditions around the fertosphere did not inhibit nitrification of released N. In urea bands, the hostile conditions associated with urea hydrolysis had largely dissipated by 35 DAI in the Vertisol (Figs. 1 – 3), which meant, despite the somewhat reduced N distribution (*cf.* Ferralsol), higher concentrations of NH_4-N were found outside the narrower zone of inhibition and were subject to rapid nitrification. In the Vertisol, this diffusion of N from the fertosphere likely occurred in response to steep concentrations gradients as aqueous NH_3 (Fig. 3), since the high CEC of this soil (Table 1) would have restricted movement of N as NH_4-N.

Unlike the Ferralsol, NH_4-N was preserved and NO_3-N formation inhibited in the DMPP-urea treatment when compared to urea (Fig. 6), with the variable efficacy of NI products between soil types previously reported by Janke et al. (2021). Effectively, the low permeability of the Vertisol *cf.* to the Ferralsol (lower CEC and coarser texture) meant that the distribution of DMPP and NH_4-N around DMPP-urea bands were more closely aligned in the Vertisol, resulting in more complete and persistent inhibition of nitrification in this soil.

The efficacy of the DMPP-urea in the Vertisol meant that the DMPP-urea/PCU blend treatments were also highly effective at reducing NO_3-N formation in this soil. Total NO_3-N production (*cf.* urea) was reduced by *ca*. 56% for the 1:2 and 2:1 DMPP-urea/PCU treatments, at 35 DAI and by 61% (1:2) and 55% (2:1) at 60 DAI (Fig. S2). This reduction was considerably greater at 35 DAI and comparable at 60 DAI to either the PCU or DMPP-urea treatments (*ca*. 46 and 53 % reduction at 35 and 60 DAI, respectively). The efficacy of the DMPP-urea/PCU blends in reducing NO_3-N formation can be attributed to the inhibitory effect of DMPP on nitrification and the persistence of DMPP in the vicinity of the band while N was slowly diffusing out of PCU granules. Slightly higher rates of nitrification were recorded in 2:1 DMPP-urea/PCU bands (*cf.* 1:2 DMPP-urea/PCU). This was consistent with the greater proportion of non-coated fertilizer and initially higher NH_4-N concentrations that contributed to more extensive diffusion of N (probably as aqueous NH_3, Fig. 3) into zones beyond the distribution of DMPP. Overall, although small differences were observed, the ratio of DMPP-urea to PCU in the blended treatments did not significantly affect the production of NO_3-N (Fig. S2) in this soil.

The N that could not be found in the urea or mineral N pools in the Vertisol was generally slightly lower than the corresponding treatments in the Ferralsol by 60 DAI (Table 2). Exceptions occurred in the PCU and the 1:2 DMPP-urea/PCU treatments where total unaccounted N was 10% and 5% higher, respectively. This corresponded to slightly lower amounts of N remaining within PCU granules applied to the Vertisol (*cf.* Ferralsol; Table 2) and suggests that quicker release of N from CRF products in the Vertisol may be linked to greater potential for N loss. As for the Ferralsol, the modification to soil chemistry at the start of the incubation suggests that volatilization may be a likely pathway of N loss from N-fertilizer treatments in the Vertisol (e.g., Figs. 1, 3, 6). However, N emissions as dinitrogen (N_2) or nitrous oxide (N_2O) may also have occurred in this soil, where the high clay content combined with a field capacity water content may have facilitated the formation of low-oxygen micro-sites that enabled denitrification. The Vertisol also has a considerable CEC (Table 1) and removal of N via sorption to soil particles cannot be discounted. Further, in both soils, consumption of N by the microbial biomass has not been accounted for. Thus, while some loss pathways may be proposed based on N transformations and soil chemistry, this study is unable to provide conclusive evidence on N loss pathways.

3.4 Effective use of EEFs varies with soil characteristics and loss conditions

These findings suggest that minimisation of fertilizer-N losses arising from NO_3-N (i.e., leaching, denitrification) will require different fertilizer-N technology and management practices in different soil types. When fertilizers are banded at the rates used in this study (150 kg N ha^{-1} equivalent), there appears to be little advantage in using a CRF, DMPP-urea or blends of the two (*cf*. urea), in soils of high permeability and poor chemical buffering (i.e., low CEC and pHBC, coarse texture) for modification of N dynamics to reduce potential N losses over a season. Similar findings were demonstrated in studies comparing N in soil solution (urea *cf*. DMPP-urea; Janke et al., 2021) and leachate NO_3^- (urea *cf*. PCU; LeMonte et al., 2016) in sandy soils, with no significant differences found between urea and the EEFs. However, both CRF and stabilized products have been observed to lower gaseous N emissions in sandy soils (Awale & Chatterjee, 2017; Hyatt et al., 2010). Controlled release products appeared to be especially effective on coarser-textured soils, predominantly through reduced NH_3 volatilization which may be more problematic in these soils. In this study, the CRF treatments reported the highest recoveries of applied N in the mineral and urea N pools (72 – 82% at 60 DAI; Table 2), possibly through reduced gaseous NH_3 losses. Some benefits of these EEF treatments have been observed in sugarcane crops grown on sandy-textured soils in field trials and these predominantly occurred in low yielding sites (Bell et al., 2021; Connellan et al., 2021) or where N loss conditions were high (Dowie et al., 2019). This suggests that in scenarios where NUE is poor due to large loss events (e.g., heavy rainfall and extensive leaching), EEFs may provide some protection against N loss, even in soils which may otherwise be poorly suited to banded EEF application.

In contrast, in soils where solute movement is restricted, and possibly where chemical changes are better buffered (i.e., high clay soils), our study indicates potential for significant reduction in losses by way of reduced NO_3^- formation with the use of banded EEFs and blends in the order of: DMPP-urea/CRF blends (higher ratio of PCU may offer small but insignificant benefits) > DMPP-urea = PCU > urea. This soil type observation is supported by field research where a greater efficacy of banded DMPP-urea/PCU blends (Bell et al., 2021) or PCUs (DiBella et al., 2013) has been demonstrated in clay and / or high organic matter soils by reduced leaching losses and greater crop N uptake. However, the implications for reduced emissions from banded EEFs and blends in heavier-textured soils is less clear. In the Vertisol, there was a trend for greater N recovery as urea or mineral N over 60 DAI in soil solution (and granules, where appropriate) in the N-fertilizer treatments containing high proportions of DMPP (i.e., DMPP-urea, and 2:1 DMPP-urea/PCU; Table 2). This suggests that some small denitrification losses may have been observed around fertilizer treatments where NO_3^- readily formed (i.e., urea and PCU). Field studies on clay soils indicate that, despite mitigation of early N_2O emissions from DMPP-urea, PCU and blends of the two, the cumulative seasonal outcomes are variable depending on whether NO_3^- formation later in the season coincides with climatic conditions which facilitate denitrification (Schwenke & Haigh, 2019; Soon et al., 2011; Wang et al., 2016a).

Irrespective of the impact of soil characteristics on N-fertilizer dynamics, the timing of loss events play a key role in the efficacy of the EEF product for mitigating N losses. Indeed, observations from field trials indicate the greatest benefits of

EEFs appear to be in mitigating N losses that occur soon after fertilizer application (Bell et al., 2021; Connellan et al., 2021). Whilst some consideration for the wider context of these findings has been discussed in this section, the dynamics of DMPP-urea, PCU, and blends of the two reported in this study do not consider the impact of crop N demand. This study was designed to examine N dynamics in banded NI-urea/CRF mixtures in a broad context (i.e., not crop specific), relative to granular urea and the individual EEF technologies. Therefore, while this study explores the principles underpinning the different N dynamics observed in blends of EEF technologies, the lack of plant N demand may limit the extrapolation of these findings to the broader portfolio of field trials examining the impacts of EEF technologies and blends on NUE (e.g., Bell et al. 2021; Connellan et al. 2021).

3.5 Potential for biodegradable CRF coatings

The POCU treatment demonstrated earlier and more rapid release of urea-N compared to PCU in both soils, although this was particularly obvious in the Vertisol (Fig. 4). Urea-N released from the POCU was rapidly hydrolysed, resulting in higher NH_4-N concentrations up to 35 DAI in the Ferralsol (Fig. 5) and up to 10 DAI in the Vertisol (Fig. 6). By 35 DAI, NH_4-N concentrations in the 0 – 5 cm zone of the POCU band were slightly lower than that of PCU in the Vertisol. This suggests rapid nitrification of the NH_4-N released earlier in the POCU treatment. In both soils, the nitrified N appeared to diffuse to zones further away from the band in response to established concentration gradients in both CRF treatments, with the distribution of NO_3-N similar for both treatments by 60 DAI (Fig. 6).

These findings suggest that a proportion of these POCU granules may have experienced coating 'failure', whereby water penetration increased the osmotic pressure within granules causing some of the POCU granules to rupture rather than swell. Typically, micropores within the coating of many CRFs are stretched and enlarged during the imbibement and swelling process, allowing release of the coated nutrient (now dissolved in water) from the granule (Shaviv, 2001). The hypothesis of POCU granule 'failure' is consistent with the observation of a greater proportion of 'burst' POCU granule coatings (i.e., POCU granules were split or contained tears) *cf*. PCU during granule recovery at sampling. In the Vertisol, the greater volumetric water content of this soil at field capacity (*cf*. Ferralsol; Table 1) may have contributed to more rapid water uptake and hence more frequent rupturing of POCU granules, resulting in the initially higher urea-N and NH_4-N concentrations in this soil (Figs. 4, 6). Further experimentation is required to elucidate the exact processes contributing to the initial 'failure' of some POCU granules and to determine the extent to which other mechanisms (e.g., microbial degradation, soil-granule contact) are also involved.

Despite the initial flush of N from apparently 'failed' POCU granules, mineral N distribution (Figs. 5, 6) and the proportion of N remaining in granules (2 – 7 % difference, Table 2) was relatively similar for bands of POCU and PCU within each soil. This suggests that once moisture uptake by POCU granules has completed, the N release characteristics were very similar to that of PCU.

4 Conclusions

Banding NI-urea and CRF technology in blends of differing proportions revealed that the NI concentration or proportion of CRF within the band did not have a significant impact on N dynamics. Both treatments slowed N release and higher NI concentrations limited the distribution of N from these fertilizer bands (*cf.* urea bands). Consequently, NH_4-N formed within blended bands was similarly protected against oxidisation by inhibitory conditions associated with band chemistry and the NI, irrespective of blend proportions. The efficacy of N preservation in blended vs 'pure' NI and CRF treatments varied depending on soil type, but in all instances the availability of N to meet potential plant demand was initially lower in treatments including the PCU. Poor synchrony of N availability to crop demand increases the risk of environmental losses, with the persistence of fertilizer N in soil once crop uptake has concluded vulnerable under wetter seasonal conditions. Importantly, soil characteristics appeared to play a large role in influencing the efficacy of EEFs and blends of NI-urea/CRF. When applied in concentrated fertilizer bands, these individual products and their blends are likely to be most effective in soils with lower permeability. This is due to better co-location of fertilizer N with any applied NI, and inhibitory conditions associated with band chemistry.

The examined plant-oil coated urea product initially released more N due to a higher prevalence of 'burst' granules, which was likely an outcome of somewhat poorer tolerance of increased osmotic pressure within granules (*cf.* PCU). However, overall dynamics and proportions of N in mineral forms (NH_4^+ and NO_3^-) were similar to that of PCU. This indicates that this technology may be a suitable option for managing the competing requirements of (i) a predictable N supply and (ii) avoiding the introduction of persistent polymers in the environment.

This study has provided fundamental understanding of the dynamics and efficacy of bands of blended NI-urea and PCU fertilizers, relative to the individual blend constituents and to granular urea. It also offers preliminary evidence to continue with the development and testing of biodegradable CRFs as substitutes for the PCU products currently in use. Findings from this study may be utilized in agronomic decisions to reduce the impact of off-farm N losses and improve on-farm NUE.

Data availability. Original data are available upon request. Data necessary for this study's findings are presented in the manuscript.

Author contributions. Chelsea K Janke and Michael J Bell conceived and designed the experiments. Chelsea K Janke performed the experiments and analysed the data. Chelsea K Janke and Michael J Bell prepared the manuscript and both authors approve the submission of this paper.

Competing interests. The authors declare that they have no conflict of interest.

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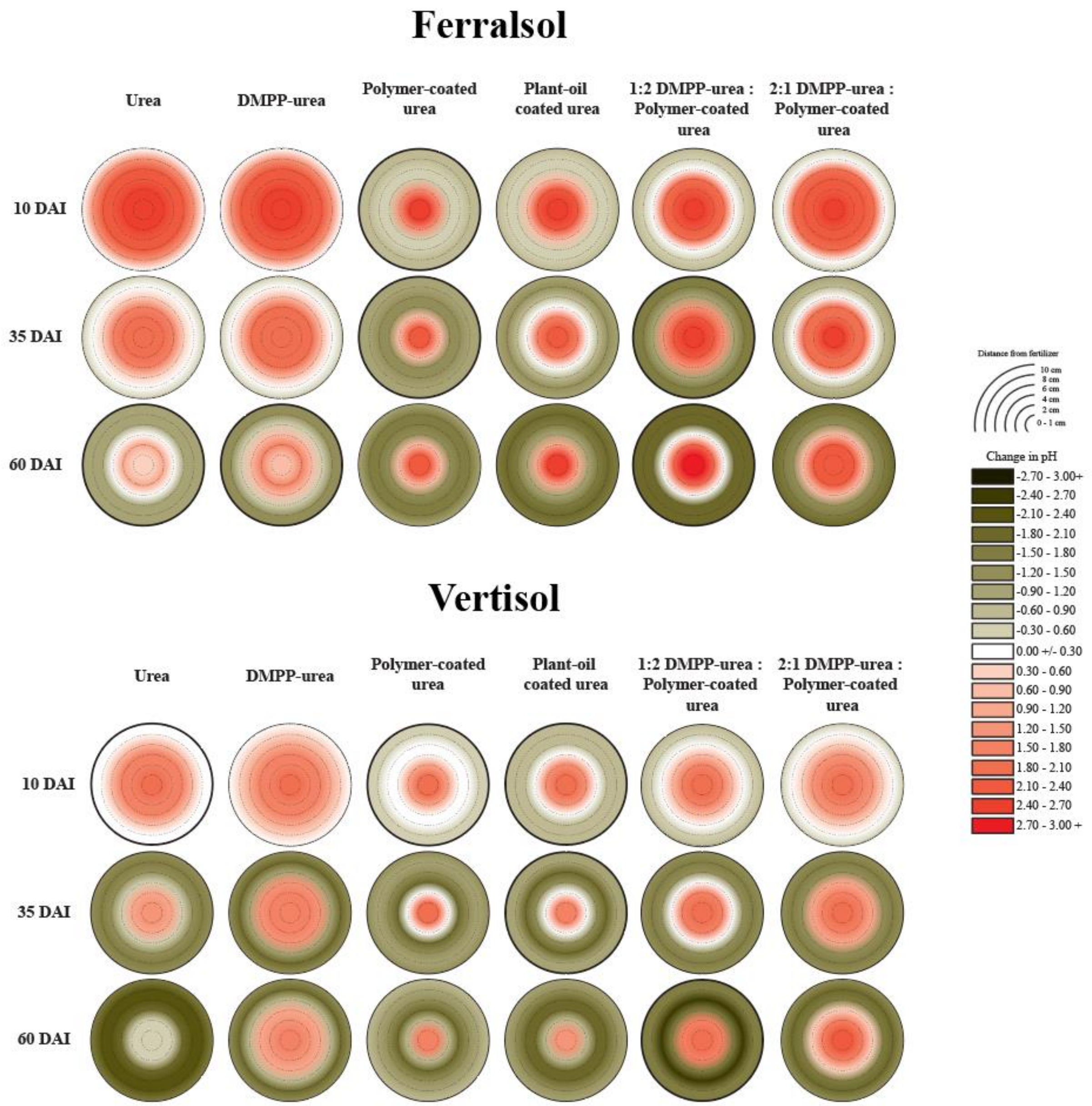

Figure 1: Heat maps displaying changes (with respect to untreated soil, Table 1) in pH distribution from bands of N-fertilizer treatments in the Ferralsol and Vertisol over time (days after incubation; DAI). Initial pH values were 6.30 (Ferralsol) and 7.15 (Vertisol). Changes in the pH of untreated soil are presented in the Supplementary Material (Part A, Table S1).

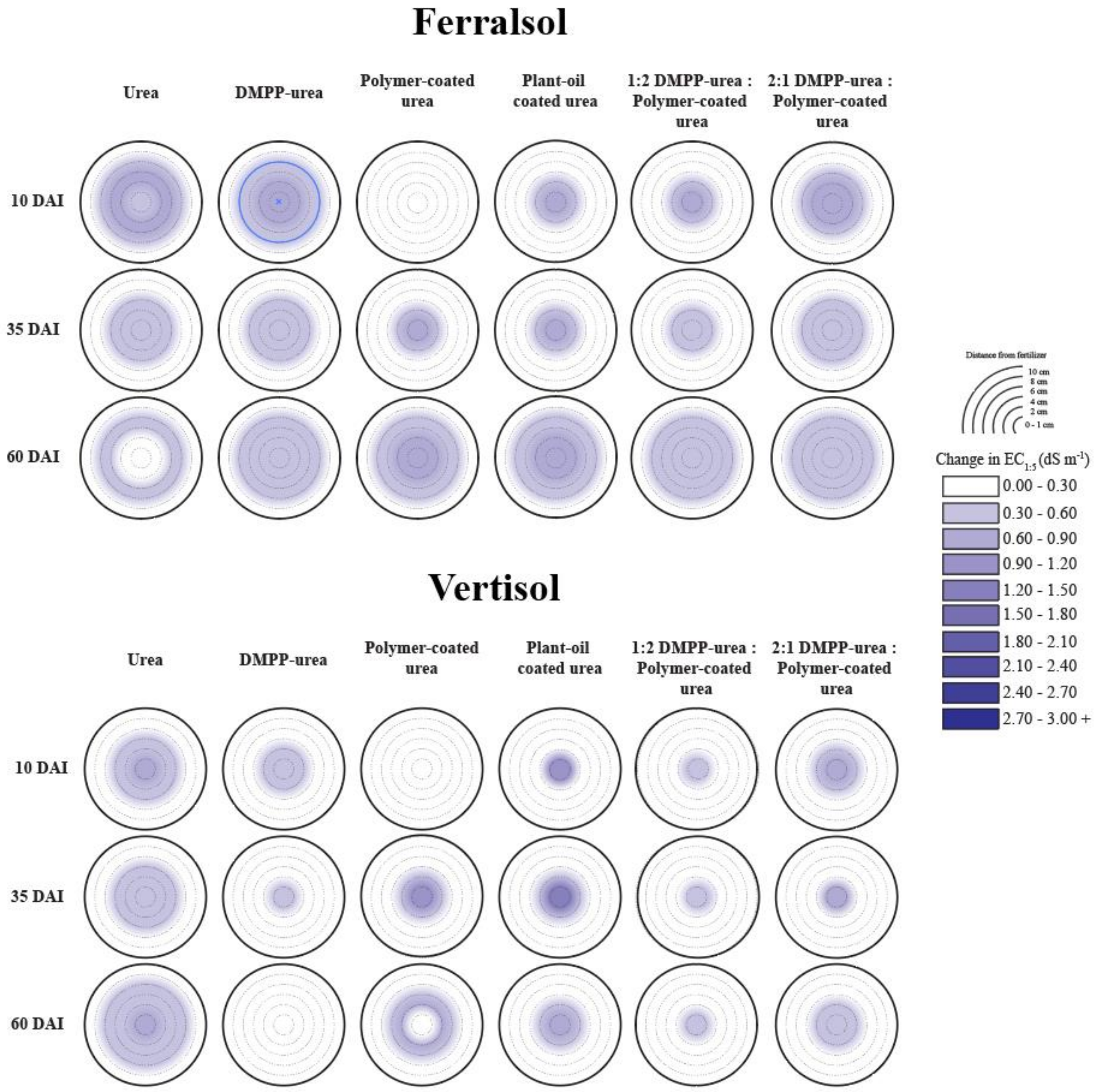

Figure 2: Heat maps displaying changes (with respect to untreated soil, Table 1) in electrical conductivity (EC, dS m^{-1}) distribution from bands of N-fertilizer treatments in the Ferralsol and Vertisol over time (days after incubation; DAI). Initial EC values were 0.07 dS m^{-1} (Ferralsol) and 0.35 dS m^{-1} (Vertisol). Changes in the EC of untreated soil are presented in the Supplementary Material (Part A, Table S1).

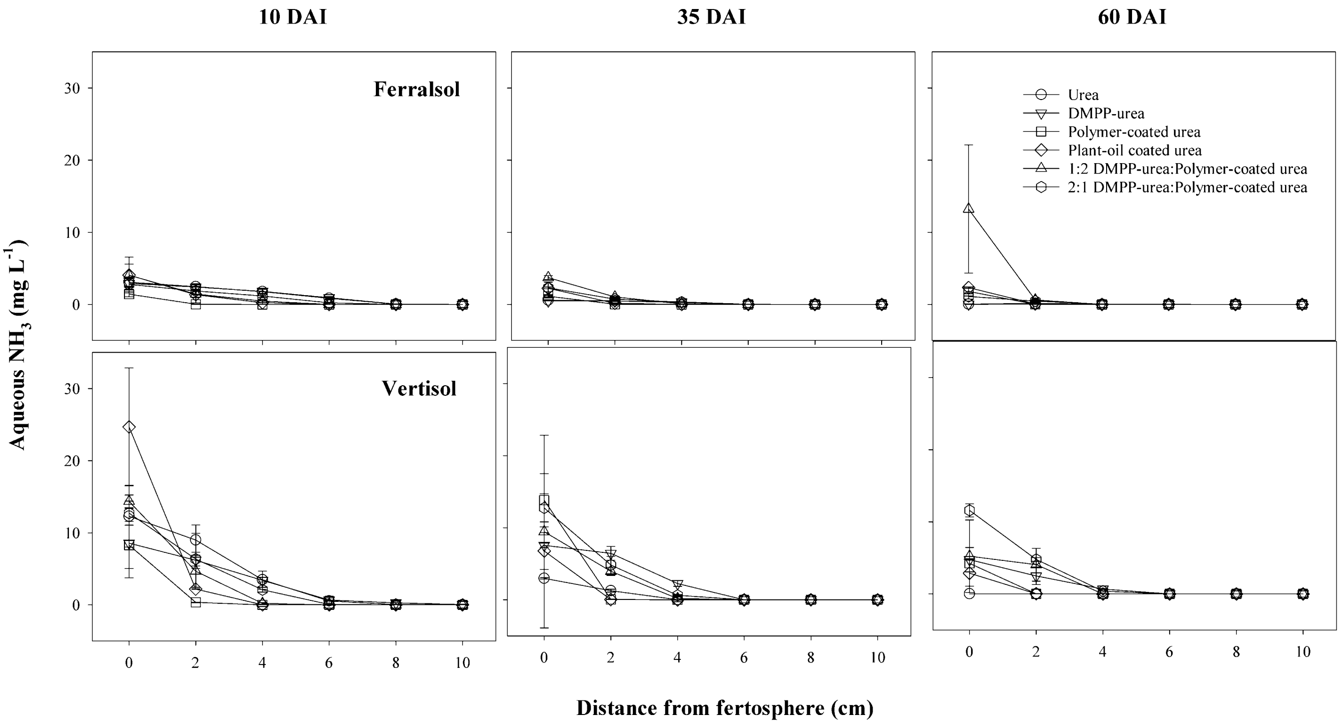

Figure 3: Aqueous NH_3 concentration (mg L^{-1}) over distance and time (days after incubation; DAI) from banded N-fertilizer treatments in a Ferralsol and Vertisol. Vertical bars represent the standard error of the mean.

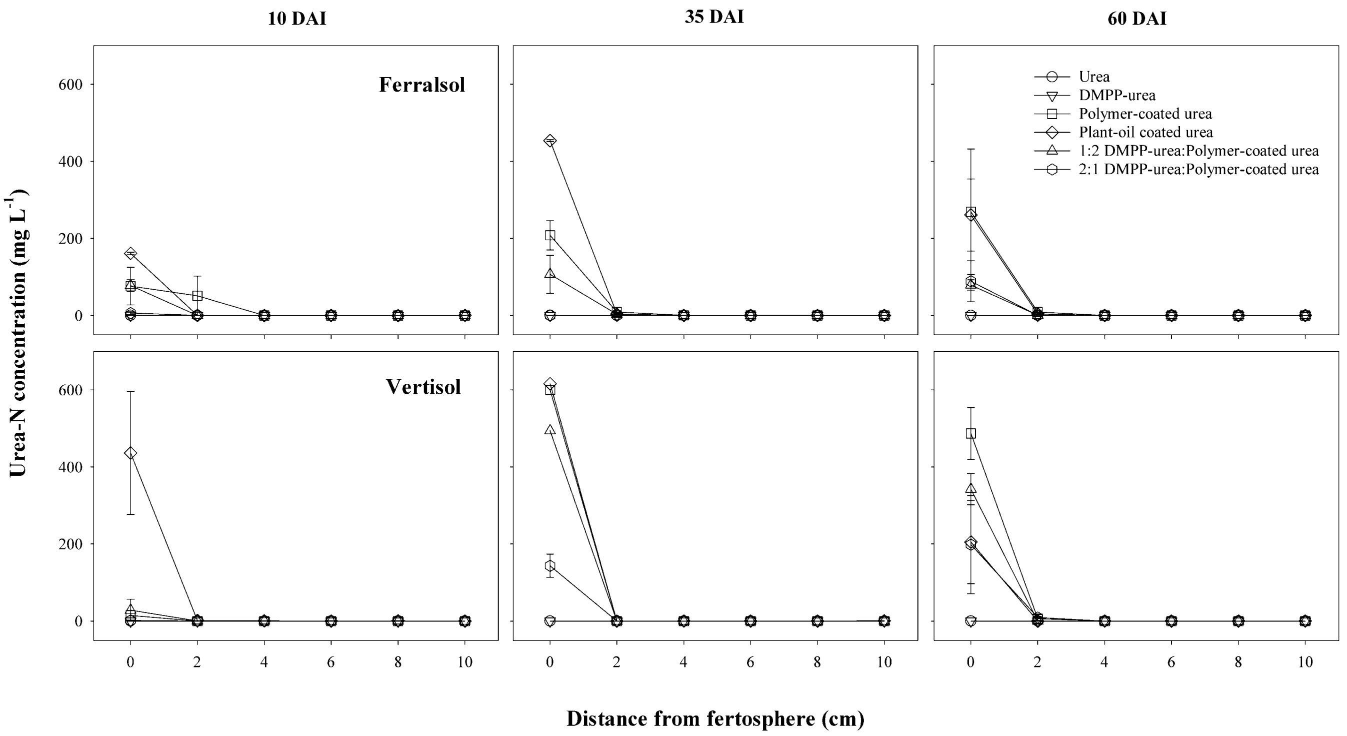

Figure 4: Urea-N concentration (mg L^{-1}) over distance and time (days after incubation; DAI) from banded N-fertilizer treatments in a Ferralsol and Vertisol. Vertical bars represent the standard error of the mean.

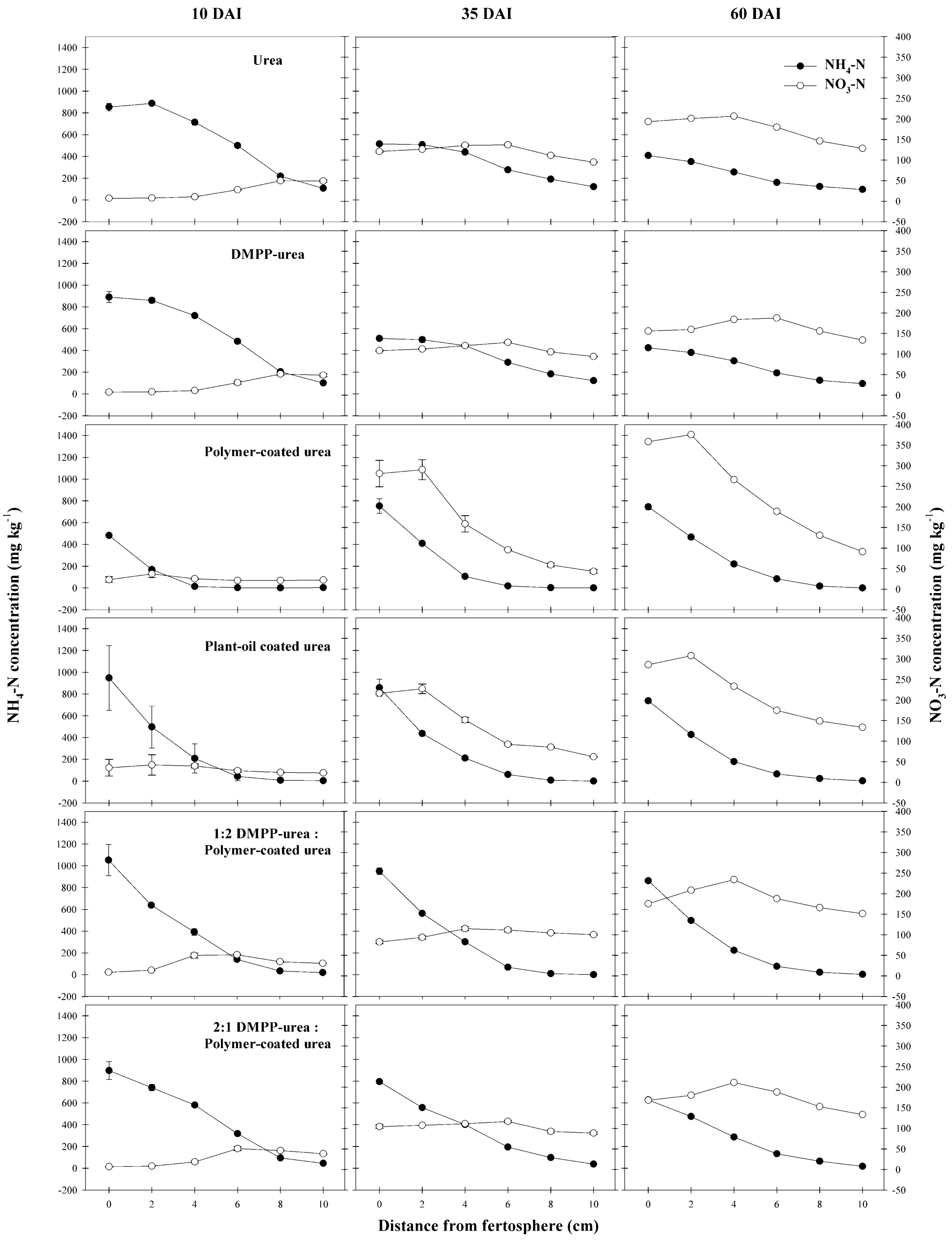

Figure 5: Concentration (mg N kg-1 soil) of mineral N species from N-fertilizer treatments in the Ferralsol during a 60-day incubation (DAI). Vertical bars represent the standard error of the mean.

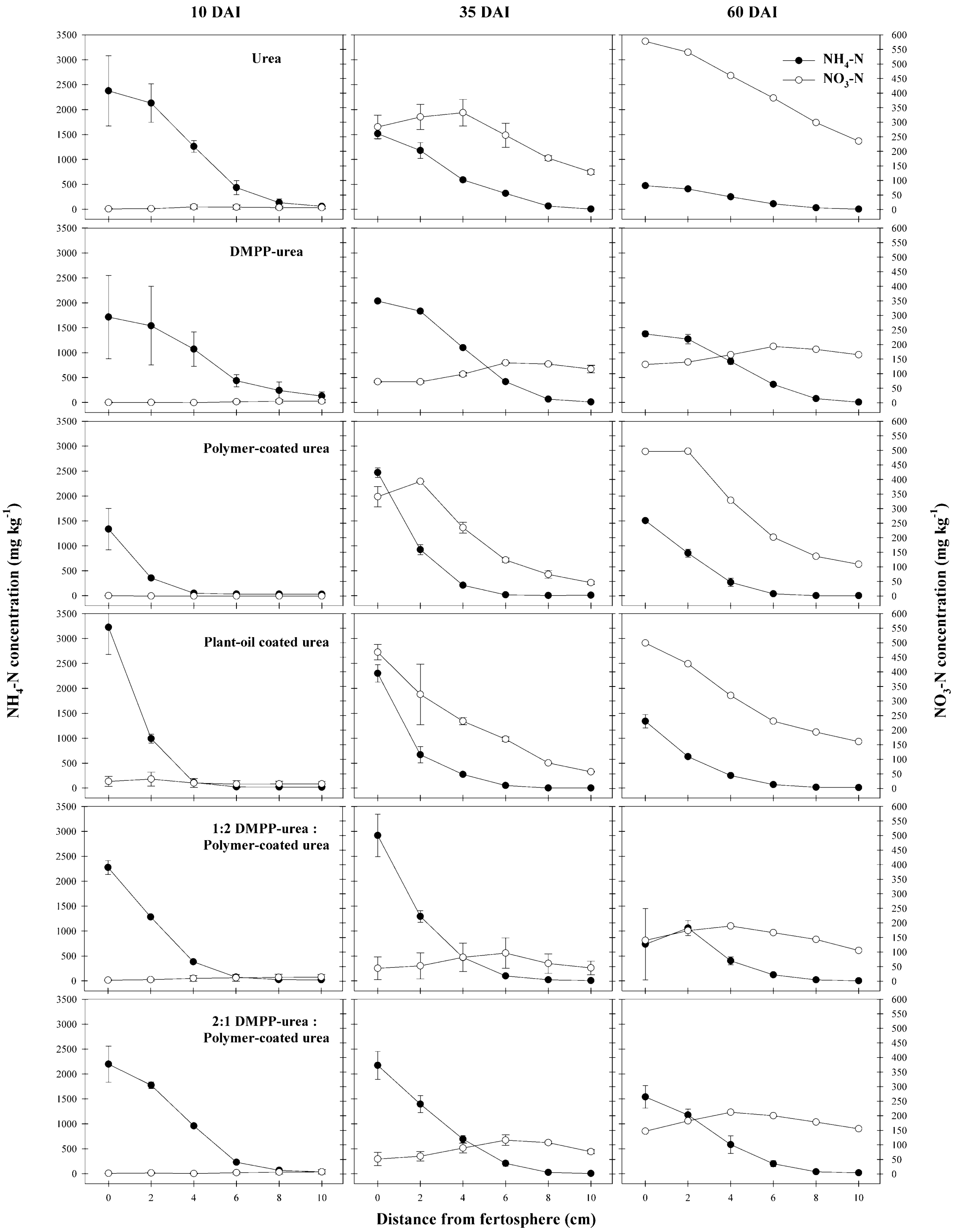

Figure 6: Concentration (mg N kg^{-1} soil) of mineral N species from N-fertilizer treatments in the Vertisol during a 60-day incubation (DAI). Vertical bars represent the standard error of the mean.

Table 1: Soil chemical properties and characteristics. Where, EC is the electrical conductivity; pHBC is the pH buffering capacity; C is carbon; TOC is total organic carbon; TN is total nitrogen; and GWC (FC) is the gravimetric water content at field capacity

		(dS m^{-1})	**(cmol OH- kg^{-1} pH unit^{-1})**	**Particle size analysis (%)**				**Exchangeable cations cmol(+) kg^{-1}**					**(%)**			**(mg kg^{-1})**		**(g g soil^{-1})**
Soil Order[1]	**pH 1:5w**	**EC 1:5**	**pHBC**	**Coarse sand**	**Fine sand**	**Silt**	**Clay**	**Ca**	**Mg**	**K**	**Na**	**CEC**	**Total C**	**TOC**	**TN**	**NH_4^+-N**	**NO_3^- -N**	**GWC (FC)**
Ferralsol	6.30	0.07	1.32	38	46	9	9	3.6	0.7	0.19	<0.08	4.5	1.21	1.17	0.06	3.2	6.8	0.12
Vertisol	7.15	0.35	3.51	5	26	21	52	12.8	13.2	0.79	1.82	28.5	2.36	2.32	0.18	4.8	8.5	0.32

[1] IUSS Working Group, 2015

Table 2 Mass N balance table for whole pots of N-fertilizer treatments in Ferralsol or Vertisol over time. Soil and granule -N values are calculated by multiplying measured concentrations in extractions by the soil or recoverable granule mass. Unaccounted N (mg) is the difference in applied N from fertilizer treatments (1350 mg N pot^{-1}) and the native soil N concentration multiplied by the total volume of soil in each pot (Ferralsol = 143 mg N; Vertisol = 159 mg N) to that recovered in soil and granules extracts. The percent of unaccounted-N is the 'mg' value divided by total starting N (applied + native N), then multiplied by 100. The intensity of the colour grading for unaccounted-N (%) values indicates the values relative to other treatments and over time, within each soil (i.e., > colour intensity = higher proportion of unaccounted N)

Soil	**Fertilizer treatment**	**10 DAI**						
		Soil-N (mg)				**Granule-N (mg)**	**Unaccounted-N (mg)**	**Unaccounted-N (%)**
		Urea	***NH_4^+***	***NO_3^-***	***Total solution N***	***Total***	***Total***	***Total***
Ferralsol	Urea	0	1011	106	1117	-	376	25
	DMPP-urea	0	982	108	1091	-	403	27
	PCU	57	53	66	177	1091	225	15
	POCU	20	230	80	329	1307	-143	-10
	1:2 DMPP-urea : PCU	9	418	106	534	944	15	1
	2:1 DMPP-urea : PCU	1	677	109	787	455	251	17
		35 DAI						
		Soil-N (mg)				**Granule-N (mg)**	**Unaccounted-N (mg)**	**Unaccounted-N (%)**
		Urea	***NH_4^+***	***NO_3^-***	***Total solution N***	***Total***	***Total***	***Total***
	Urea	1	693	330	1025	-	468	31
	DMPP-urea	1	694	312	1007	-	487	33
	PCU	34	149	262	445	750	299	20
	POCU	57	225	282	564	762	167	11
	1:2 DMPP-urea : PCU	16	290	301	607	632	254	17
	2:1 DMPP-urea : PCU	4	499	286	788	355	350	23
		60 DAI						
		Soil-N (mg)				**Granule-N (mg)**	**Unaccounted-N (mg)**	**Unaccounted-N (%)**
		Urea	***NH_4^+***	***NO_3^-***	***Total solution N***	***Total***	***Total***	***Total***
	Urea	0	451	456	907	-	587	39
	DMPP-urea	0	492	456	948	-	546	37

	PCU	40	250	474	764	453	276	18
	POCU	35	224	493	751	322	420	28
	1:2 DMPP-urea : PCU	10	263	509	781	343	369	25
	2:1 DMPP-urea : PCU	11	356	468	834	157	502	34

Soil	**Fertilizer treatment**	**10 DAI**						
		Soil-N (mg)				**Granule-N (mg)**	**Unaccounted-N (mg)**	**Unaccounted-N (%)**
		Urea	***NH_4^+***	***NO_3^-***	***Total solution N***	***Total***	***Total***	***Total***
Vertisol	Urea	1	1119	18	1137	-	371	25
	DMPP-urea	1	1075	10	1086	-	422	28
	PCU	1	157	0	158	1525	-175	-12
	POCU	46	291	40	378	1410	-279	-18
	1:2 DMPP-urea : PCU	5	434	29	468	1288	-247	-16
	2:1 DMPP-urea : PCU	0	805	13	818	471	220	15
		35 DAI						
		Soil-N (mg)				**Granule-N (mg)**	**Unaccounted-N (mg)**	**Unaccounted-N (%)**
		Urea	***NH_4^+***	***NO_3^-***	***Total solution N***	***Total***	***Total***	***Total***
	Urea	0	596	496	1092	-	417	28
	DMPP-urea	0	924	284	1209	-	300	20
	PCU	59	278	285	622	654	233	15
	POCU	64	262	314	639	701	168	11
	1:2 DMPP-urea : PCU	24	473	155	653	511	346	23
	2:1 DMPP-urea : PCU	14	598	223	835	181	493	33
		60 DAI						
		Soil-N (mg)				**Granule-N (mg)**	**Unaccounted-N (mg)**	**Unaccounted-N (%)**
		Urea	***NH_4^+***	***NO_3^-***	***Total solution N***	***Total***	***Total***	***Total***
	Urea	0	224	798	1022	-	486	32
	DMPP-urea	0	712	415	1128	-	381	25
	PCU	53	268	460	781	303	425	28
	POCU	20	255	537	812	294	403	27
	1:2 DMPP-urea : PCU	34	379	343	755	300	454	30
	2:1 DMPP-urea : PCU	27	532	429	988	159	362	24