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Improved Water Quality Outcomes from On-Farm Nitrogen Management

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The University of Queensland
Australia

Improved Water Quality Outcomes from On-Farm Nitrogen Management

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Cover photographs: (front) Silkwood runoff monitoring sites, © Bronwyn Masters; (back) Nitrogen field application using a stool splitter, © Jason Cowie

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ACRONYMS

6ES	Six Easy Steps nutrient management program
BMP	Best Management Practice
CEC	Cation Exchange Capacity
DES	Department of Environment and Science
DIN	Dissolved Inorganic Nitrogen
DoEE	Department of the Environment and Energy
DYP	District Yield Potential
EEF	Enhanced Efficiency Fertilizer
GBR	Great Barrier Reef
NESP	National Environmental Science Program
NI	Nitrification inhibitor
NRM	Natural Resource Management
NUE	Nitrogen-use efficiency
PCU	Polymer Coated Urea
PZYP	Productivity Zone Yield Potential
SRA	Sugar Research Australia
TWQ	Tropical Water Quality
UI	Urease inhibitor

ABBREVIATIONS

N	Nitrogen
ccs	commercial cane sugar (%)

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EXECUTIVE SUMMARY

Total nitrogen (N) loads entering the Great Barrier Reef lagoon have increased greatly in response to land management changes, with the extensive grazing and sugarcane industries identified as major contributors. Runoff losses of dissolved inorganic nitrogen (DIN) arising from fertilizer applications are the dominant form of runoff loss in the sugarcane industry, and represent an immediate risk to marine ecosystem health. Minimizing these losses will require a combination of management strategies that collectively maximize crop recovery of applied N and minimize the risk of loss in runoff or deep drainage. The combination of a large crop N demand and an extended period of crop N uptake that can coincide with the monsoonal wet-season in northern Australia makes this challenging.

This project is testing whether a number of inter-related strategies could be used to maintain sugarcane productivity while improving fertilizer N use efficiency and minimizing N loss in runoff and drainage. It is based on combining improved N fertilizer technology (using Enhanced Efficiency Fertilizers – EEFs) with fertilizer N rate reductions that better match the N applied to the crop demand in a productivity zone which can range in scale from intra-block, several blocks or whole farm. The performance of different EEF technologies have been benchmarked against conventional urea fertilizer under conditions consistent with applications in sugarcane fields (i.e. concentrated sub-surface fertilizer bands) in both laboratory and field experiments.

Combinations of the best available EEF products have been tested at seven field sites from Mackay to Cairns, using application rates that match the productivity zone yield potential (PZYP) of the blocks in which they were tested. These practices were benchmarked against urea applied at rates calculated using the district yield potentials (DYP) defined in the Six Easy Steps (6ES) nutrient management program (which represents current industry best management practice), and a treatment that received no fertilizer N. Sites comprised ratoon crops that were harvested in the mid-late harvest rounds, to increase the risks of inefficient fertilizer N use. Traditional crop performance indicators were collected (cane yield, ccs and sugar yield), in addition to crop biomass samplings and analyses that allowed quantification of apparent fertilizer N recovery and the efficiency of fertilizer N use. Runoff losses were quantified at the Freshwater and Silkwood sites, while estimates of N loss in deep drainage were also collected at Silkwood. This report presents findings from the first two cropping seasons.

Because results are from the first two crop seasons only, they should be considered interim findings, with additional site-years of data being collected in a two year extension to this work (Project 5.11). Results showed that yields at all sites responded to the application of urea-N fertilizer, and there were suggestions of a slight (5-10%) productivity drop if urea-N rates were lowered to those determined using PZYP at some sites. The apparent crop uptake of urea-N was generally poor (15-35% of applied N) and the agronomic efficiency of urea-N use varied significantly between sites and seasons, ranging from 2.5-11.4 kg N applied/t additional cane yield. The use of the EEF blend consistently improved fertilizer-N recovery by the crop (30-47% of applied N in biomass), but there were no consistent crop yield increases associated with this extra fertlizer N uptake except for the Silkwood site; consequently, agronomic efficiencies for the EEF blend (2.5-7.6 kg N applied/t additional cane yield) were generally only slightly lower than for urea.

Runoff losses of dissolved N (inorganic and organic forms) at the Freshwater and Silkwood sites varied between sites and seasons. Cumulative measured losses of dissolved N over the 2017 and 2018 growing seasons from the current industry standard treatment (DYP rates applied as urea) and the PZYP rates applied as the EEF blend were compared. Cumulative runoff losses at Freshwater fell from 25.8 kg N/ha (DYP, urea) to 18.2 kg N/ha (PZYP, EEF), and at Silkwood fell from 35.7 kg N/ha (DYP, urea) to 7.6 kg N/ha (PZYP, EEF). These falls represented reductions of 30% (Freshwater) to 80% (Silkwood). In addition, cumulative deep drainage losses of dissolved inorganic N (DIN) at Silkwood were reduced from 7.3 kg N/ha (DYP, urea) to 0.7 kg N/ha (PZYP, EEF) – a reduction of ~90%. These decreases in runoff and drainage losses were a result of both reductions in fertilizer N input of 23% at Freshwater (300 v 230 kg N/ha) and 38% at Silkwood (260 v 160 kg N/ha) as well as the change from urea to EEF as the N source. While very promising, it was noted that the reductions in runoff losses were lessened, in some cases reversed, if the EEF blend was applied at the higher DYP rate. This reflected additional slow release mineral N released from the EEF blend that could not be accumulated by the crop during very wet conditions.

Laboratory and field studies were undertaken as part of an associated PhD program to look at the implications of applying urea, with or without commercially available coatings or inhibitors used in EEFs, in concentrated bands. This application strategy is almost universally used in commercial cane fields, but the impact of chemical changes that occur in and around the fertilizer band as a result of fertilizer dissolution and urea hydrolysis have not been previously documented. It was hypothesized that these changes may impact on the efficacy of EFF technologies and minimize potential productivity and environmental benefits from their use.

While this work is not yet finalized, a number of important conclusions can be drawn. These include (i) Rapid hydrolysis of high concentrations of urea significantly raises pH and EC and results in development of high concentrations of aqueous NH_3 in and around the fertilizer bands, effectively inhibiting nitrification. The volume of soil affected and the persistence of these conditions vary with soil type and seasonal conditions, but particularly in lighter textured (i.e., sandier) soils, the zone of inhibition associated with urea hydrolysis may exceed the volume of soil that is influenced by the inhibitor, limiting the effectiveness of these types of EEFs; (ii) Urease inhibitors slow urea hydrolysis and therefore mitigate some of the ‘hostile’ conditions that develop in the band, but the effect lasts for < 15-20 days. The greater mobility of urea than the urease inhibitors, especially in lighter textured soils, results in urea-N rapidly moving outside the zone of influence of the urease inhibitor, further shortening the period of regulation of N transformations. Interestingly, the less hostile conditions in the band with the urease inhibitor did allow nitrification to proceed, and suggested that a blend of both urease and nitrification inhibitor modes of action may provide more effective EEF performance; (iii). Polymer-coated urea (PCU) granules released urea over an extended period, moderating the chemical changes arising from rapid urea hydrolysis and allowing relatively uninhibited nitrification to occur. The resulting formation of a steady supply of mobile nitrate-N may actually increase the window for potential N losses via leaching or denitrification pathways, compared to standard urea. The rates of urea-N diffusion out of PCU granules applied in a band were slower than expected, due to the close proximity of granules to each other resulting in a reduction in the concentration gradient along which urea diffused from inside the granule into the soil. This further extended the period of urea-N release and the resulting window for potential N losses.

Collectively, this PhD research has provided a fundamental understanding of the behaviour of urea and different EEF technologies when used in banded applications at rates typically used in the Australian sugar industry. This understanding will inform the development of improved fertilizer products and application strategies that will deliver improved crop N recovery in the future, with interest from commercial fertilizer manufacturers already developing.

1.0 INTRODUCTION

The latest estimates suggest that anthropogenic activity has more than doubled total catchment nitrogen (N) loads entering the GBR lagoon (from 20,000 to 46,500 t N/year), although the contributions and constituents of those loads vary markedly between regions and between land uses (McCloskey et al. 2016). The predominant constituent (48%) of N lost from land supporting sugarcane production is dissolved inorganic N (DIN), with this form of N rapidly taken up by pelagic and benthic algae and microbial communities (Alongi and McKinnon 2005), often leading to high levels of organic production and short-lived phytoplankton blooms during the summer season (Furnas *et al.*, 2005, 2011). The high proportion of DIN leaving sugarcane catchments and the rapid bioavailability of this form of aquatic N therefore represents a substantial risk to marine ecosystem health.

The Australian sugar industry operates in challenging environments, with high rainfall and variable soil types collectively producing difficult conditions in which to efficiently manage a mobile nutrient such as N. In addition, the crop demand for available N to support biomass growth and cane yield accumulation occurs over an extended period (typically 6-8 months – Bell et al. 2014). This extended period of crop-N demand increases the risk of loss of labile forms of N via gaseous and aqueous loss pathways, especially if the combination of fertilizer application strategies and soil N transformations result in accumulation of NO_3-N. While these loss risks vary with soil type, seasonal conditions and the timing of fertilizer application relative to the onset of the monsoonal wet season, their occurrence has resulted in the development of ‘conservative’ N management systems that have typically resulted in the application of N at rates that are in excess of crop N requirements. Current 'best' practice N management recommends rates that are based on target yields, but the recommended targets are assessed at a district scale and represent yields that are reached in only a few percent of fields (Schroeder et al. 2010). Applying N fertilizer at rates appropriate for district yield potential to consistently lower-yielding fields results in situations where N supply can greatly exceed crop N demand, and result in the formation of hot-spots for N contaminant export.

Simulation studies (Thorburn *et al*. 2017a) have illustrated the quantum and variability of such off-site N losses from conventionally fertilized sugarcane fields in Tully and Mackay over a 7-year climate string. At urea-N application rates of 150 kg N/ha applied to fine and coarse-textured soils, seasonal total N loss from fertilizer and soil N sources by denitrification and leaching was estimated to range from about 15-110 kg N/ha at Mackay and from 35-200 kg N/ha at Tully, with soil type influencing both the quantum of loss and the likely loss pathway. The extent of this variability adds considerable uncertainty to the calculation of an optimal N-fertilizer rate.

There is considerable evidence that at least part of the ‘lost’ fertilizer-N from sugarcane systems is entering the marine environment in the Great Barrier Reef lagoon, with adverse impacts on water quality and the health of the marine ecosystem (Bell et al. 2016; McCloskey et al. 2016). There is, therefore, an imperative to reduce the quantum of fertilizer-N loss from cane fields, but attempts to do this through a simplistic approach such as reducing N rates in lower yielding fields without changing other aspects of agronomic or fertilizer-N management has been shown to introduce risks to crop productivity (Thorburn *et al*. 2017b, 2018). Similarly, despite recent machinery advances that allow split N applications to be made later in the crop season, there are suggestions that this strategy used with conventional urea alone will still prove relatively ineffective at reducing fertilizer-N requirement and improving nitrogen-use efficiency (NUE) (Thorburn *et al.* 2015).

Enhanced efficiency fertilizers (EEF) attempt to modify fertilizer-N release rates or control the rate of N transformations in and around the fertilizer band to better synchronize labile-N availability with crop-N demand. While different strategies have proved more or less effective in varying soil types (Di Bella et al. 2017), their effectiveness in increasing cane yield or allowing reduced fertilizer-N rates has been variable (Verburg et al. 2017, 2018) and the higher cost of these products/kg N applied has typically resulted in a reduction in profitability, even when applied as blends with conventional urea (Kandulu et al. 2017). There has been no work quantifying the impact of EEF use on off-site N losses.

We have conducted field studies that compare the standard approach to fertilizer-N (urea) management currently documented in the SIX EASY STEPS (6ES) framework (Schroeder et al. 2014) with one in which fertilizer-N rates are derived from the productivity potential of the individual block/zone (PZYP), and the fertilizer is applied as either urea or the most effective blend of EEF products commercially available. The efficacy of these different strategies are being assessed on the basis of productivity, fertilizer NUE and runoff water quality.

This work has been supported by more fundamental studies on the performance of conventional and EEF-types of N fertilizers currently being evaluated in the sugar industry, as part of a PhD program by Ms Chelsea Janke. This work focuses on the chemical reactions that occur in and around a concentrated band of N fertilizer typical of that applied in sugarcane cropping systems, to determine whether the band environment impacts on the effectiveness of different EEF technologies.

2.0 MATERIALS AND METHODS

2.1 Field trial program

2.1.1 Field sites and fertilizer application rates

We established seven field sites after the 2016 crop harvest. All experiments were commenced after harvest of the first or second ratoon in 2016, with the exception of the Freshwater site north of Cairns (5ht ratoon). Selected site details are shown in Table 1.

The experimental design and plot size varied with site. In Silkwood, Freshwater and the Burdekin, plots were large-scale strips six to eight cane rows wide and the length of the cane block, with yield (and in the case of Silkwood and Freshwater, runoff water quality) collected from the entire treated strip. The Burdekin trial contained three replicate strips of each treatment, but due to the extensive water-quality monitoring equipment requirements at Freshwater and Silkwood, treatments were not replicated at those sites. The treated areas at Mackay were also large replicated strips, with treatments deployed in high and low yielding areas of the same block, although the harvested area in each replicate of each treatment was a 30m length of harvested cane row. At Tully, both sites consisted of smaller plot, replicated experiments in a randomized block design. Plot size was six cane rows wide each 30 m long, and all treatments were replicated four times except for the Nil N plot, which had two new replicate plots in each growing season.

The basis of fertilizer rates was either the District Yield Potential (DYP, currently used to determine the fertilizer-N rates in 6ES) or the Productivity Zone Yield Potential (PZYP, used to determine N rates aligned to a site-specific yield target based on past performance), with those targets shown for each site in Table 1. The PZYP was calculated from the mean yield of the block from mill or satellite records over two or more crop cycles, plus 2 times the standard error of that mean. As all sites were established in ratoon crops, plant-crop yields were generally excluded from this calculation, especially where those yields were markedly higher than yields of the ratoons. In situations where large variation in yields occurred between La Niña and normal or drier seasons (e.g. in the wet tropics), separate PZYP targets were calculated to reflect the expected seasonal forecast (i.e. lower PZYP targets in forecast La Niña conditions). Each site hosted a Nil N treatment each year (fertilizer-N was withheld for that growing season), but these plots/strips were moved to new plot/strip locations within the trial site annually. Having the Nil N treatment always located on a plot with a history of fertilizer-N application provided a realistic assessment of the soil N supply which the fertilizer-N application was designed to augment.

There was substantial variation in soil organic carbon (C) among sites (1.0-5.6%C), which normally modifies the recommended fertilizer-N rate in 6ES. However, there are recognized situations where the in-season soil-N mineralisation adjustment (which is based on soil organic-C content) is uncertain (e.g., sites occupying low landscape positions and with elevated C, such as the Silkwood site) and we took the opportunity at this site and at Mackay to compare rates with and without adjustment for the soil-N mineralisation.

Crop harvest and fertilizer application were conducted as in the grower's normal practice at each location, although in both years at all sites there were no crops harvested in the first round. This was considered desirable, as it was expected that the best chance to assess the risks of reduced N rates and the efficacy of EEFs would be under conditions where fertilizer-N losses were more likely to occur (i.e. where the onset of the monsoonal wet season occurred before the crop had finished the majority of biomass-N accumulation).

2.1.2 Fertilizer-N sources

The same fertilizer-N sources were used at all sites. The fertilizer-N standard was taken as granular urea, which was applied during the month following harvest of the preceding ratoon. This was compared to an EEF blend consisting of one-third by weight of the urea coated with the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP, marketed commercially as Entec®) and two-thirds the polymer-coated urea with a reported 90-day release period (product of Everris Pty Ltd and marketed as Agromaster Tropical®). This blend was chosen as the best possible combination of products that would protect fertilizer-N from risk of loss – initially by retaining the N in the NH_4-N form, and subsequently by slowing the release of urea-N into the soil solution. Both products were applied using either stool-split (Burdekin, Mackay, Freshwater and Silkwood) or subsurface side-dress (Tully) fertilizer applicators.

2.1.3 Fertilizer-N recovery, crop yield and indices of fertilizer-N use efficiency

A number of indicators of crop performance were used to assess the agronomic effectiveness of the different fertilizer strategies, with examples of a number of these shown in the attached ASSCT publication in Appendix 1. However, given the interim nature of these report findings, the focus will be confined to crop yield responses (cane and sugar yield and ccs) and crop N uptake. Fresh and dry biomass and crop-N content were determined from hand-cut biomass samples collected from 7-10 months after fertilizer application, on the assumption that at this stage, the crop-N content would be at a maximum, and most relevant to the yield-determining processes (Bell *et al*. 2015). Yields were determined by commercial harvest in the case of the large strip plots, with the bins collected from each strip weighed and CCS determined at the mill. In the case of the small plot trials, yields were determined from small-plot hand harvesting and CCS was determined by near infrared spectroscopy (Berding *et al.* 2003).

Table 1: Details of the experimental sites and fertilizer-N rate treatments.

Location	Soil type	Soil organic C (%)	District yield potential (and 6ES N rate)	Productivity zone yield potential (and N rate)	Discretionary treatment (N rate)	Variety and initial crop stage
Burdekin (Mulgrave region)	Loam over sodic clay (Sodosol)	1.0	180 t/ha (200 kg N/ha)	130 t/ha (150 kg N/ha)	Grower rate urea (170 kg N/ha)	Q240[A] (1R)
Tully 1 (well drained)	Well-drained silty light clay (Tully series)	1.0	120 t/ha (140 kg N/ha)	130 t/ha (150 kg N/ha)	(i) PZYP without mineralization discount (170 kg N/ha, urea) (ii) Wet season exploratory (120 kg N/ha, EEF)*	Q208[A] (2R)
Tully 2 (poorly drained)	Poorly drained silty clay loam (Timara series)	2.3	120 t/ha (110 kg N/ha)	130 t/ha (120 kg N/ha)	(i) PZYP without mineralization discount (170 kg N/ha, urea) (ii) Wet season exploratory (90 kg N/ha, EEF)*	Q208[A] (2R)
Silkwood**	Bulgan series (Hydrosol)	5.6	120 t/ha (160 kg N/ha*)	80 t/ha (100 kg N/ha*)	(i) Long-term Nil N (ii) subplot	Q183[A] (2R)
Freshwater (Mulgrave)	Well drained clay on alluvium (Innisfail series)	0.8	120 t/ha (150 kg N/ha)	97 t/ha (110 kg N/ha)	(i) DYP N rate as EEF blend (ii) Small plot N rate trial with urea and EEF blend	Q208 [A] (5R)
Mackay (high yield)	Gravelly yellow sodic duplex (Pindi series)	1.0	130 t/ha (150 kg N/ha)	130 t/ha (150 kg N/ha)	(i) PZYP without mineralization discount (170 kg N/ha, urea) (ii) Exploratory EEF at 80% DYP without mineralization discount (130 kg N/ha)	Q208[A] (2R)
Mackay (low yield)	Gravelly yellow sodic duplex (Pindi series)	0.7	130 t/ha (160 kg N/ha)	90 t/ha (130N kg N/ha)	(i) Exploratory EEF at 80% PZYP without min discount (105 kg N/ha)	Q208[A] (2R)

* Based on adjusting fertilizer-N rates in response to seasonal forecasts (Skocaj 2015).

** The mineralization index on this high-C Hydrosol overestimates background N mineralization; the 6ES rates, therefore, do not include the mineralization rate discount, and were applied as urea or the EEF blend.

2.1.4 Runoff and drainage losses of N

Surface water runoff was monitored in four of the fertilizer rate treatments at Freshwater and Silkwood in both seasons, with the Nil N treatment also monitored at Freshwater. Strategic sampling in the farm drain around the block was also undertaken at Silkwood. In addition, drainage losses of N below the root zone (1 m depth) were also quantified at this site using barrel lysimeters installed in each block with runoff monitoring. It should be noted that at both sites, extreme rainfall events overwhelmed runoff flumes and so data for runoff N cannot be used as a total annual runoff estimate. However, relative treatment effects can be determined.

Runoff water samples were collected by automated samplers at both sites, although load calculations were estimated differently. At Silkwood, each water sample represented an integrated composite of runoff from an individual event (event mean concentration), while at Freshwater flow weighted samples were collected across the hydrograph. Runoff samples were analysed for sediment, total nitrogen, urea, ammonium-N, and nitrate-N. Drainage samples were analysed for nitrate-N and ammonium-N concentrations.

2.2 PHD PROGRAM - Banding studies

2.2.1 Fertosphere chemistry – sealed containers

The objective of this study was to determine the effectiveness of EEF technologies within the fertosphere (soil within 2.5 cm of the fertilizer band) in a range of soils with a history of sugarcane production. Urea and EEF granules were applied to achieve fertosphere conditions that were consistent with an in-band concentration (g N / m of fertilizer band) equivalent to that experienced when 150 kg N ha-1 is applied in the field in bands 1.8 m apart. This is typical of application practices in the Queensland sugar industry.

Measurements consisted of: (i) establishing the key chemical effects and N-transformation activity within a urea-band, and (ii) contrasting these findings with nitrification inhibitor (NI) coated urea and a controlled release polymer coated urea (PCU). The incubations were conducted under static conditions over a 112- day incubation period, to cover the reported release period of the PCU product. Containers were sealed, so there was no interaction between the fertosphere soil and unfertilized soil outside the fertosphere, as would occur in a field situation.

2.2.2 Diffusion of N species and inhibitors outwards from the fertosphere

The incubation was conducted in round incubation pots (225 mm diameter PVC end-caps), using sugarcane soils with contrasting physical and chemical properties (a sandy Dermosol and a heavy clay Vertosol). Fertilizer N treatments were applied into the centre of the pot in a vertical band/column at a rate equivalent to the in-band concentration of fertilizer N applied at 150 kg N ha-1 in bands spaced 1.8 m apart. Cotton wicks were inserted vertically in the fertosphere, and in an offset pattern outwards from the fertilizer band to the extremities of the pots at regularly spaced intervals. Soils were kept moist at field capacity over incubation periods that ranged from 16 days (urea, and urea-based EEF's with urease of nitrification inhibitors) to 35 days (urea and PCUs), with unfertilized soils included in each assay.

Destructive sampling of replicated pots of each treatment was conducted at regular intervals during the incubations. Soil in each pot was collected from a 2 cm diameter central core (designated the ‘0 cm’ position), and then in increments moving outwards from that central core designated as the 2 cm, 4 cm, 6 cm, 8 cm and 10 cm samples. Soils were used to determine mineral N using standard methods.

Wicks were used to recover representative soil solution at different distances for the fertilizer bands, and were analysed for urea-N and also for the presence of the urease or nitrification inhibitors used in each product.

2.2.3 Three dimensional movement of N species in the field

The field study was conducted on a Vertosol soil at University of Queensland, Gatton Campus, over the 2017/18 summer season. Fertilizer treatments were applied in bands at 12.5cm depth at rates of 50 to 150 kg N ha-1, with each treatment replicated four times. In-band concentrations were chosen to be representative of fertilizer N rates in use in the sugarcane, grains and irrigated cotton industries.

Treatments included an unfertilized treatment, and application rates of 50, 100 and 150 kg N/ha applied as urea, or urea with the NI DMPP (Entec®). In addition, other EEF products tested included urea with a blend of DMPP and succinic acid (Entec 2, Eurochem Pty. Ltd), urea with the urease inhibitor NBPT (Green Urea NV®) and the PCU, Agromaster Tropical®. After fertilizer application, the distribution of urea-N and mineral N were monitored over a 71 day period, with samplings based on likely duration of EEF efficacy and in response to significant rainfall or irrigation events. Plots were maintained free of plants during this period.

At sampling events, soil monoliths were collected at right angles to the fertilizer band and dissected into zones that allowed quantitation of vertical (both above and below the fertilizer band) and lateral movement of N out of the fertilizer band, in response to both diffusion and mass flow. Samples were collected over a 30cm vertical distance (12.5cm above and below a fertosphere 5cm wide), and out to a distance of 12.5 cm horizontally. At all sampling times, chemical conditions in and around the fertilizer band were monitored, along with urea-N and mineral N species.

3.0 KEY FINDINGS

The results reported from the field sites represent interim findings that cover only two crop seasons, and particularly for the Tully location, neither season represented a very wet year. However, there have been some promising trends emerging, and these are summarised in Section 3.1.1 (productivity impacts) and 3.1.2 (water quality benefits). More detailed coverage of the agronomy and water quality outcomes for a subset of these sites are outlined in a paper presented at the 2019 ASSCT conference (Appendix 1).

Some of the findings from the studies exploring the impact of banded fertilizer applications on the efficacy of different EEF products are still being collated and analysed, with the PhD thesis to be submitted in late 2019. A short summary of the key findings from the laboratory incubations and a preliminary assessment of performance in the field studies are provided in Section 3.2. At this stage, one technical paper has been published (Appendix 2), with another 4 manuscripts in the late stages of development or in external review. It is anticipated these will all be published during 2019.

3.1 Field studies

3.1.1 Crop productivity

In this discussion, productivity results have been assessed relative to that of crops receiving urea-N at rates determined using the 6ES Best Management Practice (BMP) protocols – the current industry standard. Those N rates are shown in Table 1, with crop performance compared to that of treatments where either urea, or a blend of EEF products, were applied at rates corresponding to the PZYP at each site. These reduced rates are also shown in Table 1. It should be noted that at some sites (e.g. Tully) the PZYP and DYP were effectively equal, and so there was no assessment of a reduced rate of urea N (Fig. 1a, b). Similarly, data are presented illustrating crop performance with a combination of PZYP N rates and substituting the EEF bend for urea, relative to the urea-DYP standard, in Fig. 2 (a, b). Results for the Tully sites in this comparison simply represent the effect of changing to the EEF blend, rather than using urea.

For all sites and seasons, there were no statistically significant differences between cane yields (Fig. 1a) or sugar yields (Fig. 1b) for crops receiving a urea-N application rate based on PZYP rather than DYP. The extent of the reduction in urea-N rates in the PZYP treatment varied from 30-60 kg N/ha (Table 1), and represented a relative reduction between 20%and 40% compared to the industry standard. However, while not statistically significant at any single site, there was a consistent pattern for slightly lower cane and sugar yields with the PZYP N rates which collectively represented an average productivity loss of 8% in both yield parameters, relative to industry standard rates. At some sites and seasons (e.g. Mackay in 2018 and Silkwood in 2017), the relative losses were much higher (viz, 24% at Silkwood in 2017, and 18% at Mackay in 2018).

Similarly, for all sites and seasons there were no statistically significant differences between cane yields (Fig. 2a) or sugar yields (Fig. 2b) for crops receiving the industry standard N rate as urea (determined using DYP) or a rate of N corresponding to PZYP for each individual block and applied as a blend of EEF products. The lower N rates applied as the EEF blend were identical to those applied as urea in Fig. 1, but unlike in Fig. 1, there was no longer any slight depression in either cane or sugar yields evident relative to the industry standard rates as urea. It should be noted that the data in Fig. 2 for the Tully sites represent the same N rate applied as urea or the EEF blend, as the yields determined using DYP or PZYP were identical for those sites.

These results are encouraging, as at this early stage they suggest that EEF technology may be a way to reduce or eliminate the productivity risk associated with reduced N rates based on a defensible PZYP calculation. These results are preliminary only, and may change as the lower N rates are applied over a longer period in the crop cycle (eroding the existing N surplus at each site). Results from the extension of this work in NESP TWQ Hub Project 5.11 will help to address these uncertainties. Regardless, the additional cost of the EEF products is significant, with the cost/kg N applied increasing significantly compared to urea. The actual cost of EEF-N will depend on the products and proportions of each in the blend, but could increase the cost of fertilizer N by 50-100%. Without productivity increases to offset those costs, or compensation to growers to offset any additional fertilizer cost, widespread commercial adoption of this strategy is unlikely.

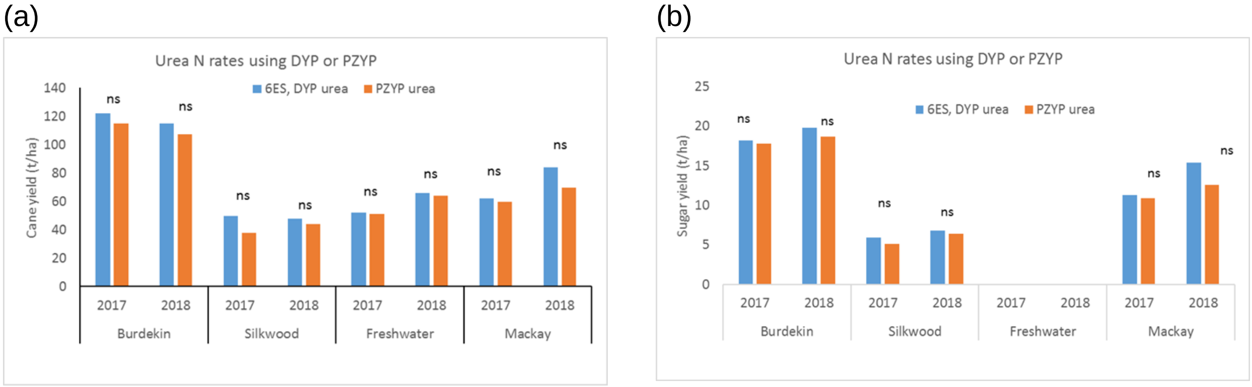

Figure 1: Effects of application of urea-N at rates determined using DYP (current industry standard) or PZYP (derived from production records for each block) for (a) cane yield or (b) sugar yield) for the 2017 and 2018 growing seasons. Statistical differences are denoted by * ($P<0.05$), with ns indicating yield differences were not statistically significant.

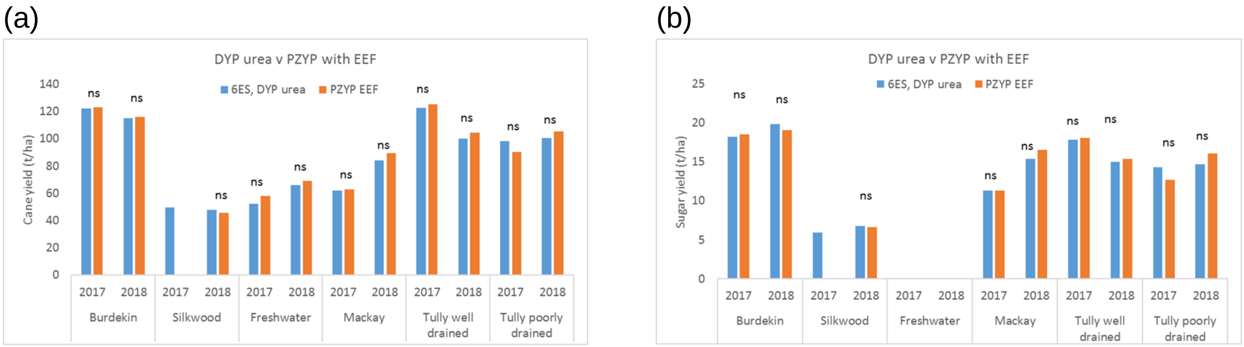

Figure 2: Effects of fertilizer N applications of urea at a rate determined using DYP (current industry standard) or of a blend of EEF fertilizers applied at rates determined by PZYP (derived from production records for each block) for (a) cane yield or (b) sugar yield) for the 2017 and 2018 growing seasons. Statistical differences are denoted by * (P<0.05), with ns indicating yield differences were not statistically significant.

3.1.2 Crop N uptake

The productivity responses recorded in the contrasting N management strategies were consistent with measured crop N contents (Fig. 3). While not always statistically significant, reducing urea N rates from the current standard to a rate determined using PZYP typically resulted in lower crop N acquisition, with an average biomass N content that was 17% lower than with the current DYP benchmark rates (Fig. 3a). In contrast, substituting the EEF blend for urea at those lower N rates was generally able to achieve similar crop N contents as that with DYP urea (Fig. 3b), and showed a significant improvement in fertilizer N recovery by crops at all sites.

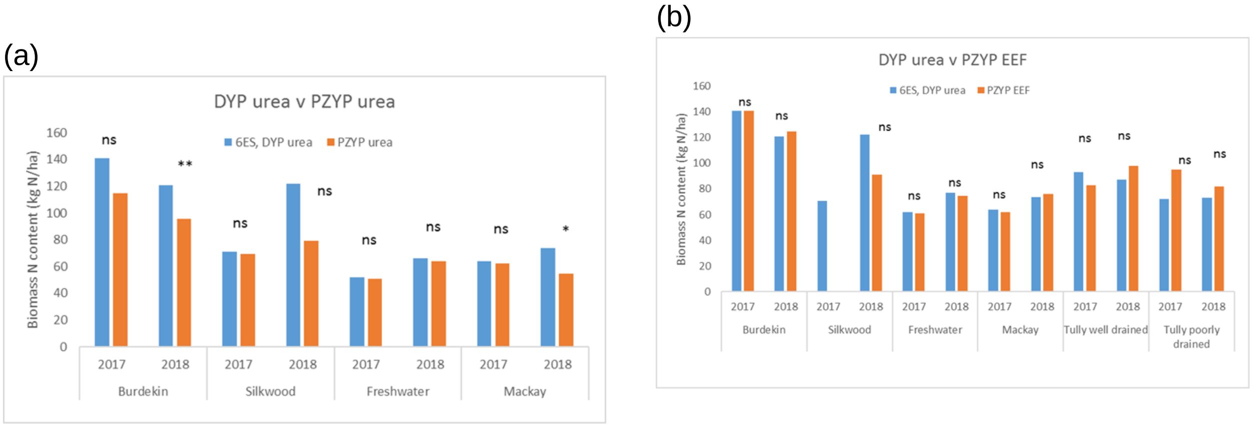

Figure 3: Effects of application of (a) urea-N at rates determined using DYP (current industry standard) or PZYP (derived from production records for each block) or (b) urea-N at rates determined using DYP or an EEF applied at rates based on PZYP on biomass N accumulation by ratoon crops in the 2017 and 2018 growing seasons. Statistical differences are denoted by ** (P<0.01) or * (P<0.05), with ns indicating treatment differences were not statistically significant.

3.1.3 Runoff and drainage losses

The total quantities of dissolved N measured in runoff in the 2017 and 2018 crop seasons are shown in Figure 4, with the relative losses over the 2 crop seasons compared to those recorded from the DYP-urea treatment at each site shown as a percentage. The two clear observations that can be made for these data are that: (i) reducing N rates from that derived by DYP to a PZYP rate resulted in 28-60% reductions in dissolved total N measured in runoff, while (ii) switching from urea to EEF at the same N rate could result in runoff losses that were higher (DYP rates at Silkwood), similar (Freshwater at PZYP) or lower (Silkwood at PZYP and Freshwater at DYP). However, when losses from the current industry standard (DYP-urea) are compared to the EEF blend applied at PZYP (where yields were similar), reductions in dissolved total N in runoff were reduced by 60% at Silkwood and 32% at Freshwater. In absolute terms, this represented reductions of 19 kg N/ha and 8.5 kg N/ha at Silkwood and Freshwater sites, respectively.

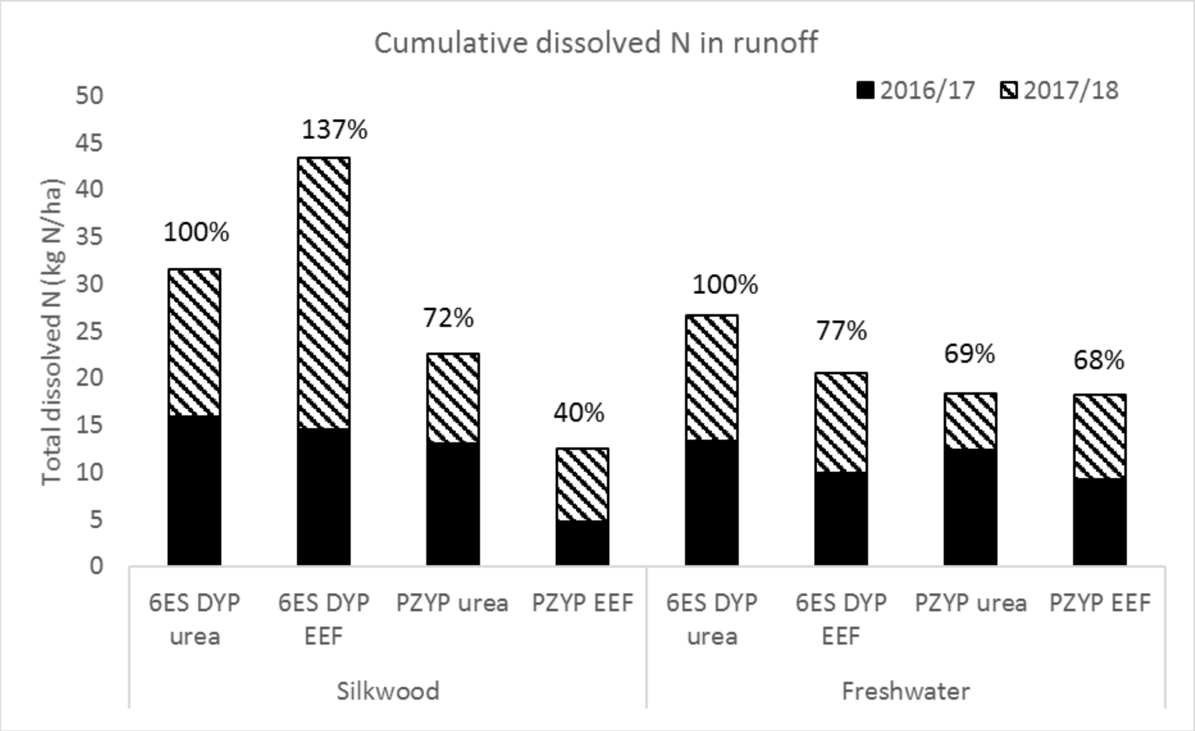

Figure 4: Runoff losses of dissolved total N at the Silkwood and Freshwater sites for the 2017 and 2018 crop seasons. Losses were recorded for N application rates determined using DYP (industry standard) or PZYP, with each rate applied as either urea or a blend of EEF products. Runoff losses were collected from unreplicated strips at both locations, so statistical comparisons cannot be made. In addition, seasonal totals did not represent total N lost in runoff, as flumes were overwhelmed by flooding events in each season.

In addition, the combination of PZYP N rates and use of the EEF blend also produced much lower deep drainage losses of dissolved inorganic nitrogen (DIN) than that from the urea-DYP rate at Silkwood. In this instance, cumulative drainage DIN losses were reduced from 7.4 kg DIN/ha to 1.3 kg DIN/ha, or a reduction of more than 80%. If the runoff and drainage losses at Silkwood are considered collectively, the PZYP-EEF combination reduced aquatic N losses by 65% (from 38.9 to 13.8 kg N/ha).

3.2 Laboratory studies

The key findings from the laboratory studies are presented as a series of extracts from the abstracts of technical manuscripts either already published (Appendix B) or currently in review. We have not presented any data in tables or figures, but readers are referred to the full manuscripts which will be uploaded into e-Atlas as they are published.

3.2.1 Initial fertosphere studies in sealed systems

A 112-day incubation experiment was conducted with the EEFs band-applied in three contrasting soils with a history of sugarcane production. In standard urea and NI-urea treated soils, the pH within the fertosphere significantly increased to a maximum of ~pH 9.2–9.3. Alkaline conditions and high ammonium concentrations promoted elevated aqueous ammonia concentrations, resulting in complete nitrification inhibition. The PCU granules released ~40% of total urea-N content within 14 days, followed by subsequent release at significantly lower rates. The initial rapid urea-N release was attributed to damaged polymer coats, while the close proximity of neighbouring granules within the band may have contributed to the subsequent slower release phase through reduced concentration gradients and restricted diffusion from granules. Variation between soils suggests that soil properties such as clay content and pH buffer capacity may influence urea hydrolysis, but not nitrification. These results suggest that both NI and controlled-release technology may not have the expected impacts on N transformations and availability when applied in a concentrated band.

3.2.2 Diffusion of N species and inhibitors outwards from the fertosphere

In a 16-day laboratory incubation, the efficacy of the nitrification inhibitor (NI), 3,4-dimethylpyrazole phosphate (DMPP) and the urease inhibitor (UI), N-(n-butyl) thiophosphoric triamide (NBPT) was investigated by incubating two commercially available urea-based products containing these additives in bands at concentrations equivalent to 150 kg N ha^{-1} (row spacing 1.8 m). These products were assessed relative to a band of granular urea applied at the same rate and the study was conducted in two soil types differing in physical and chemical characteristics (a Vertosol and a Dermosol).

The urea band produced substantial increases in soil pH, EC, and aqueous NH_3 concentration which influenced ureolytic activity and nitrification within the fertosphere and surrounding soil for both soil types. However, key soil physico-chemical factors including cation exchange capacity (CEC), impedance (to diffusion) and pH buffering capacity (pH_{BC}) influenced the size and persistence of the impacted zone, resulting in substantial soil-type variation.

When compared to granular urea alone, the inclusion of DMPP in the urea band did not provide any inhibitory benefits except when the inhibitor was able to diffuse beyond the zone affected by urea-N hydrolysis. Within that zone, severe inhibition of nitrification was already occurring. The benefit of the NI was therefore observed in the soil with higher clay, organic matter and pH buffering capacity, which restricted the zone in which ureolytic-induced chemical changes and resulting nitrification inhibition occurred. In contrast, the urease inhibitor NBPT provided some temporary benefits by slowing the rapid rise in pH, EC and aqueous NH_3 observed in standard urea bands, although the effects were short-lived (*ca*. 9 days) in both soils. The benefits of NI and UI technology are likely to vary considerably between soils and application methods when compared to a standard urea band, and these studies are providing a physico-chemical approach to determining where and when the benefit of ‘stabilising’ EEF technology may be realised.

Two additional experiments over 35 and 91 day incubation periods compared the N dynamics of a urea band against a band of PCU granules, with the focus on N release from the band and its subsequent diffusion. The N was applied at in-band concentrations equivalent to those when 150 kg N ha^{-1} is applied in bands 1.8m apart, with the same contrasting soil types used as the inhibitor studies. Compared to the granular urea standard, PCU granules provided a sustained release of urea-N to the soil solution, with the lower urea-N concentrations limiting the development of the toxic conditions associated with rapid urea hydrolysis. Differences were observed between soil types, but these were relatively small. However, the close proximity of PCU granules to each other in a band restricted the diffusion-driven release of urea-N from the granules, and soil moisture content and mass flow are likely to be strong drivers of the effect on N release. The relatively mild fertosphere conditions for the PCU (compared to standard urea) resulted in relatively greater proportions of PCU-derived mineral N being oxidised to nitrate, potentially increasing N-loss risk.

3.2.3 Three dimensional movement of N species in the field

This study took a mechanistic approached to investigating the potential of banded nitrification inhibitors (NIs), a urease inhibitor (UI) and a controlled release polymer-coated urea (PCU) for improving NUE under field conditions. A 71-day field trial was conducted at Gatton, Australia, with fertilizer treatments banded at rates of 50, 100, 150 kg N ha^{-1} at a band spacing of 1.8m. Excavation of soil profile cross sections allowed quantification of urea- and mineral N species in the fertosphere and surrounding soil at set sampling intervals.

The addition of NIs extended the inhibition observed in a standard urea band for up to *ca*. 40 days. This occurred primarily in the fertosphere and soil immediately below, and was observed at application rates as low as 50 kg N ha^{-1}, although the duration of the inhibitory period was shorter at low N rates. The UI had a transient effect, with urea hydrolysis limited for 7 – 21 days after fertilizer application, and resulted in N moving more rapidly into lower profile layers due to leaching of preserved urea-N. The PCU released urea-N slowly over time with the lower concentrations in soil protecting N from early N losses, but the lack of inhibitory conditions associated with hydrolysis of concentrated urea enabled high rates of nitrification to occur with time. This resulted in greater proportions of fertilizer N being susceptible to leaching and denitrification losses over the PCU ‘life-time’.

4.0 RECOMMENDATIONS AND CONCLUSION

While results are based on only two field seasons, they have been able to consistently demonstrate more efficient fertilizer N recovery by crops when EEF technology is used, compared to conventional urea. This project chose to use a blend of commercially available NI and PCU products, with the results of the laboratory studies suggesting there are likely to be benefits from combining controlled release and N-stabilizing technologies in this fashion. The particular blend used in these studies was based on the best products commercially available at the inception of this project. It is recognized that the availability and efficacy of these technologies will evolve, but the concepts explored in the field and laboratory components of this project will be relevant and a useful guide to fertilizer manufacturers. At this time, results show the potential benefits of enhanced efficiency technology in delivering greater fertilizer NUE in the sugar industry.

Enhanced fertilizer technologies have also enabled what appear to be a significant rationalization of fertilizer N inputs to better match finer scale productivity. While N fertilizer inputs in high-yielding blocks may not change using this local productivity approach, this project has demonstrated that there should be opportunities to make substantial rate cuts in poorer performing blocks without an increased risk of a productivity drop. Interestingly, making these rate adjustments without addressing N losses through use of EEF technology will result in an increased risk of productivity drop.

This project has demonstrated that reducing fertilizer N rates, regardless of fertilizer technology, is likely to reduce the runoff and deep drainage losses of fertilizer N from cane fields. However, the combination of reduced N rates and EEF technology will deliver the greatest water quality benefits. The quantum of that reduction is uncertain, given the inability to fully capture all runoff during extreme events at both detailed monitoring sites, but the relative reduction in losses has so far been between 30 and 60%.

The water quality data has also provided a cautionary note regarding the use of EEF technology. When the current EEF blend was used at rates equivalent to the current industry standard based on DYP, there were situations where runoff losses actually equalled (Freshwater 2018) or exceeded (Silkwood 2018) those from urea N. This was not due to a failure of the EEF technology, but rather an example of a controlled release N supply that was not able to be utilized by the crop in high risk situations (e.g. heavy rainfall and/or prolonged waterlogging). There were suggestions of higher cane yields at both sites with DYP rather than PZYP N rates with EEF products, but the yield benefits were small and at the expense of a greater water quality risk. While cost-prohibitive at present, future research is needed to define where a change to EEFs without reducing N rates may deliver increased productivity without a greater N loss risk.

In conclusion, while the research program has so far found evidence to support our hypothesis, that EEFs will reduce the risk of productivity loss from reduced N rates and improve water quality, these treatments need to be exposed to at least a full crop cycle and to a wider range of seasonal conditions. The NESP TWQ Hub Project 5.11, which extends these sites for a further two years, is helping to meet this requirement. However, it should also be noted that our field program chose sites and fertilizer N application times that represented moderate-high risk of offsite N loss and inefficient use of fertilizer N. This was done deliberately, to test the combination of reduced N rates and EEFs under the most challenging conditions, but it means that it is not appropriate to extrapolate findings across the broader sugarcane industry.

There will be a significant financial impost associated with using EEF products rather than conventional urea. As such, it is clearly important to identify where and when EEFs are most effective, either in increasing productivity or maintaining productivity at lower N rates, so that appropriate cost-benefit analyses can be undertaken. Some of this work is currently underway in the Reef Trust 4/EEF60 project, with which this project and NESP TWQ Hub Project 5.11 are closely linked, and in industry-funded simulation studies. Collectively, these studies will help to provide guidance to industry, natural resource management (NRM) groups and government about the costs and benefits of improved fertilizer N use in the sugar industry.

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APPENDIX 1: PAPER PUBLISHED IN 2019 ASSCT PROCEEDINGS

Peer-reviewed paper

Can new fertilizer technology facilitate a reduction in fertilizer-N rates and improved water quality without compromising sugar production?

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Abstract Optimizing nitrogen (N) application rates to both sustain high levels of productivity and minimize any impacts on the surrounding ecosystem is challenging, especially under monsoonal wet-season conditions in northern Australia. The inability of existing application strategies and fertilizer-N products to achieve synchrony of mineral N supply with crop demand, or prevent rapid formation of nitrate-N (that is vulnerable to loss via gaseous or aqueous loss pathways) increases risks of inefficient N use. A blend of enhanced efficiency fertilizers (EEFs) with different modes of action has the best chance of lowering the risk of N losses and increasing crop-N recovery, providing an opportunity to reduce fertilizer-N rates without increasing the risks of productivity loss. Seven field trials were established from Mackay to the wet tropics, with data from consecutive ratoon crops at sites in Tully, Silkwood and the Burdekin reported here. Yields and indices of N use efficiency were developed for crops receiving urea-N at rates equivalent to that derived from the local SIX EASY STEPS guidelines, or as urea or a blend of EEF's applied at N rates calculated using a block-specific yield target (PZYP) based on mill records. Results showed that yields at all sites responded to the application of urea-N fertilizer, and there were suggestions of a slight productivity drop if rates were lowered to those determined using PZYP at some sites. The apparent crop uptake of urea-N was generally poor (15-30% of applied N) and the agronomic efficiency of fertilizer-N use varied significantly between sites and seasons (2.5-11.4 kg N applied/t additional cane yield). The use of the EEF blend consistently delivered improved fertilizer-N recovery (30-47% of applied N), but the lack of any yield increases at sites other than Silkwood resulted in similar agronomic efficiencies (2.5-7.6 kg N applied/t additional cane yield). The impacts of the EEF blend on runoff and drainage losses at Silkwood were confounded by inadequate closure of the fertilizer trench during stool splitting.

Key words Urea, enhanced efficiency fertilizers, nitrogen, productivity zone yield potential, dissolved inorganic nitrogen

INTRODUCTION

The Australian sugar industry operates in challenging environments, with high rainfall and variable soil types collectively producing difficult conditions in which to efficiently manage a mobile nutrient such as nitrogen (N). In addition, the crop demand for available N to support biomass growth and cane yield accumulation occurs over an extended period (typically 6-8 months – Bell *et al*. 2014). This extended period of crop-N demand increases the risk of loss of labile forms of N via gaseous and aqueous loss pathways, especially if the combination of fertilizer application strategies and soil N transformations result in accumulation of NO_3-N. Simulation studies (Thorburn *et al.* 2017a) have illustrated the quantum and variability of such off-site N losses from conventionally fertilized sugarcane fields in Tully and Mackay over a 7-year climate string. At urea-N application rates of 150 kg N/ha applied to fine and coarse-textured soils, seasonal total N loss from fertilizer and soil N sources by denitrification and leaching was estimated to range from about 15-110 kg N/ha at Mackay and from 35-200 kg N/ha at Tully, with soil type influencing both the quantum of loss and the likely loss pathway. The extent of this variability adds considerable uncertainty to the calculation of an optimal N-fertilizer rate.

There is considerable evidence that at least part of the 'lost' fertilizer-N from sugarcane systems is entering the marine environment in the Great Barrier Reef lagoon, with adverse impacts on water quality and the health of the marine ecosystem (Bell *et al.* 2016; McCloskey *et al.* 2016). There is, therefore, an imperative to reduce the quantum of fertilizer-N loss from cane fields, but attempts to do this through a simplistic approach such as reducing N rates in lower yielding fields without changing other aspects of agronomic or fertilizer-N management has been shown to introduce risks to crop productivity (Thorburn *et al.* 2017b, 2018). Similarly, despite recent machinery advances that allow split N applications to be made later in the crop season, there are suggestions that this strategy used with conventional urea alone will still prove relatively ineffective at reducing fertilizer-N requirement and improving NUE (Thorburn *et al.* 2015).

Enhanced efficiency fertilizers (EEF) attempt to modify fertilizer-N release rates or control the rate of N transformations in and around the fertilizer band to better synchronize labile-N availability with crop-N demand. While different strategies have proved more or less effective in varying soil types (Di Bella *et al*. 2017), their effectiveness in increasing cane yield or allowing reduced fertilizer-N rates has been variable (Verburg *et al.* 2017, 2018) and the higher cost of these products/kg N applied has typically resulted in a reduction in profitability, even when applied as blends with conventional urea (Kandulu *et al.* 2017). There has been no work quantifying the impact of EEF use on off-site N losses.

Our study compares the standard approach to fertilizer-N (urea) management currently documented in the SIX EASY STEPS (6ES) framework (Schroeder *et al.* 2014) with one in which fertilizer-N rates are derived from the productivity potential of the individual block/zone (PZYP) and the fertilizer is applied as either urea or the best available blend of EEF products commercially available. The approach is assessed on the basis of productivity, fertilizer NUE and runoff water quality.

METHODS

Field sites and fertilizer application rates

We established seven field sites after the 2016 crop harvest, but results from only the Burdekin, Tully and Silkwood sites are reported in this paper due to the delay in obtaining harvest results from the 2018 crop season at the Freshwater and Mackay locations. All experiments were commenced after harvest of the first or second ratoon in 2016, with selected site details shown in Table 1. There was substantial variation in soil organic carbon (C) among sites (1.0-5.6%C), which normally modifies the recommended fertilizer-N rate in 6ES. However, there are recognized situations where the in-season soil-N mineralisation adjustment (which is based on soil organic-C content) is uncertain (e.g., wet sites occupying low landscape positions and with elevated C, such as the Silkwood site) and we took the opportunity at this site to compare rates with and without adjustment for the soil-N mineralisation.

The experimental design and plot size varied with site. In Silkwood and the Burdekin, plots were large-scale strips six to eight cane rows wide and the length of the cane block, with yield (and in the case of Silkwood, runoff water quality) collected from the entire treated strip. The Burdekin trial contained three replicate strips of each treatment, but due to the extensive water-quality monitoring equipment requirements at Silkwood, treatments were not replicated. At Tully, both sites consisted of smaller plots, replicated experiments in a randomized block design. Plot size was six cane rows wide each 30 m long, and all treatments were replicated four times except for the Nil N plot, which had two new replicate plots in each growing season.

The basis of fertilizer rates was either the District Yield Potential (DYP, currently used to determine the fertilizer-N rates in 6ES) or the Productivity Zone Yield Potential (PZYP, used to determine N rates aligned to a spatially relevant yield target), with those targets shown for each site in Table 1. The PZYP was calculated from the mean yield from block or satellite records over two or more crop cycles, plus 2 times the standard error of that mean. As all sites were established in ratoon crops, plant-crop yields were generally excluded from this calculation, especially where those yields were markedly higher than yields of the ratoons. In situations where large variation in yields occurred between La Niña and normal or drier seasons (e.g. in the wet tropics), separate PZYP targets were calculated to reflect the expected seasonal forecast (i.e. lower PZYP targets in forecast La Niña conditions). Each site hosted a Nil N treatment each year (fertilizer-N was withheld for that growing season), but these plots/strips were rmoved to new plot/strip locations annually. Having the Nil N treatment always located on a plot with a history of fertilizer-N application provided a realistic assessment of the soil N supply which the fertilizer-N application was designed to augment.

Table 1. Details of the experimental sites and fertilizer-N rate treatments.

Location	Soil type	Soil organic C (%)	District yield potential (and 6ES N rate)	Productivity zone yield potential (and N rate)	Discretionary treatment (N rate)	Variety and initial crop stage
Burdekin (Mulgrave region)	Loam over sodic clay (Sodosol)	1.0	180 t/ha (200 kg N/ha)	130 t/ha (150 kg N/ha)	Grower rate urea (170 kg N/ha)	Q240[A] (1R)
Tully 1 (well drained)	Well-drained silty light clay (Tully series)	1.0	120 t/ha (140 kg N/ha)	130 t/ha (150 kg N/ha)	(i) PZYP without mineralization discount (170 kg N/ha, urea) (ii) Wet season exploratory (120 kg N/ha, EEF)*	Q208[A] (2R)
Tully 2 (poorly drained)	Poorly drained silty clay loam (Timara series)	2.3	120 t/ha (110 kg N/ha)	130 t/ha (120 kg N/ha)	(i) PZYP without mineralization discount (170 kg N/ha, urea) (ii) Wet season exploratory (90 kg N/ha, EEF)*	Q208[A] (2R)
Silkwood**	Bulgan series (Hydrosol)	5.6	120 t/ha (160 kg N/ha*)	80 t/ha (100 kg N/ha*)	Long-term Nil N subplot	Q183[A] (2R)

* Based on adjusting fertilizer-N rates in response to seasonal forecasts (Skocaj 2015).

** The mineralization index on this high-C Hydrosol overestimates background N mineralization; the 6ES rates, therefore, do not include the mineralization rate discount, and were applied as urea or the EEF blend

Crop harvest and fertilizer application were conducted as in the grower's normal practice at each location, although in both years at all sites there were no crops harvested in the first round. This was considered desirable, as it was expected that the best chance to assess the risks of reduced N rates and the efficacy of EEFs would be under conditions where fertilizer-N losses were more likely to occur (i.e. where the onset of the monsoonal wet season occurred before the crop had finished the majority of biomass-N accumulation).

Fertilizer-N sources

The same fertilizer-N sources were used at each site. The fertilizer-N standard was taken as granular urea, which was applied during the month following harvest of the preceding ratoon. This was compared to an EEF blend consisting of one-third of the urea coated with the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP, marketed commercially as Entec®) and two-thirds the polymer-coated urea with a reported 90-day release period (product of Everris Pty Ltd and marketed as Agromaster Tropical®). This blend was chosen as the best possible combination of products that would protect fertilizer-N from risk of loss – initially by retaining the N in the NH_4-N form, and subsequently by slowing the release of urea-N into the soil solution.

Both products were applied using either stool-split (Burdekin and Silkwood) or subsurface side-dress (Tully) fertilizer applicators, although at Silkwood in particular, the stool-split applicators did not always effectively close the fertilizer trench and cover the fertilizer band with soil. This suboptimal application strategy contributed to some confounding of the benefits of EEF use in some seasons due to greater loss risks to both the atmosphere and in runoff.

Fertilizer-N recovery, crop yield and indices of fertilizer-N use efficiency

Fresh and dry biomass and crop-N content were determined from hand-cut biomass samples collected from 7-10 months after fertilizer application, on the assumption that at this stage, the crop-N content would be at a maximum, and most relevant to the yield-determining processes (Bell *et al*. 2015). Crop-N was partitioned between leaf/cabbage/dead leaf and stalks at that time. In situations where biomass sampling was conducted a little earlier than desirable (e.g. due to an impending cyclone), fewer whole-stalk samples were again collected for dry matter and N concentration immediately prior to harvest (to determine the partitioning of N between harvested and non-harvested portions of the crop), and stalk-N concentration from the final harvest was used in combination with cane yields to estimate crop-N removal.

Yields were determined by commercial harvest in the case of the large strip plots, with the bins collected from each strip weighed and CCS determined at the mill. In the case of the small plot trials at Tully, yields were determined from small-plot hand harvesting and CCS was determined by near infrared spectroscopy (Berding *et al.* 2003).

Two indices of N use efficiency were calculated from these data, using calculations adapted from Ladha *et al.* (2005):

- *Agronomic efficiency of fertilizer-N use (AgronEff$_N$)* = Fertilizer-N rate/(Yield$_{N1}$ – Yield$_{N0}$) = kg fertilizer-N required to produce an additional tonne of cane yield. In this calculation, Yield$_{N1}$ is the cane yield at fertilizer rate N$_1$, while Yield$_{N0}$ is the yield with no N applied.
- *Nitrogen uptake efficiency (NUpE)* = (Crop-N1 – Crop-N0)/Fertilizer-N rate = the additional crop-N uptake/kg fertilizer-N applied. In this calculation, N1 is the biomass-N content for N rate 1, while N0 is the biomass-N content with no applied N fertilizer.

Runoff and drainage losses of N

Surface water runoff and drainage below the root zone (1 m depth) were monitored in four of the fertilizer rate treatments at Silkwood in both seasons, excluding the Nil N treatment, in addition to strategic sampling in the farm drain around the block. Surface water samples were collected by automated samplers, with each water sample representing an integrated composite of runoff from each individual runoff event (event mean concentration). Runoff samples were analysed for sediment, total nitrogen, urea, ammonium-N, and nitrate-N. Drainage samples were collected from five lysimeter barrels in each of the treatments with runoff monitoring (totalling 20 barrels) on a weekly to monthly basis, depending on rainfall. Drainage samples were analysed for nitrate-N and ammonium-N concentrations.

RESULTS AND DISCUSSION

Cane yield response to N rate and fertilizer form

There were statistically significant cane yield, CCS and sugar yield responses to fertilizer-N application at all sites in both years (data not shown), with cane yields without fertilizer-N in 2017 representing 45-60% (mean 53%) of yields of treatments receiving the recommended 6ES fertilizer rate applied as urea, and a slightly higher 53-80% (mean 66%) of the yields from the same benchmark treatment in 2018. However, at sites where statistical comparisons could be made between the core treatments shown in Table 2 (i.e., excluding Silkwood), there was no significant response to either N rate or the use of EEFs in terms of cane or sugar yields and CCS. There was, however, an interesting trend for 6-8% higher yields with the EEF blend compared to urea at the PZYP N rate across both seasons in the Burdekin, with the yields in the EEF treatment receiving 150 kg N/ha effectively identical to those receiving 200 kg N/ha as urea.

Whilst not able to be compared statistically, yields at Silkwood in the 2017 season responded strongly to increased N rates as urea (cane yields with 160 kg N/ha were 31% higher than those with 100 kg N/ha), and at the 160 kg N/ha rate, increased by a further 23% when the N was applied as the EEF blend. However, while the maximum yield with urea-N was similar in the 2018 crop (47.5 t/ha in 2018 versus 49.6 t/ha in 2017), there was no apparent yield response to urea-N rates above 100 kg N/ha. By comparison, in strips where N was supplied as the EEF blend, yields increased by 22% as the N rate increased from 100 kg N/ha to 160 kg N/ha, and at the 160 kg N/ha rate the EEF treatment produced 16% higher yields than the equivalent rate of urea.

Accumulation of N by the cane crop

Biomass sampling at 7-10 months after fertilizing was assumed to approximate the time of maximum crop-N uptake (Bell *et al.* 2015; Moody and Connellan 2018), and data from across all sites was initially pooled in an analysis of the relationship between crop-N content and final cane yield (Fig. 1). This analysis suggested distinctly different relationships for the crops grown at Silkwood versus the crops grown at the Burdekin or Tully sites. In both datasets, there was a linear relationship between crop-N content and cane yield up to crop-N contents of about 100 kg N/ha, after which there was little or no further increase in cane yields despite greater N accumulation. However, for the same crop-N content, the yields at Silkwood were always 50-60 t/ha less than crops at the other sites, and the crops at those sites were much more efficient at using additional N accumulation to produce increased cane yield. To illustrate this, crops containing <100 kg N/ha at both Tully sites and the Burdekin required an additional 0.81 kg N in above ground biomass to produce an additional tonne of cane yield, while crops at Silkwood needed 1.93 kg biomass-N to produce an additional tonne of cane yield. Collectively, these data suggest that while crops at Silkwood were responsive to N application, other limitations to yield at that site (e.g., waterlogging) were playing a much greater role in determining crop yields.

Table 2. Effect of fertilizer rate and product on cane yield (t/ha), CCS and sugar yield (t/ha) for the 2017 and 2018 crop harvests*.

Location	Season	Cane	CCS	Sugar	Cane	CCS	Sugar	Cane	CCS	Sugar	Cane	CCS	Sugar
		200N, urea			150N, urea			150N, EEF			170N, urea		
Burdekin	2017	121.8	15.0	18.2	115.2	15.5	17.8	122.7	15.	18.5	115.5	15.3	17.7
	2018	115.3	17.2	19.8	106.5	16.7	18.7	115.6	16.6	19.1	112.8	17.3	19.4
Tully 1		150N, urea			150N, EEF			170N, urea			120N, EEF		
	2017	122.4	14.5	17.8	125.1	14.7	18.1	125.4	14.9	18.3	112.1	14.7	16.5
	2018	100.0	15.0	15.0	104.3	14.7	15.4	106.6	15.1	16.1	104.8	14.8	15.5
Tully 2		120N, urea			120N, EEF			170N, urea			90N, EEF		
	2017	98.3	14.5	14.3	90.2	14.1	12.7	100.9	14.6	14.7	91.9	14.7	13.5
	2018	100.6	14.9	14.7	105.3	15.3	16.1	111.1	14.7	16.3	91.2	14.9	13.6
Silkwood**		100N EEF blend			100N urea			160N EEF blend			160N urea		
	2017	-	-	-	37.8	11.9	5.11	61.1	11.9	5.96	49.6	11.9	7.27
	2018	45.4	14.6	6.6	43.9	14.6	6.4	55.3	14.3	7.9	47.5	14.6	6.8

*Statistical testing for treatment effects showed no statistically significant differences (ns) for any parameter in either crop season at Burdekin, Tully 1 or Tully 2 sites. Treatments at Silkwood were applied as unreplicated strips, so statistical comparisons cannot be made

**Fertilizer-N rates were based on the 6ES DYP rate, with or without the soil-N mineralization adjustment, for urea and EEF blends.

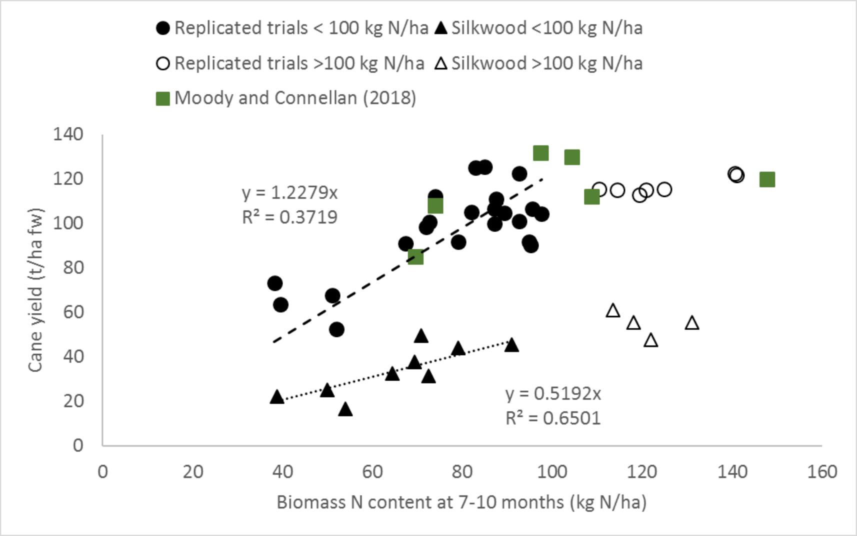

Figure 1. Relationship between biomass-N content of sugarcane crops in all experiments in 2017 and 2018 and cane yields harvested in that growing season. Data have been pooled for the Burdekin and both Tully replicated experiments and contrasted with data from the Silkwood strip trial. Individual trial data from the Burdekin (Moody and Connellan 2018) are shown on this figure for sites where cane yields were <140 t/ha.

It is interesting to note the similarity between the findings from the Tully and Burdekin sites from this study, and those reported by Moody and Connellan (2018) for sites in the Burdekin. The trial data points from Moody and Connellan (2018) for crop yields <140t/ha (slightly above the best recorded in our Tully and Burdekin trials) have been added to Figure 1, and there is clear overlap between these data sets. The pooled data continue to suggest that above-ground N content >100-110 kg N/ha did not necessarily result in higher cane yields, and when a pooled regression was fitted to all data (excluding Silkwood) for crop-N <110 kg N/ha the slope was effectively unchanged ($y = 1.2297x$; $R^2 = 0.44$), as was the calculated 0.81 kg biomass-N/t cane requirement. Moody and Connellan (2018) have suggested an additional 15% of the measured above ground biomass N is sequestered below ground in the stool and shallow roots of the cane crop, and so applying this adjustment, the combined data would suggest the crop needs to acquire 0.94 kg N to produce each t of cane yield.

Efficiency of recovery and use of fertilizer-N

The size of the cane yield response to applied N and the efficiency with which that applied fertilizer was used to produce additional cane yield (AgronEff_N) are shown for the 2017 and 2018 harvests at all sites in Table 2. Consistent with the lack of statistically significant differences in cane yields (Table 2), there was a similar agronomic response to applied N in terms of additional cane produced (Table 3), although the size of that response varied between seasons in the Burdekin (e.g. an average 55 t/ha yield increase in 2017 versus 21 t/ha in 2018) and to a lesser extent at the well-drained Tully site (an average 48 t/ha yield increase in 2017 versus 36 t/ha in 2018). The reasons for these trends were quite different, with the reduced N response in 2018 in the Burdekin due to a higher yield without applied N (92 t/ha versus 64 t/ha in 2017), while at the well-drained Tully site the yields without N were similar in both seasons (73 versus 68 t/ha), but the average yield with applied N was substantially lower in 2018 (103 t/ha) than in 2017 (121 t/ha) (Table 2).

Table 3. Agronomic responses in cane yields and crop-N uptake from the fertilized treatments at each site. Data are used to derive indices of AgronEff_N and NUpE for the different fertilizer-N treatments.

Location	Year	Agronomic response to fertilizer-N t cane/ha (kg N applied/t extra cane yield)					Apparent fertilizer-N uptake kg fertilizer-N/ha (% applied N)				
Burdekin		200N, urea	150N, urea	150N, EEF	170N, urea	*LSD (0.05)*	200N, urea	150N, urea	150N, EEF	170N, urea	*LSD (0.05)*
	2017	58.1 (3.4)	51.6 (2.9)	59.0 (2.5)	51.8 (3.3)	*ns (0.5)*	52.5 (26%)	26.1 (17%)	52.2 (35%)	22.0 (13%)	*27.3 (0.19)*
	2018	23.5 (10.0)	14.7 (11.4)	23.8 (7.6)	21.0 (14.1)	*ns (ns)*	41.8 (21%)	16.6 (11%)	45.7 (31%)	40.2 (24%)	*19.3 (11.9)*
Tully, well drained		150N, urea	150N, EEF	170N, urea	120N, EEF	*LSD (0.05)*	150N, urea	150N, EEF	170N, urea	120N, EEF	*LSD (0.05)*
	2017	49.3 (3.0)	52.0 (2.9)	52.3 (3.3)	39.0 (3.1)	*ns (ns)*	54.5 (36%)	44.8 (30%)	46.8 (28%)	35.8 (30%)	*ns (ns)*
	2018	32.5 (4.6)	36.8 (4.1)	39.1 (4.4)	37.3 (3.2)	*ns (ns)*	36.2 (24%)	46.6 (31%)	36.2 (21%)	38.4 (32%)	*ns (ns)*
Tully, poorly drained		120N, urea	120N, EEF	170N, urea	90N, EEF	*LSD (0.05)*	120N, urea	120N, EEF	170N, urea	90N, EEF	*LSD (0.05)*
	2017	45.7 (2.6)	37.6 (3.2)	48.3 (3.5)	39.3 (2.3)	*ns (ns)*	20.0 (17%)	43.2 (36%)	40.7 (24%)	42.8 (48%)	*18.4 (16.3)*
	2018	36.9 (3.6)	41.6 (2.8)	47.4 (3.5)	27.5 (3.2)	*ns (ns)*	33.2 (28%)	42.5 (35%)	48.0 (28%)	27.8 (31%)	*ns (ns)*
Silkwood		100N EEF blend	100N urea	160N EEF blend	160N urea		100N EEF blend	100N urea	160N EEF blend	160N urea	
	2017	-	15.7 (6.4)	39.0 (4.1)	27.5 (5.8)	*na*	-	30.5 (31%)	74.6 (47%)	31.9 (20%)	*na*
	2018	20.2 (5.0)	18.7 (5.4)	30.1 (5.3)	22.3 (7.2)	*na*	41.0 (41%)	29.0 (29%)	68.0 (43%)	72.0 (45%)	*na*

Given the similarity in cane yields between fertilizer treatments at each site, differences in AgronEff_N among treatments (only significant in the Burdekin site in 2017) were due primarily to N rate (i.e. similar yield responses from lower N rates). However, there did seem to be situations where this reduced rate effect on AgronEff_N was at least countered, if not reversed, by a constrained crop yield response when N rate was below the optimum. For example, reducing the urea N rate from 160 kg N/ha to 100 kg N/ha at Silkwood in 2017 (a 37.5% reduction) was accompanied by 43% reduction in the cane yield response to applied N and a slight increase in AgronEff_N. Similarly, the reduction in EEF N rates from 150 to 120 kg N/ha (20%) in the well-drained site at Tully in 2017, and from 120 to 90 kg N/ha (25%) at the poorly drained site in 2018, resulted in reductions in the cane yield response to applied N of 25% and 34%, respectively and slight increases in AgronEff_N. There was substantial variation in AgronEff_N between seasons and among sites, with the AgronEff_N ranging from a relatively efficient 2.5-3.0 kg N applied/tonne additional cane produced (in the Burdekin and the poorly-drained Tully site in 2017) to a relatively inefficient 6.0-7.0 (Silkwood) to 11.0-14.1 (Burdekin 2018) kg N/additional tonne of cane produced. These site and seasonal differences in AgronEff_N did not appear to be related to site differences in fertilizer-N application rates, or to the amount of fertilizer-N recovered by crops (Table 3).

The average apparent fertilizer-N uptake by crops ranged from 36-53 kg N/ha, with only small differences (<10 kg N/ha, and often much less) between seasons at each site (Table 3). The greatest apparent N recovery was at the Silkwood site (an average NUpE of 36% of applied N), which was consistent with what appeared to be very low N availability and consequent strong fertilizer-N responses recorded at that site (Tables 2 and 3). Within sites, the NUpE of the EEF blend was often significantly greater than that for the equivalent rate as urea, with the instances where this occurred most commonly representing situations where waterlogging and high N-loss situations would be expected (e.g. the flood-irrigated Burdekin site, the poorly drained Tully site, and Silkwood in the 2017 season).

The contrasting NUpE of urea-N at the Silkwood site provides an interesting insight into the importance of the timing and quantity of rain (and hence the potential for fertilizer-N loss) in the period following fertilizer application. In the 2017 crop, N was applied in early December 2016, and in the following 3 months there was a total of 1570 mm of rainfall, with over 710 mm falling in January 2017. By contrast, much less total rainfall (960 mm) fell in the 3 months following the late November fertilizer application in the 2018 crop, with the first large falls and major runoff not occurring until 2 months after fertilizer application. The higher rainfall and greater N loss risk for urea experienced in the 2017 crop was consistent with the poor N recovery in the 160N urea treatment (NUpE of only 20%), with both urea treatments only able to provide about 30 kg/ha of crop-N. In the 2018 crop, the relatively drier period after fertilizer application allowed much greater crop-N recovery in the 160 kg N-urea treatment and NUpE as high as 45%.

Despite this clear demonstration of the vulnerability of urea-N to environmental losses in the contrasting seasonal conditions at Silkwood, the NUpE of the EEF blend at 160 kg N/ha was relatively unaffected at 43% and 47% in 2017 and 2018, respectively. The lower rate of the EEF blend also provided NUpE benefits relative to urea in the 2018 crop – the only time that contrast was present. This consistency of EEF blend performance in terms of fertilizer NUpE was also evident across both seasons in the Burdekin and similarly at both sites at Tully, with the exception of the inexplicably poor performance of the 90 kg N/ha rate in the poorly drained site at Tully in 2018.

Water-quality implications from reduced N rates and EEF use

The combination of crop yields that were often unresponsive to increasing N rate, and apparent crop recovery of applied N that was similar across most of the N rates tested (with some notable exceptions), suggests that the amount of remnant fertilizer-N vulnerable to environmental losses should fall with falling N rates. Similarly, the consistently greater NUpE recorded for EEFs in higher loss situations (Table 3) suggests that losses from the EEF blend would be expected to be less than for conventional urea. Our data from the Silkwood site for the 2018 crop season (Fig. 2) were only partly consistent with these hypotheses. The combined DIN loss from runoff and drainage for the 100 kg N/ha application rate was only 25% of the loss recorded at 160 kg N/ha (i.e., 5.1 kg DIN/ha compared with 20.0 kg DIN/ha), and at the 100 kg N/ha application rate, the EEF blend produced only 42% of the combined losses from the same rate as urea. However, there was a clear anomaly that occurred in the EEF treatment applied at 160 kg N/ha, due to unexpectedly large runoff DIN losses.

Sequential soil sampling showed that significantly higher mineral N concentrations were maintained in the fertilized topsoil layers in the EEF160 treatment, compared to the equivalent rate of urea N, for a period from 50-150 days after fertilizer application (data not shown). While this behaviour was consistent with the objectives of having a controlled-release N fertilizer that released N in synchrony with crop-N demand, the reason for the elevated runoff losses that occurred over this period was consistent with high NO_3-N concentrations in topsoil layers. While this may have been associated with high water tables and limited N redistribution into deeper layers at this site, it was also consistent with inappropriate placement of the fertilizer in the soil profile. At the time of fertilizer application in November 2017 there was visible evidence of a failure to close the slot after the stool split fertilizer application. As a consequence, the more gradual release of mineral N from the controlled release granules provided a continual renewal of soil mineral N in a position that was vulnerable to runoff loss in each subsequent rainfall event.

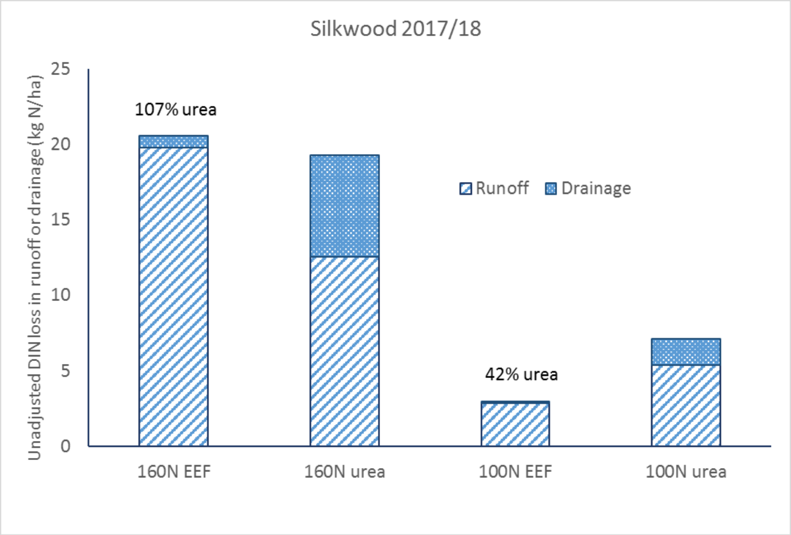

Figure 2. Measured losses of dissolved inorganic Nitrogen (DIN) in runoff and deep drainage at the Silkwood site for the third-ratoon crop harvested in the 2018. Values represent total DIN losses and cannot solely be attributed to fertilizer application, as the Nil N treatment was not able to be monitored to determine background DIN loads.

It is interesting to note that the higher DIN runoff losses from the 160N EEF treatment were almost totally compensated for by elevated drainage losses from the equivalent rate of urea. This would have been consistent with rapid mineralization and generation of nitrate-N in the urea treatment, which was rapidly moved (in runoff or deep drainage) from the vulnerable topsoil layers. Collectively, these data illustrate the critical importance of appropriate N application strategies, in addition to choice of appropriate rates and products, if N-use efficiency and water quality are to be improved.

SUMMARY AND CONCLUSIONS

This paper reports the first results from a subset of the sites established in the National Environmental Science Program and will be the precursor to the more extensive assessment of the performance of combinations of reduced N rates and use of new N fertilizer technology in the Reef Trust 4/EEF60 program. However, while these results are at an early stage of the trial program, they do illustrate important factors that need to be considered in any rationalization of fertilizer-N management in the sugar industry.

Firstly, for crops ratooning after second or final harvesting rounds, the apparent NUpE of applied urea N is poor (typically <30%, and sometimes <20%). Fortuitous combinations of delayed or low intensity rainfall for an extended period after fertilizing can sometimes moderate losses and result in improved NUpE, but it would be impossible to predict these occurrences with sufficient certainty to influence a fertilizer decision.

Secondly, a blend of EEF fertilizer products is providing higher NUpE and a more consistent supply of available N to the sugarcane crop than occurs with urea. This improved NUpE is only rarely reflected in greater crop yields relative to the same rate of urea, although when these situations occur (typically in conditions conducive to large fertilizer-N losses), the yield benefits may be substantial.

Thirdly, the combination of EEF fertilizers and lower fertilizer-N rates offer real potential for reducing the loss of DIN in runoff and drainage. However, this will not happen (and in fact runoff losses may be exacerbated) unless fertilizer is placed well below the soil surface and there is adequate closure of the fertilizer slot to minimize off-site losses. There have already been discussions about the need to ensure effective soil cover of both fertilizers and pesticides applied in-crop, and there is tillage equipment currently being evaluated that should reduce the risks of losses in such situations. However, the extent of inadequate fertilizer trench closure has not been determined, and there would appear to an urgent need to conduct regional surveys after the main fertilization periods to quantify the extent of this problem.

Finally, the research has not been running for long enough to make any firm conclusions about fertilizer rates. There are suggestions that reducing rates to match PZYP in either low or higher yielding situations will be a greater productivity risk when the fertilizer used is urea, but that switching to a blend of EEF products will mitigate that risk somewhat by improving the NUpE and ensuring greater crop-N contents. There is an emerging relationship between crop-N content at 7-10 months and final cane yield that may prove to be a useful guide to the quantum of N required in different productivity zones. The challenge is to maximize the chances of the crop acquiring the N it needs, and the best opportunity to do this lies with rapidly improving EEF technology.

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APPENDIX 2: FIRST PAPER PUBLISHED FROM THE LABORATORY STUDIES ON BANDED N FERTILIZERS

Biochemical effects of banding limit the benefits of nitrification inhibition and controlled-release technology in the fertosphere of high N-input systems

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Abstract. Enhanced efficiency fertilisers (EEFs) may have an important role in improving nitrogen (N) use efficiency in agricultural systems. The performance of EEFs when applied by broadcasting and incorporation is well documented; however, little information is available for sub-surface banded N-fertiliser. This study aimed to determine the effectiveness of EEFs within the fertosphere in several soils. This was determined by: (i) establishing the key chemical effects and N-transformation activity within a urea band, and (ii) contrasting these findings with nitrification inhibitor (NI)-coated urea and a controlled-release polymer-coated urea (PCU). A 112-day incubation experiment was conducted with the EEFs band-applied in three contrasting soils with a history of sugarcane production. In standard urea and NI-urea treated soils, the pH within the fertosphere significantly increased to a maximum of ~pH 9.2–9.3. Alkaline conditions and high ammonium concentrations promoted elevated aqueous ammonia concentrations, resulting in complete nitrification inhibition. The PCU granules released ~40% of total urea content within 14 days, followed by subsequent release at significantly lower rates. The initial rapid urea release was attributed to damaged polymer coats, while close proximity of neighbouring granules within the band may have contributed to the subsequent slower release phase through reduced concentration gradients and restricted diffusion from granules. Variation between soils suggests that soil properties such as clay content and pH buffer capacity may influence urea hydrolysis, but not nitrification. These results suggest that both NI and controlled-release technology may not have the expected impacts on N transformations and availability when applied in a concentrated band.

Additional keywords: fertiliser, nitrogen, nitrification inhibitors, polymers, soil fertility.
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Introduction

Improving nitrogen (N) use efficiency (NUE) in agricultural production systems has become increasingly important, with widespread reports of the detrimental effects of N lost from agricultural activities to the wider environment, including groundwater and aquatic ecosystems, forest ecosystems, coastal marine ecosystems, and atmospheric composition (Hatfield and Follett 2008). In climates and agricultural systems where N-fertiliser losses are exacerbated by surface application and/or where zero tillage systems limit the opportunities to incorporate broadcast fertiliser into soil, N-fertiliser may be applied as a sub-surface band at/or before planting or by side-dressing during the growing season

(Passioura and Wetselaar 1972; Creamer and Fox 1980; Zebarth *et al*. 1999; Bell *et al*. 2014; Raczkowski *et al*. 2016; Zou *et al*. 2017).

Banding of fertiliser N is critical to the sugarcane industry in tropical and sub-tropical regions of Queensland, Australia, where high crop residue loads on the soil surface, high temperatures, and high rainfall can result in substantial N losses following surface application of fertiliser (Prammanee *et al*. 1989; Denmead *et al*. 1991). Granular urea is typically applied as a sub-surface band at ~10 cm below the soil surface, which has the effect of increasing assimilation of fertiliser N into the soil N pool by reducing ammonia ($NH_{3(g)}$) volatilisation losses to the atmosphere and minimising the possibility of off-site loss in surface runoff. Sub-surface banding at planting (plant cane) or by stool splitting after harvest (ratoon crops) also ensures that the position of N is in close proximity to the developing root system of the sugarcane crop. However, in addition to climatic constraints, rapid crop growth limits the opportunities for N-fertiliser application to a single window very early in the growing season (generally less than 3 months after planting or harvest of the previous crop). This fertiliser must meet the N demands of the sugarcane crop, which has a 9–16 month growing season in the Australian sugarcane cropping system.

Enhanced efficiency fertilisers (EEFs) could be a key strategy for improving fertiliser NUE in sugarcane production by synchronising fertiliser N availability with crop requirements, thus reducing the chance of environmental losses by aquatic or atmospheric pathways and providing opportunities to reduce fertiliser application rates. Currently, commercial EEFs encompass a range of technologies with varying properties that generally utilise one of two key mechanisms: controlled release of N from the granule, or stabilisation of N in forms that are less volatile or mobile in the soil profile. Controlled-release fertilisers (CRFs) regulate the rate, pattern and duration of N release under known environmental conditions (Shaviv 2001) through the use of coating materials such as sulfur, wax, and polymers. Release of N from soil-incorporated CRFs is temperature dependent, with granules largely unaffected by wet–dry cycles, pH, and microbial activity (Christianson 1988). In contrast to CRFs, stabilised fertilisers are those that reduce the rate of N transformation at specific steps, regulating the formation of N compounds that may be easily lost. There are two key steps that are widely targeted by stabilising technology – (i) the hydrolysis of urea to ammonium carbonate ($(NH_4)_2CO_3$) by urease inhibitors (UIs) (Andrews *et al*. 1984); and (ii) the oxidisation of ammonium (NH_4^+) to nitrite (NO_2^-) (Robertson and Groffman 2015) by nitrification inhibitors (NIs).

A substantial amount of literature exists on the performance and effectiveness of EEFs in situations where the fertiliser is broadcast and incorporated into soil through tillage, or in incubations whereby the fertiliser treatment is mixed through the soil (Shaviv *et al*. 2003*a*, 2003*b*; Chen *et al*. 2008; Chen *et al*. 2015; Mahmood *et al*. 2017). However, there is little reported research on the effects of EEFs applied in a concentrated band below the soil surface, which is common practice in many cropping industries. Nitrogen fertiliser applied as a band creates a different biochemical environment to fertiliser mixed through soil. Several key effects have been identified in research on banded urea, including elevated pH (Hauck and Stephenson 1965; Pang *et al*. 1973), phytotoxic effects as a result of elevated NH_3 concentrations (Hauck and Stephenson 1965; Passioura and Wetselaar 1972; Creamer and Fox 1980) and the accumulation of NO_2^- (Hauck and Stephenson 1965). In contrast, dilute and/or dispersed urea application is not likely to result in persistent, localised regions of high pH (>8), which reduces the risk of NO_2^- accumulation and NH_3 toxicity to nitrifying organisms, enabling rapid nitrification (Hauck and Stephenson 1965). Thus, there is a substantial contrast in the chemical and biological effects of banded vs dispersed N-fertilisers on the soil solution, and these factors need to be considered in the development of fertiliser products and application strategies.

The laboratory incubation conducted in this study was aimed at determining the impact of contrasting EEF technologies within the immediate zone (soil within 2.5 cm) surrounding banded N-fertiliser (the ‘fertosphere’) in contrast to a granular urea standard. This study does not correspond to conditions likely to be encountered beyond the fertosphere, which is the subject of ongoing investigations. The study quantified the release and hydrolysis of urea from fertiliser granules, and the effects of EEF technologies on key chemical impacts of urea bands, including pH increase, elevated aqueous NH_3 concentrations, accumulation of NO_2^--N, and the subsequent effects on N-transformation activity. The incubation was conducted over 112 days using three soils of contrasting characteristics collected from sugarcane fields, under temperature and moisture conditions typical of sugarcane-growing regions.

Materials and methods

Soil collection, characterisation, and preparation

Soils were collected from the top 10 cm profile layer of sugarcane research sites at Silkwood (GDA94 Zone 55, 17°44′43″S 146°2′55″E – Hydrosol), Homebush (GDA94 Zone 55, 21°15′37″S 149°05′01″E – Sodosol) and Granville (GDA94 Zone 56, 25°32′00″S 152°43′49″E – Dermosol), in coastal Queensland, Australia. Samples were kept cool during transport to the laboratory and stored at 4°C until further preparation. Key soil characteristics are presented in Table 1. Herein, the soils are referred to by their soil order (Isbell 2016). Soil was oven-dried at 40°C, and sieved to <2 mm. The moisture content at field capacity for each soil was determined using the column method described in Asher *et al*. (2002).

Incubation experiment

Oven-dried (40°C) and sieved (<2 mm) soil was added to 50 mL tubes (15 g soil per tube) and the bulk density adjusted to 0.3 cm^3. Soil moisture was subsequently adjusted to pre-determined field capacity levels of 0.29, 0.16 and 0.21 g g^{-1}, for the Hydrosol, Sodosol, and Dermosol respectively. Fertiliser granules were placed onto the soil in the incubation tube at an in-band concentration (27 g N per m of fertiliser band) equivalent to that experienced when 150 kg N ha^{-1} is applied in the field in bands 1.8 m apart, which is typical of application practices in the sugar industry. After fertiliser was applied, a further 15 g soil was added on top, positioning the fertiliser band ~3.25 cm from the soil surface. Bulk density and moisture content for this upper soil layer was adjusted as for the soil at the bottom of the tube.

An unfertilised control and five N-fertiliser treatments were established for each soil type, and are identified as: (i) nil; (ii) standard urea granules; (iii) standard urea granules treated with liquid nitrapyrin (eNtrench™); (iv) 3,4-dimethylpyrazole phosphate (DMPP) coated on standard urea granules (ENTEC®); (v) 3,4 dimethyl pyrazole glycolate (DMPG) coated on standard urea granules with proprietary solvent or wetting agent for improved inhibitor retention on the fertiliser granule; and (6) polymer-coated urea (PCU) granules (Agromaster Tropical®) with an approximate release period of 90 days (determined by the industry standard method of dissolution in water at a constant temperature). Where nitrapyrin was used in Treatment (iii), eNtrench™ (nitrapyrin conc. of 17.79%) was applied at a rate equivalent to 2.5 L ha^{-1} (3.33 mg nitrapyrin g N^{-1}), as per label instructions. The quantities of DMPP and DMPG applied with an N rate of 150 kg N ha^{-1} are equivalent to 600 g ha^{-1} (2.16 mg DMPP g N^{-1}), and 254 g ha^{-1} (0.92 mg DMPG g N^{-1}) respectively. Tubes were capped with lids containing three small holes for aeration and incubated at 30°C for 112 days. A beaker containing water was placed in the incubator to maintain humidity and minimise moisture loss from the incubation tubes, and soil moisture was manually adjusted by weight fortnightly. Data were collected by destructively sampling incubation tubes at 7, 14, 28, 56, 84, and 112 days. All treatments were in triplicate, and incubation tubes were rotated weekly in the incubator to minimise any effects of temperature or humidity gradients.

pH and electrical conductivity experiment

Syringe tubes (50 mL; i.d. 3 cm) were utilised for measurements of pH and electrical conductivity (EC), with soil and N-fertiliser treatments established in a similar fashion to that for the 50 mL incubation tubes. These tubes had the top end removed, plunger fully drawn and were sealed using parafilm with three pin-holes. Moisture of soil in these tubes was adjusted as for the incubation tubes. At the requisite sampling times, soil was placed in beakers and DI water added to achieve a ratio of 1 : 5 (w/v) soil : water. Separate probes were used to measure EC, followed by pH, with stirring for both measurements (Rayment and Lyons 2010). The samples for pH and EC analysis were collected only on Days 7, 27, and 112.

Table 1. Chemical and physical characteristics of soils used in the incubation assays. Values were determined before incubation experiment pH refers to 1 : 5 (soil : water) measurement; PSA, particle size analysis; pHBC, pH buffering capacity; EC, electrical conductivity; eCEC, effective cation exchange capacity; TN, total nitrogen; TOC, total organic carbon

Order[A]	Location	Colour	PSA (%)				pH	pHBC (cmol (+) g^{-1} soil pH $unit^{-1}$)	EC (dS m^{-1})	eCEC ($cmol_c$ kg $soil^{-1}$)	TN (%)	NO_3^--N (mg kg $soil^{-1}$)	TOC (%)
			Coarse sand	Fine sand	Silt	Clay							
Hydrosol	Silkwood	Dark, poorly-draining	11	33	20	35	5.40	0.223	0.03	1.82	0.28	7	4.87
Sodosol	Homebush	Hard-setting brown-yellow	17	45	26	16	5.25	0.068	0.06	4.17	0.09	19	1.26
Dermosol	Granville	Brown-grey	17	36	32	23	6.68	0.089	0.14	9.89	0.09	4	1.08

[A] Isbell (2016).

Nitrogen extraction

Extraction of mineral N followed standard methods (Rayment and Lyons 2010), using a 1 : 5 (w/v) ratio with 2 M KCl. After thorough mixing to ensure even suspension of soil in solution, a sub-sample of 5 mL was taken from the 1 : 5 soil-2 M KCl slurry before extraction and 10 µL of urease inhibitor (0.0072 M Ag_2SO_4) was added to stabilise urea-N (Lambert *et al*. 2004). Both soil-N extraction and urea-N extraction (5 mL sub-sample with urease inhibitor) solutions were shaken end-over-end for 1 h. A 10 mL aliquot was taken from the soil-N extraction solution and centrifuged at 1760 ×*g* for 9 min, followed by pouring off and re-centrifuging of the supernatant. Organic material on the solution surface was removed with vacuum suction. A 2 mL aliquot of the 5 mL urea-N extraction subsample was filtered to 0.45 micron, and subsequently frozen until analysis. The 10 mL aliquot (without urease inhibitor) was used to determine NH_4^+-N (Searle 1975), NO_2^--N and NO_x^--N (Best 1976; Bremner 1965) by segmented flow analysis (SFA). Urea-N concentrations were determined by ultraviolet HPLC (HPLC-UV) (MicroSolv 2010) from the 5 mL subsample with urease inhibitor. Soil-N and urea-N extraction data were collected at 7, 14, 28, 56, and 84 days.

At each sampling time, recoverable PCU granules were removed from the soil before extraction. These granules were counted, weighed, crushed, and dissolved in 10 mL DI water. Urease inhibitor (10 µL 0.0072 M Ag_2SO_4) was added to samples to inhibit urease activity (Lambert *et al*. 2004), and full dissolution of residual urea in the granules was achieved by end-over-end shaking for 1 h. Samples were frozen until analysis by HPLC-UV.

Ammonia ($NH_{3(g)}$) and nitrogen gas sampling

An additional set of all fertiliser–soil combinations in triplicate was placed in sealed 50 mL centrifuge tubes. An $NH_{3(g)}$ trap of 10 µL 5M H_2SO_4 on filter paper (6 mm diameter) was suspended with a stainless-steel wire at the top of the tube (Brooks *et al*. 1989). A single trap containing 10 µL 5 M H_2SO_4 permits a maximum of 1400 mg N to be captured; weekly recovery of gaseous N from H_2SO_4 traps did not exceed 1.6 mg N, indicating a lack of saturation in single measurement period. In the N-fertiliser treatments, it was assumed that the predominant N gas form was $NH_{3(g)}$ as nitrification and denitrification processes, which produce other forms of gaseous N, were negligible. In control treatments, the total N detected in traps may comprise a combination of $NH_{3(g)}$ and trace amounts of nitrous oxide (N_2O) (Nunn 1958), a minor by-product of aqueous NH_3 oxidisation in the nitrifying process which was active in these soils, although the specific N forms ($NH_{3(g)}$ or N_2O) were not identified. The $NH_{3(g)}$ and total gaseous N (control values) data allow general inferences on patterns of $NH_{3(g)}$ volatilisation and gaseous N emissions with respect to soil type and N-fertiliser treatment. Filter paper traps were removed and replaced weekly, with the removed traps placed immediately into sealed vials. Analysis was conducted by combustion (TruMac CN) of samples using high temperature and a pure oxygen stream, with N content being determined by detection of N_2 gas, reduced in a Cu-catalyst tube (Yeomans and Bremmer 1991; Rayment and Lyons 2010; LECO Corporation 2011). Ammonia and gaseous N emission data were collected from 7 through to 99 days.

Data transformation and statistical analysis

Data from SFA are expressed as mg N kg soil^{-1}. Concentrations of NO_3^--N were determined by calculating the difference between NO_x^--N and NO_2^--N (Best 1976; Bremner 1965). Urea-N values from HPLC-UV analysis were reported as mg N kg soil^{-1} (1 : 5 w/v extraction ratio), and were accordingly converted to the percent total of applied urea-N.

Nitrogen values from combustion analysis of $NH_{3(g)}$ traps were reported as percent N of the total mass of the filter paper traps, and were converted to total $N_{(g)}$ captured (mg) per kg soil over a 7-day period. The background N of filter paper was subtracted from all reported values.

Ammonia (aqueous NH_3) concentrations were calculated by applying the pK_a value of the $NH_4^+ \rightleftharpoons NH_3$ reaction at 30°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 (Erickson 1985). Concentration values were expressed as mg NH_3 kg soil^{-1}.

Values for pH were arithmetically averaged from triplicate samples, and this was checked against the geometrical mean of H^+ concentrations to ensure correct interpretation (Boutilier and Shelton 1980). The EC values were likewise averaged from three replicate samples.

Statistical analysis of urea-N, NH_4^+-N, NO_2^--N, NO_3^--N, NH_3, and $NH_{3(g)}$ values involved a two-way ANOVA for time and N-fertiliser treatment effects, within each soil type. Statistically significant differences were assessed using Tukey honest significant difference (HSD) testing between pairs of means within each soil type ($P < 0.05$). A subsequent three-way ANOVA for the effect of soil type, time, and N-fertiliser treatments on urea-N, NH_4^+-N, NO_2^--N, and NO_3^--N values was conducted, with post-hoc Tukey HSD pairwise comparison determining significant differences between soil types ($P < 0.05$). Control values were omitted from the three-way ANOVAs to avoid misinterpretation of overall soil effects on the N-fertiliser treatments. The impact of treatment on pH and EC was determined by two-way ANOVA for time and N-fertiliser treatment, within each soil type. Statistically significant differences were assessed using Tukey HSD testing between pairs of means within each soil type ($P < 0.05$). Inter-soil analysis for pH and EC was conducted in a three-way ANOVA, with control values omitted, and post-hoc analysis using the Tukey HSD method ($P < 0.05$).

Significant interaction effects from two-way and three-way ANOVAs were not included in the results and discussion, as significant variation over time was expected and provides little clarity in answering research questions. Soil effects were best determined by individual factor results from the three-way ANOVA, and thus were not considered in interaction effects in two-way and three-way ANOVA results.

Results

Due to similarity of results and for conciseness of reporting, not all soils are presented in every dataset within the manuscript; a complete dataset for all soils is provided in the Supplementary material, available on request.

Detection of fertiliser-derived urea-N in soil

Urea-N concentrations in soil solution from fertiliser treatments varied greatly over time and also differed significantly between soil types (Fig. 1). In all soils, recovery of urea-N was higher in the urea and NI-urea treatments than PCU over the first 27 days after incubation initiation (DAI), after which urea-N represented <0.02% of applied N. In the Sodosol there was still a substantial proportion of fertiliser N as urea at 27 DAI, ranging from ~30% in the NI treatments to 37% in soil treated with standard urea granules. In the PCU treatment, urea was recovered up to 84 DAI although quantities were very low in all soils.

The recovery of applied N-fertiliser as urea was greatest in the Sodosol (12%) when compared with the Dermosol and the Hydrosol (both 2%).

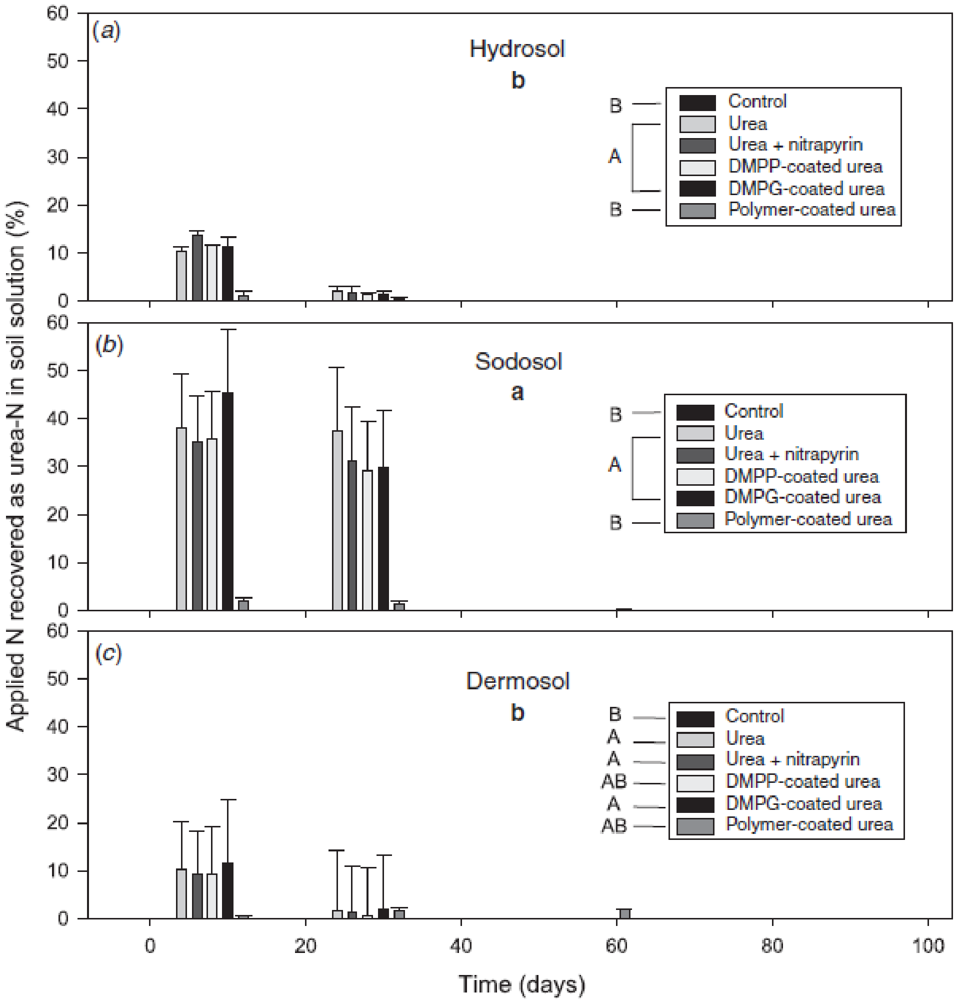

Fig. 1. Applied N recovered as urea-N (%) from 2 M KCl extraction of N-fertiliser treatments in (*a*) Hydrosol, (*b*) Sodosol, and (*c*) Dermosol. Capital letters show significantly different means of overall urea-N release from the N-fertiliser treatments. Lowercase letters note the significant variation in average urea-N release between the soil types, using post-hoc Tukey HSD analysis ($P < 0.05$). Error bars indicate the standard error of the mean.

Recovery of urea-N from PCU

Urea in the standard urea and NI-urea treatments was completely dissolved with no granules present at 7 DAI in all soils. However, granules of PCU could be recovered for the entire duration of the incubation (112 DAI). Over time, PCU granules became transparent and swollen, and ‘cracked’ shells were observed. At 7 DAI, up to 43% of the urea-N was released from PCU granules in the Hydrosol, 40% in the Sodosol, and 34% in the Dermosol (Fig. 2). Little urea-N was released over the following 7 days but by 27 DAI ~60% of applied urea-N had been released from the PCU granules in the Hydrosol and Sodosol. Only 54% of urea-N had been released into the Dermosol at 27 DAI (Fig. 2). At the end of the incubation (84 DAI) urea-N release from PCU granules was similar in all soils at ~82%. There was no significant effect of soil type on urea-N release from PCU granules; however, time had a significant effect, with large volumes of urea-N released within the first 14 DAI, compared with later stages of the incubation. After 14 DAI, the release of urea-N from PCU granules was generally linear (Fig. 2).

Subsequent transformation activity on N

Concentrations of NH_4^+-N were elevated (above control values) in all soils treated with N-fertiliser, with a gradual decline over the duration of the incubation (Fig. 3*a*, Fig. S1, available as Supplementary material). In contrast, the concentration of extractable NH_4^+-N increased in untreated soils over the 84-day incubation.

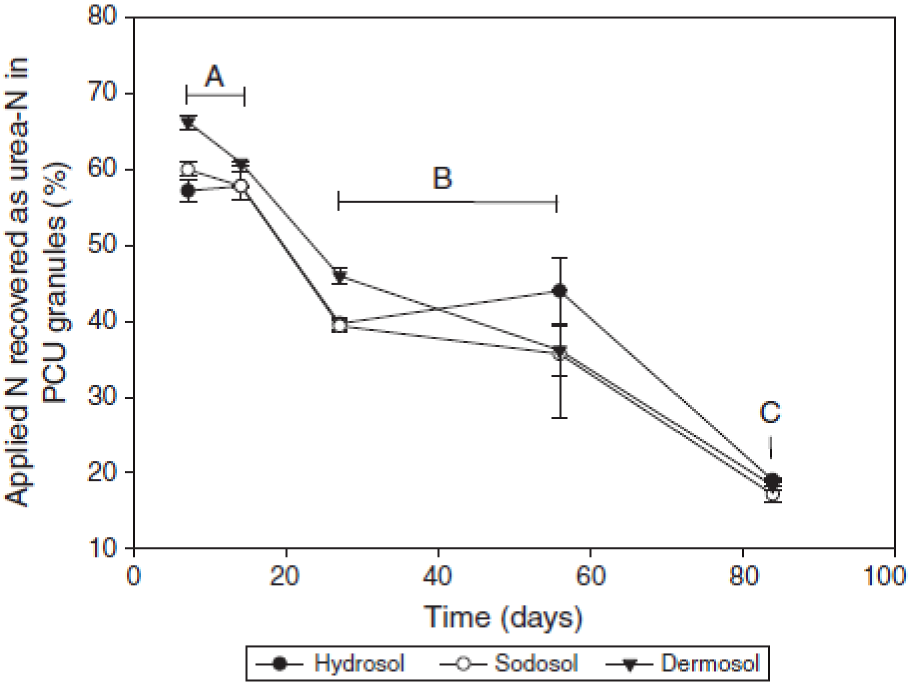

Fig. 2. The retention of urea in PCU granules (% of applied urea-N) in a Hydrosol, Sodosol, and Dermosol Capital letters indicate the statistically significant variation of recoverable urea-N over time as determined by post-hoc Tukey HSD analysis ($P < 0.05$). The different groupings (A, B, and C) correspond to Phases 1, 2, and 3 of urea-N release.

Within each soil type, concentrations of NH_4^+-N did not vary significantly between urea and NI-urea treatments over time. However, in the Hydrosol (Fig. 3) and Dermosol (Fig. S1*b*), PCU-treated soil demonstrated an increase in NH_4^+-N concentration up to ~27 DAI before plateauing. In the Sodosol (Fig. S1*c*), the PCU treatment exhibited a sustained, gradual increase in NH_4^+-N concentration over the duration of the incubation. At 84 DAI, concentrations of NH_4^+-N were not significantly different within soils treated with urea, NI-urea, and PCU (Figs 3, S1).

Accumulation of NO_2^--N was not apparent in this incubation with detected NO_2^--N concentrations in the range of 0–30 mg N kg^{-1} for all soils (Fig. 3*b*). Some statistically significant variation between treatments was observed in the Dermosol (Fig. S1*b*) and Sodosol (Fig. S1*c*); however, relative to concentrations of NH_4^+-N, these differences were small.

Formation of NO_3^--N was significantly inhibited in all soils treated with banded N-fertiliser, with no significant variation between the N-fertiliser treatments or soil types (Figs 3*c*, S1). There was an increase in NO_3^--N over the duration of the incubation in untreated soils, and no significant differences between the soil types (Fig. S1). Final NO_3^--N concentrations in control soils ranged from 830 mg N kg^{-1} (Sodosol) to 900 mg N kg^{-1} (Hydrosol) and 955 mg N kg^{-1} (Dermosol) (Figs 3*c*, S1).

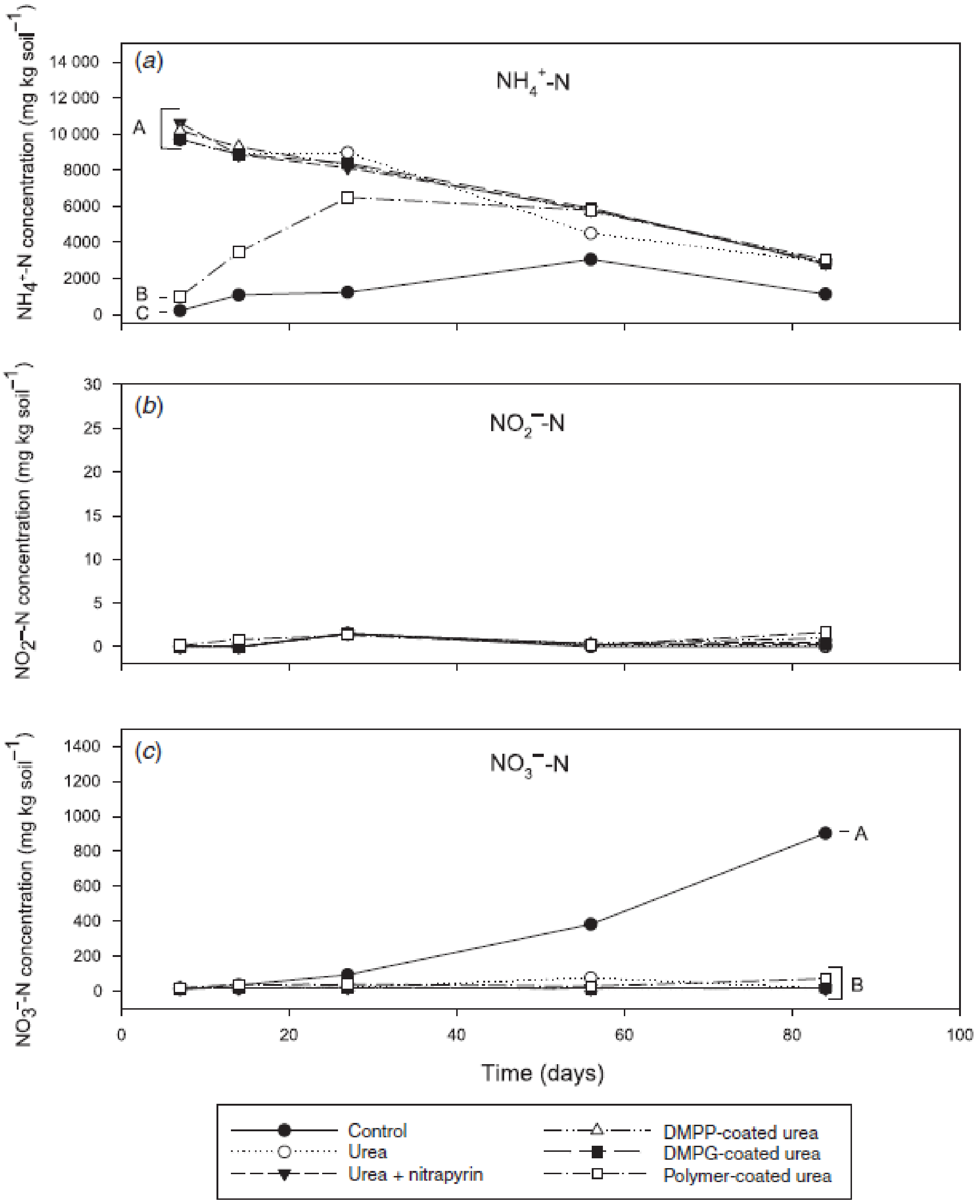

Fig. 3. Nitrogen species profile, including (*a*) NH_4^+-N, (*b*) NO_2^--N, and (*c*) NO_3^--N, of N-fertiliser treatments over time in the Hydrosol. Capital letters indicate statistically different groups of N-fertiliser treatments tested within each N species over the duration of the incubation by post-hoc Tukey HSD analysis ($P < 0.05$).

Against a backdrop of negligible and unchanged aqueous NH_3 concentrations in all control soils, effects of fertiliser addition were significant and dynamic (Figs 4*a*, S2). Soil solution NH_3 concentrations increased significantly in all soils for the first 14 DAI following application of urea and NI-urea treatments (Figs 4*a*, S2), after which aqueous NH_3 concentrations decreased but remained higher than control values for the duration of the incubation. The PCU differed from the other fertilised treatments in that formation of NH_3 was delayed by ~14 days, at which point aqueous NH_3 concentrations steadily increased and either plateaued (in the Sodosol and Dermosol) or slowly decreased (Hydrosol) in the later stages of the incubation. Significant differences in aqueous NH_3 concentrations over time were observed up to 56 DAI in both the Hydrosol and Dermosol: urea and NI-urea treatments > PCU > control. After 56 DAI, aqueous NH_3 was higher in the PCU treatment compared with urea and NI-urea in these soils (Figs 4*a*, S2). Whilst a similar trend was evident in the Sodosol (Fig. S2), aqueous NH_3 concentrations for the NI-urea treatments were intermediate and not statistically different to either the urea or the PCU treatments up to 56 DAI. Significant variation in aqueous NH_3 concentration was seen between all the treated soils, with the highest overall mean concentration reported in the Hydrosol (1290 mg NH_3 kg^{-1}), followed by the Dermosol (990 mg NH_3 kg^{-1}), and then the Sodosol (650 mg NH_3 kg^{-1}) (Fig. S2).

There was significantly more $NH_{3(g)}$ volatilised from soils treated with N-fertilisers compared with the untreated soils (Figs 4*b*, S3), with no significant variation between N-fertiliser treatments over the duration of the incubation. Average weekly $NH_{3(g)}$ emissions varied significantly between treated soil types over the incubation period with the Sodosol (0.94 mg $NH_{3(g)}$ kg $week^{-1}$) > the Dermosol (0.81 mg $NH_{3(g)}$ kg $week^{-1}$) > the Hydrosol (0.71 mg $NH_{3(g)}$ kg $week^{-1}$) (Fig. S3).

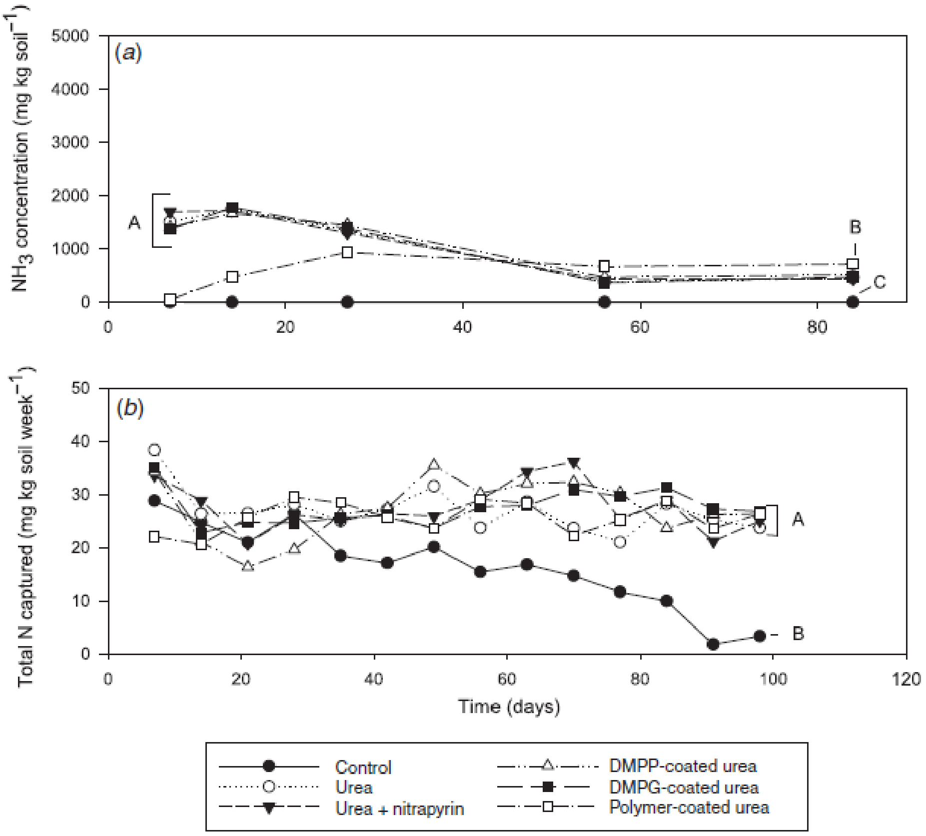

Fig. 4. (*a*) Calculated aqueous NH_3 concentrations from N-fertiliser treatments in the Dermosol. Capital letters show significantly different means of overall NH_3 concentrations corresponding to the different N-fertiliser treatments, using post-hoc Tukey HSD analysis ($P < 0.05$). (*b*) Measured $NH_{3(g)}$ and gaseous N emissions in the Dermosol over time. Capital letters indicate significant difference between N-fertiliser treatments for the duration of the incubation, as determined by post-hoc Tukey HSD analysis ($P < 0.05$).

Changes to soil chemistry

A rapid increase in pH to ~9.2–9.3 occurred by 7 DAI in all soils treated with urea and NI-urea (Figs 5*a*, S4). Soils treated with PCU also demonstrated a pH increase, but at a slower rate and only reached pH 9.2–9.3 at 27 DAI. Untreated soils showed a pH increase to ~27 DAI, and then a drop in pH thereafter (Figs 5*a*, S4). Whilst the pH increase in treated soils was significantly higher when compared with untreated soils, there were no significant differences between N-fertiliser treatments, with this effect consistent across all soil types. The average pH over the duration of the incubation was significantly different between soils, with the Dermosol demonstrating the highest mean pH (9.23), followed by the Sodosol (9.10), and then the Hydrosol (8.93) (Fig. S4).

Over the 112-day incubation, the control soils showed a steady increase in EC (Figs 5*b*, S5). In contrast, the treatments receiving urea and/or NI-urea showed a rapid increase in EC over the first 7 DAI, followed by a steady decrease to EC values less than the control soil by the end of the incubation period. The PCU treatment produced much slower changes in EC and did not achieve the same quantity of EC increase as recorded in the urea and NI-urea treatments. The average EC over the incubation period for the PCU treatment was not significantly different from that of the control treatments, although EC dynamics over that time were quite different (Figs 5*b*, S5). Significant variation between soil types was observed for EC when averaged over the monitoring period, with EC of the Hydrosol (2.72 dS m^{-1}) > the Dermosol (2.38 dS m^{-1}) > the Sodosol (1.37 dS m^{-1}) (Fig. S5).

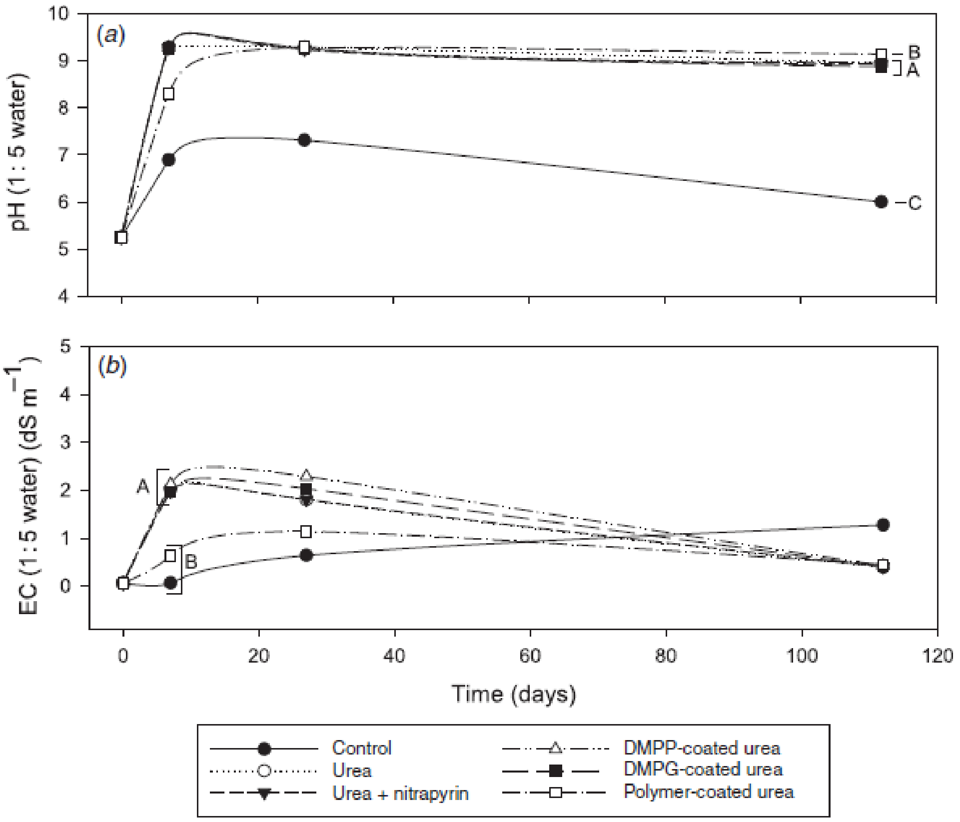

Fig. 5. (*a*) Changes in soil pH (1 : 5 soil : water) in response to banded N-fertiliser addition in the Sodosol. Capital letters show significant effects of N-fertiliser treatments for the duration of the incubation as determined by post-hoc Tukey HSD analysis ($P < 0.05$). (*b*) Mean values of recorded electrical conductivity (1 : 5 soil : water) in the Sodosol over time. Capital letters show significant variation of the overall mean electrical conductivity in response to N-fertiliser treatments, as determined by post-hoc Tukey HSD analysis ($P < 0.05$).

A linear relationship between mineral N (NH_4^+-N plus NO_3^--N) and EC was observed with 96%, 85%, and 95% of the variation in EC explained by changes in mineral N concentration in the Hydrosol, Sodosol, and Dermosol respectively (Fig. 6).

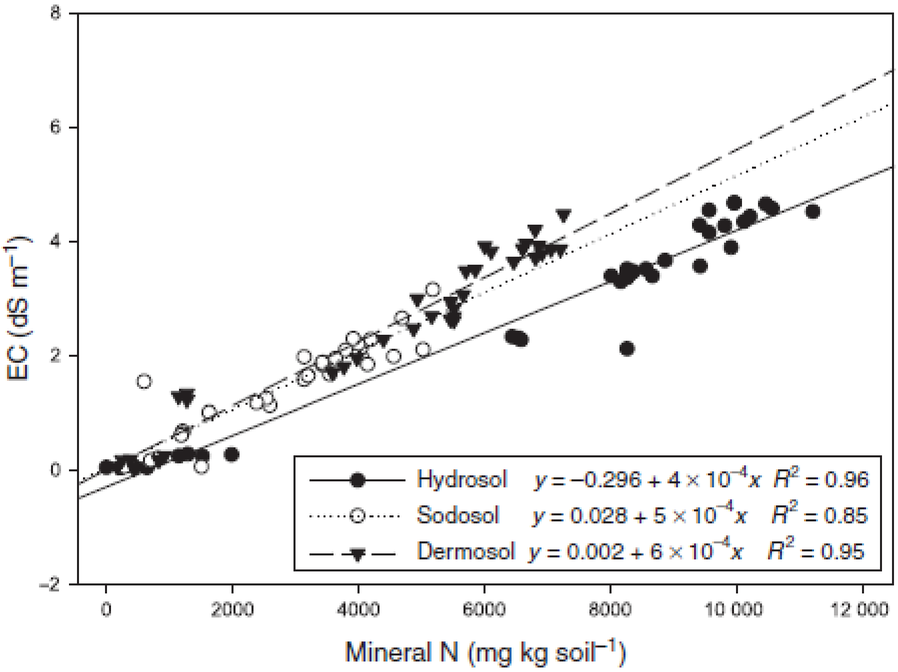

Fig. 6. Correlation of mineral N to electrical conductivity (EC) in 1 : 5 (w/v) soil : water extracts. The R^2 values indicate the proportion of variation that can be explained by the associated equation for each soil type.

Discussion

Fertosphere environment of banded urea

Urea concentrations

In soil where urea fertiliser is dispersed, such as in a mixed or broadcast application, urea-N is typically undetectable after ~2–4 days (Antil *et al*. 1992; Christianson *et al*. 1993). However, in this experiment, all soils treated with banded urea recorded significant amounts of urea-N up to 27 DAI (Fig. 1), indicating that band-applied urea, at high concentrations, produced more urea-N than could be effectively processed by the immediate soil solution. Hauck and Stephenson (1965) concluded that the soil immediately surrounding a dissolving granule must influence the type and rate of transformation processes that initially act on the fertiliser granule, and the subsequent reactions in the wider soil environment. In particular, the activity of urease (urea amidohydrolase) present in soil within the fertosphere is likely to be a key soil constituent influencing the 'processing' capability of soils. Urease is a soil enzyme that facilitates the transformation pathway of urea to NH_4^+. It exists either intracellularly or extracellularly on soil clay and humic phases (Bakshi and Varma 2011). Briefly, urease catalyses reactions between urea and water to form $(NH_4)_2CO_3$, which in turn consumes protons from the soil solution during the formation of NH_4^+. The recovery of substantial concentrations of urea-N up to 27 DAI suggests highly concentrated urea solutions within the fertosphere may have induced substrate saturation to the extent that the enzyme is unable to catalyse urea transformations fast enough. This would result in an extended period of urea-N presence in the fertosphere. This phenomenon has been reported previously in microbial culture incubations (Singh and Nye 1984; Bhat *et al*. 2011), with urease activity increasing with substrate (urea) concentration up to ~20 300 mg urea-N L^{-1} (equiv. 101 500 mg urea-N kg $soil^{-1}$) (Bhat *et al*. 2011), after which further increases in urea-N concentrations actually decrease urease activity. While this value is substantially greater than the highest values recorded in this study (17 500 mg urea-N kg soil^{-1}), the enzyme concentration was likely much higher in the culture study by Bhat *et al*. (2011), permitting higher concentrations of urea before the onset of saturating conditions. Further, the sensitivity of urease to high pH (i.e. > pH 7.0), may reduce the affinity of urease to urea molecules, even at low (5600 mg urea-N L^{-1}; equiv. 28 000 mg urea-N kg soil^{-1}) concentrations (Singh and Nye 1984). The pH observed in this study was consistently above pH 8.0 in N-fertiliser treated soils, in comparison to the Bhat *et al*. (2011) study where the authors note the lack of alkaline conditions.

The capacity of soils to hydrolyse urea may therefore vary according to the potential activity of urease within each soil. While urease concentration was not directly measured, properties such as high clay and organic carbon content, and pH (optimum = 6–6.8 depending on urea concentration) are known to favour urease presence and activity in soil (Singh and Nye 1984; Bakshi and Varma 2011; Bhat *et al*. 2011). The Hydrosol had a considerably higher clay and organic carbon content than the other soils (Table 1) and, similarly, the Dermosol had a higher percent of clay compared with the Sodosol. These properties may have contributed to increased hydrolysis of urea in the Hydrosol and Dermosol as demonstrated by a significantly lower detection of urea for the duration of the incubation compared with the Sodosol (Fig. 1). While the original $pH_{(1:5\ soil:water)}$ of 5.4 in the Vertosol (Table 1) was below the optimum for urease activity, initial urea hydrolysis altered the fertosphere pH very rapidly, suggesting initial pH values of the soils may not greatly influence urease hydrolysis in the vicinity of a urea band. Rather, pH buffer capacity (pHBC), may contribute to higher ureolytic activity, where both the Vertosol and Dermosol had higher pHBC than the Sodosol. Of note, the total organic carbon of the Dermosol (1.08%) was slightly lower than that of the Sodosol (1.26%), indicating that clay content and pHBC may be the dominant factors affecting urea hydrolysis.

Changes in pH

During the incubation period, the $pH_{(1:5\ soil:water)}$ in the unfertilised soils appeared to increase slightly during the first 7–27 days, before dropping to values at or below the starting pH in all soil types (Figs 5*a*, S4). The reason for the initial increase in pH in untreated soils is unknown, but may be due to an initial flush of ammonification that typically follows re-wetting of air-dry soil. This phenomenon was identified in all three soils. The subsequent prolonged drop in pH in all soils is consistent with nitrification (Bloom and Skylberg 2012) and the substantial increase in NO_3^--N over the incubation period in untreated soils (Figs 3, S1).

The pH dynamics that were observed in treatments receiving urea-N were quite different. The chemical reactions that occur during the hydrolysis of urea, as described in detail by Bloom and Skylberg (2012), resulted in the formation of extremely alkaline conditions within the band for the duration of the incubation in urea treated soil (Figs 5*a*, S4). Significant pH increases have been recorded in a range of soils (acid, neutral, and alkaline soils) where urea-N was applied in bands, with the effect being most dramatic near the fertiliser band itself (Pang *et al*. 1973). Hauck (1985) found that in the vicinity of the urea granule, nitrification was inhibited in response to increased pH and subsequent NO_2^- accumulation. Larger granules generated a wider alkalising effect in soil (Hauck 1985), which can be extrapolated to the situation when two or more granules are very close together (Bezdicek *et al*. 1971), such as in a fertiliser band.

Elevated pH to levels of ~9.2–9.3 within the band of urea represents unfavourable conditions for both urease and nitrifying microorganisms. The effect of pH on soil microorganisms is primarily associated with changes to chemical equilibria of NH_4^+ □ NH_3 and NO_2^- □ nitrous acid (HNO_2). Un-ionised aqueous NH_3 and HNO_2 may penetrate cell walls when the extracellular pH is higher (NH_3 toxicity) or lower (HNO_2 toxicity), than intracellular pH (Warren 1962; Erickson 1985; Claros *et al*. 2013). Urease activity is minimal above pH 8.5, with an optimum range of pH 6–6.8 depending on urea concentration (Singh and Nye 1984). Thus, the potential inhibition of urease by substrate saturation (Fig. 1) is magnified by the increased pH in the fertosphere (Figs 5*a*, S4). A negative feedback system for the hydrolysis of concentrated urea-N in soil therefore exists, whereby urea hydrolysis raises soil pH, which subsequently inhibits the hydrolysing enzymes until the pH of soil solution is reduced. *Nitrosomonas*, an important NH_3-oxidising bacterial genus, is reportedly less sensitive to pH changes than nitrite-oxidising bacteria (NOB), and is able to adequately function within a pH range of ~6.5–9.5, with an optimum pH of 8.1 (Grunditz and Dalhammar 2001). Nitrite-oxidising microbes, such as *Nitrobacter*, are more sensitive to elevated pH and can function at pH values in the range of 6.0–9.0, with an optimum of 7.9 (Grunditz and Dalhammar 2001). Thus, high concentrations of NO_2^- may accumulate when the pH is such that the less sensitive ammonia-oxidising bacteria (AOB) are able to function, but NOB are not. In this study, the pH within the fertosphere exceeded optimum levels for both AOB and NOB (Figs 5*a*, S4) and resulted in no net accumulation of NO_2^--N or NO_3^--N (Figs 3, S1).

Changes to soil EC

The EC is a measure of dissolved salt concentration in solution, with values of 4 dS m^{-1} considered saline in soils (Allison *et al*. 1954). High concentrations of soluble salts may affect soil microbes by two primary mechanisms: (1) osmotic effects, and (2) specific ion effects (Yan *et al*. 2015). Concentrations of aqueous NH_3 well above known toxicity thresholds likely induced specific ion effects on soil nitrifying microbes, with the specific toxicity effects of aqueous NH_3 discussed in the subsequent sections. However, EC values of ~4.53 dS m^{-1}, 1.90 dS m^{-1}, and 3.87 dS m^{-1} in urea treated soils by 7 DAI in the Hydrosol, Sodosol (Fig. 5*b*), and Dermosol respectively (Fig. S5), represent a significant increase from control values, likely inducing osmotic pressure on soil microbes. McCormick and Wolf (1980) found the nitrification process was moderately inhibited (10–37% decrease) at an EC of 0.7 dS m^{-1}, whereas McClung and Frankenberger (1985, 1987) identified nitrification inhibition in a range of soils from 8% to 98% in response to salt solutions (with added urea and NH_4^+-N fertilisers) with a threshold of 3–6 dS m^{-1}. The variation in the EC toxicity thresholds to nitrification processes in these studies were likely a result of variability in initial EC values, cation or anion exchange capacities, and tolerances of nitrifying microbes specific to the studied soils. In this study, the inhibitory effect of elevated EC on nitrification may have decreased over the duration of the incubation as EC values declined in urea-treated soils. It is hypothesised that a substantial increase in EC in response to the addition of banded urea-based N-fertilisers may increase salinity within the fertosphere, to levels that induce full or partial inhibition of nitrification. However, the initial and/or continued influence of EC on nitrification could not be quantified in this study, as other inhibiting factors such as elevated pH were confounding, and specific soil type effects in the literature are not well characterised.

Shift in solution NH_3

In addition to elevated pH, high NH_4^+-N concentrations in the fertosphere resulted in the concentration of aqueous NH_3 increasing to levels potentially toxic to nitrifying bacteria (Figs 4*a*, S2). *Nitrosomonas* is inhibited within a range of 10–150 mg L^{-1} aqueous NH_3 (equiv. 50–750 mg NH_3 kg soil), and *Nitrobacter* within a range of 0.1–4.0 mg L^{-1} NH_3 (equiv. 0.5–20 mg NH_3 kg soil) (Anthonisen *et al*. 1976; Suthersan and Ganczarczyk 1986; Bae *et al*. 2001). As noted earlier, high pH will potentially amplify the toxicity effects of the already raised aqueous NH_3 concentrations by creating a pH differential between soil solution and the intra-cellular environment of living organisms. These minimum aqueous NH_3 thresholds suggest that the absence of NO_2^--N and NO_3^--N within the fertosphere of all soils (Figs 3, S1) was not solely an effect of pH on nitrifying organisms, but also of

NH_3 toxicity. These data clearly suggest that banding urea at in-band concentrations similar to those found when 150 kg N ha^{-1} is applied in the field for wide-row crops such as sugarcane will create an inhibitory effect on nitrification within the fertosphere.

Volatilisation of $NH_{3(g)}$

Significant $NH_{3(g)}$ volatilisation (Figs 4*b*, S3) was the predominant end result of the elevated $NH_4^+ \rightleftharpoons$ aqueous NH_3 equilibrium in all soils. These gaseous N losses were the main driver for the decrease in concentrations of NH_4^+-N and aqueous NH_3 over the incubation period. In larger soil volumes (i.e. outside the fertosphere), this loss pathway may not be so active, as gaseous loss of $NH_{3(g)}$ from the fertosphere is likely to be converted back to NH_4^+ as $NH_{3(g)}$ comes into contact with soil pore water (Bezdicek *et al*. 1971).

Effects of nitrification inhibitors on the chemistry of urea bands

The key function of NIs is to restrict the first step of nitrification which is the oxidisation of NH_3 to NO_2^- by the enzyme ammonia mono-oxygenase (AMO) and hydroxylamine oxidoreductase (HAO) (Cantera and Stein 2007; Robertson and Groffman 2015). By limiting the formation of NO_2^-, and thus NO_3^-, NIs may enable N to remain closer to the zone of application in the form of NH_4^+, which would be retained on soil cation exchange sites.

Urea-N concentrations measured in the nitrapyrin, DMPP, and DMPG treatments were not significantly different to those recorded in soil treated with urea alone (Fig. 1), and concentrations of fertiliser-derived NH_4^+ behaved similarly (Figs 3, S1), demonstrating that the addition of NIs had no effect on urea hydrolysis. Accordingly, the pH (Figs 5*a*, S4) and aqueous NH_3 concentrations (Figs 4*a*, S2) reached levels that potentially inhibit nitrification within the fertosphere of soil treated with NI-urea. Consequently, low NO_2^--N and NO_3^--N concentrations (Figs 3, S1) were recorded in soils treated with the NI-urea compounds, and concentrations were no different to that of untreated urea. Likewise, EC levels in soil treated with NI-urea were not significantly different from that treated with standard urea (Figs 5*b*, S5), and as for banded urea, the increase in soil EC was primarily driven by mineral N (largely, NH_4^+-N) increases. Nitrification inhibitors also did not affect the loss of N to $NH_{3(g)}$ volatilisation, relative to standard urea treatments (Figs 4*b*, S3), and the same differences between soil types in the extent of urea hydrolysis, evidenced by elevated NH_4^+ concentrations and pH increases, were observed. Thus, as a result of the chemical conditions created from initial urea hydrolysis, NIs were effectively made redundant within the fertosphere of banded urea granules. Within the confined volumes of the incubation chambers in this study, the absence of any significant variation in NO_3^--N concentration between the different soils treated with urea and NI-urea suggests soil properties do not moderate the inhibitory effects to nitrification within the fertosphere. However, while the inhibition persisted for the duration of the experiment (84 days) in this study, it is likely that in the field (where the soil volume is unrestricted) dissipation of this inhibitory effect will occur more quickly because of mass flow and diffusion of fertiliser products away from the fertosphere in soil water.

Fertosphere performance of banded PCU

Polymer-coated urea aims to improve NUE by controlling the release of urea-N to the soil solution, in a manner that allows a slow release of N and minimises the volatilisation loss of N that can result from rapid hydrolysis and also NO_3^--N loss by drainage and/or denitrification following nitrification reactions (Shaviv 2001). Although urea-N was recovered up to 54 DAI from soil with banded PCU granules, the total recovery of urea was significantly lower than other N-fertiliser treatments over the duration of the incubation (Fig. 1), accounting for only a small percentage of the applied N. It is likely that the relatively infrequent sampling times may have limited the ability to effectively account for urea release, as the smaller concentrations would have allowed larger proportions of any released urea to hydrolyse between sampling events. The granule-retention data therefore provide a more appropriate insight into the urea-N release dynamics of PCU granules.

Three distinct time-related phases of urea-N release are identified in this incubation (Fig. 2), whereby over the first 14 DAI an average 40% of applied urea-N was released from PCU granules. Over the following 42 days, a further 20% was released, and a final 22% was released from 56 to 84 DAI (Fig. 2). Given a release claim of 100% over 90 days, the magnitude of the initial urea release in Phase 1 cannot be fully explained by water movement into granules and subsequent diffusion via enlarged pores in the coating. Coupled with observations of 'burst' granules at sampling, it is therefore likely that the dominant mechanism of urea release over the first 14 DAI was due to cracks in the polymer coating, resulting in granules that behaved like uncoated urea. However, the subsequent phases were characterised by very low diffusion rates with ~0.48% applied urea release day^{-1}, and 0.79% applied urea release day^{-1} for Phases 2 and 3 respectively (Fig. 2). It is hypothesised that, when applied in a band, the PCU granules may have slower than expected release of urea-N over Phases 2 and 3 due to the interference of neighbouring granules on the granule-soil urea-N concentration gradient, upon which the diffusion mechanism of N release by polymer products relies (Shaviv *et al.* 2003*b*). This effect would be exacerbated by the significant release of urea to soil over the first 14 DAI.

Concentrations of NH_4^+-N were significantly lower (~44% less in all soil types) in PCU-treated soil (Figs 3, S1) than in those treated with urea or NI-urea. Low NO_2^- and NO_3^--N concentrations (Figs 3, S1) in the PCU treatment rule out the possibility that nitrification led to the low NH_4^+ concentrations, and collectively these data suggest there was less urea-N available to hydrolyse than in urea and NI treatments over the duration of the incubation. This is supported by approximate N budgeting data using soil extractable N (not shown), with the PCU treatments in all soils recording substantially lower extractable mineral N than the urea and NI-urea treatments, except when the urea-N in recoverable PCU granules was included. This indicated that a substantial amount of urea remained in PCU granules over the duration of the incubation. The EC values of PCU-treated soil show lower salt concentrations than in other N-fertiliser treatments (Figs 5*b*, S5), supporting the theory of restricted release. As for urea and NI-urea treatments, the changes in EC concentration in PCU-treated soil were driven by an increase in NH_4^+-N concentration (Figs 3, 6, S1).

Despite the apparently slower and/or incomplete release of urea-N in the PCU treatment, urea concentrations and subsequent ureolytic activity were sufficient to raise the pH in these treatments to values similar to those in the urea and NI-urea treatments, although it required ~20 days to reach these values (Figs 5*a*, S4). Likewise, the development of NH_3 toxicity also occurred in soil treated with PCU following a delay. At 7 DAI the concentration of aqueous NH_3 in soil treated with banded PCU was within the toxicity range for *Nitrobacter* but not *Nitrosomonas* in all soils, while by 27 DAI, aqueous NH_3 concentrations in all soils had reached levels toxic to all nitrifying bacteria, and remained within these thresholds for the duration of the incubation (Figs 4*a*, S2). The combination of slow diffusion of urea-N from PCU granules and the 'neighbour' effect of granules in a fertiliser band did not mitigate the development of fertosphere chemistry that inhibited nitrification.

Soils receiving PCU emitted $NH_{3(g)}$ at rates similar to those of urea and NI-urea treatments within each soil type, suggesting that beyond a certain NH_4^+-N concentration and pH threshold, formation of gaseous $NH_{3(g)}$ from banded urea will proceed at the maximum rate of $NH_{3(g)}$ emission (Figs 4*b*, S3) for each soil type. This indicates an NH_3-saturated soil solution within the fertosphere of all N-fertiliser treatments.

Based on the findings from this study, there are two important issues identified as possible limitations to improving NUE by using banded PCU: (1) the potential risk of 'locking' N in granules as a result of impaired diffusion due to the proximity of neighbouring granules and the effect on concentration gradients; and (2) the occurrence of a significant proportion of compromised polymer coats that may induce the same biochemically hostile conditions as banded urea.

It is expected that under field conditions, a larger volume of soil may partially alleviate these effects by allowing diffusion of released urea away from the band, thus lessening the impact on the concentration gradients between granules and soil solution in the fertosphere. This finding further suggests that in soils of low hydraulic conductivity (e.g. heavy clays) or in weather conditions that restrict the diffusion of urea away from the band (i.e. dry periods), the release of urea from PCU granules may be much slower than anticipated.

Conclusions

This study found that within the fertosphere of highly concentrated urea, NIs did not provide any inhibition of nitrification compared with standard urea, as nitrification was already inhibited by the development of hostile chemical conditions associated with urea hydrolysis. Banded applications of PCU slowed the release of urea-N. However, an initial rapid release of urea, likely due to compromised polymer coatings, produced quantities of urea and the associated ureolytic activity sufficient to elevate pH and induce aqueous NH_3 concentrations which inhibit nitrification. Furthermore, banding of PCU introduced a neighbour-granule effect whereby the concentration gradient between individual granules and the soil solution was reduced, slowing the release of urea-N from polymer-coated granules and resulting in incomplete release of granule N.

Soil type may influence ureolytic activity and, to a certain extent, the consequent chemical conditions in the vicinity of the fertiliser band, but these effects did not contribute to mitigation of the inhibition of nitrification.

Thus, within the fertosphere and compared with a concentrated granular urea standard, EEF technologies including NIs and polymer coating did not appear to induce the required responses to nitrification or N release that would enable substantial reductions in environmental losses and enhanced crop N uptake.

Conflicts of interest

The authors declare no conflicts of interest.

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