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4 **Urea contributions to dissolved ‘organic’ nitrogen losses from**
5 **intensive, fertilised agriculture.**
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ABSTRACT: While nearly 60% of global nitrogen fertilizer use is in the form of urea, and urea is increasingly implicated in aquatic eutrophication, little is known of the scale or temporal dynamics of urea export from intensive agriculture. Annual paddock urea nitrogen exports in surfacewater runoff were quantified across multiple years from several sugarcane farms across Australia's Great Barrier Reef catchment area. Study results suggest that runoff of undegraded urea can represent a significant proportion of the total 'dissolved organic nitrogen' pool leaving paddocks, and an important form of nitrogenous export from fertilised agricultural land uses. Situations where substantial rainfall or irrigation-driven surfacewater runoff occur within 1-2 weeks of fertiliser application particularly provide scope for major, and in some cases dominant, losses of undegraded urea from paddocks. Fertiliser derived urea can be a significant, bioavailable and anthropogenic form of dissolved 'organic' nitrogen export that warrants further attention in many field and catchment scale research applications.

Keywords: nitrogen export; eutrophication; water quality; fertiliser

1. Introduction

Despite a long-standing focus on what are perceived to be more biologically available nitrogen forms (i.e., ammonium ($\text{NH}_4^+\text{-N}$) and nitrate ($\text{NO}_3\text{-N}$)) in agricultural and catchment water quality research,

dissolved organic nitrogen (DON) is significant, and often dominant contributor to nitrogen exports from intensive agriculture at both field and catchments scales (Jordan et al., 1997; Filoso et al., 2003; van Kessel et al., 2009). DON constituents include free and protein-bound amino acids, amino sugars (from cell walls), nucleotides, and by-products of cellular metabolism such as urea (Jorgensen, 2009). Urea ($\text{CO}(\text{NH}_2)_2$) presents a somewhat special form of dissolved 'organic' nitrogen, as it can be derived from both natural and anthropogenic processes. The world's most popular fertiliser, industrial production of urea fertiliser is currently approaching 70 million metric tons yr^{-1} (Glibert et al., 2006), with a twofold increase in application expected by 2050 (Millenium Ecosystem Assessment, 2005). With applied fertiliser urea anticipated to hydrolyse within days to plant-available ammonium and nitrate (Vlek and Craswell, 1979; Yadav et al., 1987), urea was long-assumed to make negligible direct contribution to aquatic eutrophication (Meisinger and Randall, 1991). With recent research highlighting substantial transmission of urea to aquatic environments, and disproportionate roles in some eutrophication issues, urea is now also regarded as a significant anthropogenic nitrogen form within some aquatic DON pools (Solomon et al., 2010; Bogard et al., 2012; Glibert et al., 2014). Despite long-standing appreciation of the off-site movement potential of unhydrolysed urea (Dunigan et al., 1976), there has been surprisingly little subsequent research on the specific dynamics and scale of off-site loss of applied fertiliser urea from agriculturally developed land uses (although see Daigh et al., 2014).

Coastal eutrophication is a key water quality management issue in Australia's Great Barrier Reef (GBR) World Heritage Area (Brodie et al., 2011; 2012). Key management responses in the Great Barrier Reef Catchment Area (GBRCA) include end-of-catchment load reduction targets for inorganic nitrogen, landholder incentives for adoption of land management practices that reduce the run-off of nutrients, as well as paddock and catchment water quality monitoring and modelling initiatives to both quantify and/or predict water quality improvements associated with specific management changes (Brodie et al., 2012; Carroll et al., 2012). With urea not traditionally measured in GBRCA monitoring programs, however, it's potential contribution to agricultural nitrogen exports and catchment nutrient loadings is currently unknown. Most paddock, catchment and marine water quality monitoring in the GBRCA has instead focussed on more traditional eutrophication indicators such as total nitrogen,

particulate nitrogen, various inorganic nitrogen species (ammonium, nitrate and nitrite), and DON in its entirety (with urea an undefined constituent within the broader DON pool) (Bainbridge et al., 2009; Wallace et al., 2014).

Sugarcane (*Saccharum officinarum* L.) is the dominant crop the GBRCA (~380,000 ha of the whole GBR catchment area; Furnas, 2003), and is primarily reliant on urea-based solid (granular) and liquid nitrogenous fertilizers. Dissolved inorganic nitrogen export from sugarcane has been identified as a key contributor to nutrient loading to the GBR marine environment (Bainbridge et al., 2009; Thorburn et al., 2011; 2013; Brodie et al., 2012). With the addition of urea analysis to recent paddock scale monitoring we present here a summary of the role of urea to paddock-scale losses of dissolved nitrogen, and aspects of its temporal loss dynamics.

2. Material and Methods

2.1 Study sites

A range of site agronomic, hydrological, bioclimatic and water quality data was collected over 2-4 years from six study paddocks on multiple commercial scale sugarcane farms across several of the major GBRCA sugarcane growing districts (Carroll et al., 2012). Monitored paddocks included predominantly rainfall-fed sites (Wet Tropics and Mackay-Whitsunday regions), as well as fully furrow irrigated sites in the dry-tropical lower Burdekin region (Supplemental Information Fig. A.1). Monitored paddocks were selected to be representative of local farming districts and encompassed a range of the predominant soil types, fertiliser application methods and rates, tillage and crop residue management systems utilised across the GBRCA sugarcane industry (Table 1). Sugarcane in the GBRCA is a semi-perennial crop, mainly planted in autumn (April–July) and mechanically harvested 13–16 months later (harvesting season is June–December), with cane stools then allowed to re-grow (ratoon), usually for 4-5 harvests until productivity declines. The crop is fertilised with a basal application at planting, then remaining fertiliser is applied 3-5 months later. Ratoon cane is fertilised typically 1-2 months after harvest. Annual fertiliser applications on all sites (Tables 1 and A.1) were

predominantly surface-applied liquid or sub-surface granular urea treatments (stool split via coulters into the cane row at a depth ~10 cm). Nitrogen application rates reflected current generalised industry recommendations for each district established through regional yield response functions (Calcino, 1994), or best management practice application rates based on a combination of district yield potential and a soil nitrogen mineralisation index (Schroeder et al., 2010).

2.2 Data collection and water quality analysis

Surfacewater runoff volumes were measured at each instrumented plot using either San Dimas flumes (300 mm) or ultrasonic dopplers installed in paddock drainage outfalls collecting runoff from 4-30 cane rows plus inter-rows. Adjacent to the flume or monitored drainage pipe outflow was a monitoring station that included a refrigerated ISCO automatic water sampler and a tipping bucket pluviometer. Water samples during paddock runoff events were collected as composited (“bulked”) samples for each event, or multiple discrete samples collected during individual events according to pre-defined height or discharge triggers. In irrigated farms systems such as the lower Burdekin, irrigation inflow samples were also regularly collected for water quality analysis. Runoff and irrigation water samples were analysed for total nitrogen (TN), particulate nitrogen (PN), DON, total filterable-dissolved nitrogen (TDN), ammonium nitrogen (AN), oxidised nitrogen (ON: nitrate + nitrite) and total suspended solids (TSS). Samples for TN, TDN were digested in an autoclave using an alkaline persulfate technique (modified from Hosomi and Sudo, 1986) and the resulting solution simultaneously analysed for ON by segmented flow auto-analysis using an OI Analytical (Texas, USA) Flow Solution IV. The analyses of ON, and AN were also conducted using segmented flow auto-analysis techniques following standard methods (APHA, 2005). Particulate nitrogen concentrations were estimated by the subtraction of the total filterable nutrient concentrations from the total nutrient concentrations. Similarly, DON was estimated by the subtraction of ON and AN from the TDN concentration. A specific urea assay was also conducted to quantify the urea component of DON using a segmented flow analyser modification of the procedures developed by Marsh et al. (1965). Samples for TSS analyses were filtered through pre-weighed Whatman (England)

GF/C filter membranes (nominally 1.2µm pore size) and oven-dried at 103–105°C for 24 h and reweighed to determine the dry TSS weight as described in APHA (2005).

Surfacewater loads for nutrient and sediment runoff at sites were calculated by multiplying the total event discharge by event concentration for composited samples from individual events, or via linear interpolation techniques combining continuous time series discharge data and discrete point source water quality data. For full site histories, monitoring procedures and detailed management practices see Table A.1 and Davis et al. (2013), Armour et al. (2013a), and Rohde et al. (2013).

2.3 Data analysis

Urea data were presented as total and cumulative monitored annual urea loads (kg ha⁻¹) and proportionate contribution of urea to annual dissolved nitrogen surfacewater loads exported from paddocks. Previous research has suggested environmental variables such as rainfall or irrigation timing in relation to fertiliser application, antecedent rainfall and runoff volumes as potentially important variables in driving urea losses from paddocks in agricultural scenarios (Dunigan et al., 1976; Glibert et al., 2006). A random forest model (Breiman, 2001) was used to identify potential relationships between a range of environmental predictors and urea losses (total annual urea loadings, and proportionate urea contributions to annual dissolved nitrogen load exports) from paddocks.

Random forest models are a machine learning method that incorporate the combined output of many decision tree models (via bootstrapping), such that the predictions of the final model are an averaged prediction from those trees. Random forests show high predictive accuracy, are minimally influenced by highly correlated variables or samples sizes, data distributions, can accommodate mixed variable datasets, and can capture non-linear relationships involving complex high order interaction effects. We ran random forests using the *randomForest* package (Liaw and Wiener, 2002), with variable importance calculated using the mean decrease in predictive accuracy when specific variables were randomly permuted across the dataset (Strobl et al., 2007).

Because model averaging approaches like random forests comes at the expense of some loss of interpretability, the same predictor and response variables were used as input into classification and

regression tree (CART) models. The non-parametric recursive partitioning structure of CART models offer greater ease of interpretation, and like random forests are ideal for uncovering complex dependencies among predictor variables (Breiman et al., 1998). We ran CART using the *rpart* package (Therneau et al., 2011). Explanatory variables used in all random forest and CART models included; time interval from fertiliser application to first paddock runoff (days), interim rainfall totals occurring between fertiliser application and first runoff event (mm), total annual rainfall and irrigation applied to the paddock (mm), annual fertiliser application (kg ha^{-1}), irrigation/rainfall total causing first runoff event (mm), annual paddock runoff volume (mm), paddock slope (m/m), and monitored annual suspended sediment loads (kg ha^{-1}) as continuous variables, and; soil type, fertiliser application methods (surface or sub-soil applied), tillage practices (minimum tillage or conventional multiple cultivation), crop residue practices (green cane trash blanket retention or burnt cane) and fertiliser type (liquid or granular) as categorical variables. All random forest and regression tree models were implemented using R (R Core Team, 2015).

3. Results and Discussion

Annual loads and proportionate contributions of all nitrogen species in runoff varied substantially across sites in relation to both climatic and site soil characteristics (Fig. 1, Fig. A.2). Particulate nitrogen made variable contributions to total nitrogen loads (Fig. A.2), and we limit focus in this study to dissolved nitrogen forms. DON in its entirety was the dominant nitrogen form lost in paddock runoff in 65% of the 20 monitored years. Urea-N was a major, and in several cases dominant, contributor to both the DON pool, and also overall total dissolved nitrogen load losses from all paddocks. Urea-N was a larger contributor to nitrogen runoff exports than ammonium-N and oxidised-N in 55% and 25% respectively of year's monitored across all sites. Total annual urea load losses were, however, highly variable across sites, ranging from up to $\sim 16 \text{ kg ha}^{-1}$ (representing $\sim 8\text{--}9\%$ of the year's applied nitrogen) to $< 0.01 \text{ kg ha}^{-1}$, but also highly variable within sites (i.e., ranging from $0.3\text{--}16 \text{ kg ha}^{-1}$ over three years at one Mackay-Whitsunday site). Urea-N was only detected in

negligible concentrations in irrigation inflow water, so runoff loads can be assumed to be largely attributable to undegraded fertiliser urea.

According to both random forest and CART modelling, much of this variability evident in the annual contribution of urea to nitrogen exports could be explained by annual variations in climatic and hydrological variables experienced at paddocks. Random forest models identified the time interval between fertiliser application and the first paddock surfacewater runoff event as the best predictor for annual variability in both urea proportionate contribution to annual TDN exports and total urea-N loads. Interim rainfall between application and initial paddock runoff, annual runoff volumes and sediment loads were also among the most important explanatory variables for observed data. Overall randomforest models respectively explained ~55% and 64% of dataset variance in urea proportionate contribution and annual load exports (Fig. 2). For both total loads, and proportionate contributions, CART models attributed similar importance to the same variables, specifically identifying major paddock runoff occurring within 10 days of fertiliser application associating with higher urea losses (Fig. A.3, Table A.2).

In relation to specific data, the highest recorded urea load losses from any site ($\sim 16 \text{ kg ha}^{-1} \text{ year}^{-1}$ and $\sim 60\%$ of annual TDN losses) occurred at a Mackay site where applied fertiliser in one year received a 130 mm rainfall event within 3 days of application (Fig. 3a, Table A.1). This urea load loss total was the highest of any nitrogen pool constituent documented from all monitored sites throughout the entire study period (and exceeded combined oxidised-N and ammonium-N loads from this particular site for the entire 3-year monitoring period). This $16 \text{ kg ha}^{-1} \text{ year}^{-1}$ urea load loss also exceeded any annual total nitrogen runoff loss documented from previous sugarcane research conducted across the GBRCA (see Thorburn et al., 2011; Webster et al., 2012). Urea losses from the same paddock in the subsequent year were markedly lower when the first runoff event occurred ~ 75 days post-fertiliser application (i.e. 0.3 kg ha^{-1} and $<10\%$ of annual dissolved nitrogen load losses), and with $\sim 200 \text{ mm}$ of interim rainfall. Similarly, the highest annual load losses of urea in the irrigated lower Burdekin sites ($\sim 2.5 \text{ kg ha}^{-1}$ and 30% of annual dissolved nitrogen losses at Site 1) occurred when the trial paddock was furrow irrigated immediately following crop harvest and fertilisation (~ 1 - 2 day delay). Cumulative urea-N load losses in runoff water through time (Fig. 3a) highlighted that in

circumstances where major urea loss occurred, the dominant proportion of loss occurred almost entirely in the initial paddock surfacewater runoff event following application. Urea-N losses (in terms of both loads and proportionate contribution to the DON losses) occurring after these initial events was relatively minimal, suggesting a short, but key risk period for substantial urea mobility in surfacewater runoff.

Results align with previous suggestions that irrigation or rainfall soon after application will facilitate direct fertiliser urea movement from paddocks and into receiving aquatic ecosystems (Dunigan et al. 1976; Glibert et al., 2006). In the cases of the most substantial urea losses documented here, applied urea probably had insufficient time to hydrolyse to ammonium or oxidised nitrogen, and left paddocks in unhydrolysed (undegraded) form. In cases of longer delays between fertiliser application and first paddock runoff, urea loads and proportionate contribution to annual loads tended to be minimal (Fig. 3a-b), with the dominance of other N forms likely reflecting greater opportunity for more complete conversion of fertiliser urea to ammonium and nitrate-N. This is also illustrated in the contrasting nitrogen dynamics at one of the Mackay-Whitsunday sites following identical 200 kg ha⁻¹ applications of urea-based nitrogen fertiliser in concurrent years (Fig 4.). In 2010, when runoff occurred only 3 days after fertiliser application, urea dominated the early runoff dynamics, but decreased rapidly, while oxidised nitrogen forms became dominant contributor in later runoff events (likely reflecting the time interval required for urea conversion to oxidised nitrogen). In the subsequent 2011 year, when the first runoff event occurred 76 days after application, oxidised nitrogen dominated runoff loads and urea-N made only minimal contribution to runoff loads (reflecting longer opportunity times for more complete urea conversion to nitrate). The broader, annual scale datasets analysed here did, however, only account for 50-60% of dataset variability. Finer scale research highlighting the role of additional variables such as soil moisture and temperature (Yadav et al., 1987), the role of other macro- and micronutrients or specific management practice impacts on nutrient dynamics (see Daigh et al., 2014), will be required to improve understanding of urea fertiliser transformations and loss partitioning across different farming systems.

The increasing addition of urease inhibitors to fertilisers to delay urea hydrolysis for several weeks or more (Glibert et al., 2006), will likely increase both the likelihood that agricultural runoff

contains unhydrolyzed urea, and increase the length of time post-application in which urea could make a significant component of nitrogen load loss from paddocks. A notable gap in this study was the lack of assessment of groundwater nitrogen losses, which can be substantial under some GBRCA sugarcane farming systems (Thorburn et al., 2011; Armour et al., 2013b). Recent syntheses have highlighted DON as an often significant (and overlooked) nitrogen leaching pathway (van Kessel et al., 2009). While rarely assessed, urea leaching losses to groundwater can be substantial under certain conditions (see Svensen and Singh, 1997), and have been cited as potential reasons for unexpectedly high fertiliser derived DON losses in nitrogen tracing studies where urea-N was not explicitly assessed (Zhao et al., 2009).

This significant, but previously cryptic role of urea in paddock runoff also has a range of implications for nitrogen research over multiple scales in the GBRCA. Other GBRCA sugarcane studies of field scale nitrogen export have consistently documented runoff loads can be dominated by DON (i.e. >50% of total nitrogen: Masters et al., 2008; Webster et al., 2012). Using traditional analytical approaches, while direct fertiliser-derived urea contributions will be captured in the DON fraction of total nitrogen losses, it's specific scale is indeterminate, and anthropogenic fertiliser urea contributions will not be distinguishable from other organic nitrogen forms. An understanding of specific loss pathways and their role and scale in transferring contaminants from land to water is an important pre-requisite for effectively quantifying the relative water quality impacts of different management measures, currently a major research investment in the GBR catchment area (Carroll et al., 2012). Many recent water quality policy instruments both in the GBR (Brodie et al., 2012) and internationally (see Kroon et al., 2014 and references therein), similarly emphasize targets based around 'inorganic' or 'anthropogenic' nitrogen loadings and/or nutrient budget approaches based on indicators such as ammonium-N and oxidised-N (nitrate + nitrite) which may not accurately capture the true scale of fertiliser nitrogen export from agriculture. It is also becoming increasingly apparent that urea may be preferentially used over inorganic nitrogen, and contribute disproportionately to total nitrogen used by phytoplanktonic communities during algal blooms (Solomon et al., 2010; Glibert et al., 2014). With nutrient stimulated development of marine phytoplankton blooms in flood plumes

identified as a key threat to the GBR (Fabricius et al., 2010; Brodie et al., 2011), the potential role of urea as a nitrogen substrate in these processes will also be worth investigating.

4.0 Conclusions

Urea nitrogen emerged in this study as a significant contributor to paddock nitrogen losses, often representing a large fraction of the total dissolved ‘organic’ nitrogen pool, paralleling the emerging role of urea in the DON pool in some aquatic environments (i.e., Solomon et al., 2010). Undegraded fertiliser urea also frequently exceeded runoff loads of more traditionally monitored dissolved nitrogen species such as ammonium and oxidised nitrogen. With current, and projected increased future usage, and technological advances which may increase potential for fertiliser urea losses, improved understanding of urea dynamics in terms of loss pathways and soil transformations is essential to mediate potential water quality degradation. At the very least, quantification of urea contribution to the DON pool exported from paddocks or catchments would seem an important future consideration for water quality monitoring, particularly so in cases where major runoff-producing rainfall or irrigation occurs in close proximity to key periods of fertiliser application (see Monaghan et al., 2016). Based on study findings, and the ease of urea analysis (this study; Revilla et al., 2005), we recommend that future GBRCAs water quality research over multiple spatial scales include urea determinations.

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426

Figure captions

Fig. 1. Proportionate dissolved nitrogen species contributions to annual monitored nitrogen surfacewater runoff loads from Great Barrier Reef catchment area sugarcane farms (DON has had the urea contribution subtracted from total DON load, and particulate nitrogen is excluded).

Fig. 2. Variable importance in random forest models (a) predicting urea as a proportion of annual dissolved nitrogen loading in surfacewater runoff, and (b) total urea runoff loads ($\text{kg} \cdot \text{ha}^{-1}$). Variable importance is measured as the normalized difference (Inc%MSE) between the prediction error (MSE; mean square error) measured when permuting the out-of-bag portion of the data and the MSE when permuting the given variable (larger Inc%MSE indicates higher variable importance in the random forest model). Explanatory variables acronyms used in all models included time interval from fertiliser application to first paddock runoff (DaysApp), interim rainfall totals occurring between fertiliser application and first runoff event (InterimRain), total annual rainfall and irrigation applied to the paddock (AnnualWater), soil type (Soil), annual fertiliser nitrogen application (Nrate), irrigation/rainfall total causing first runoff event (EventVol), paddock runoff volume (Runoff), application methods (ApplM), crop residue treatment (Cover), crop tillage system (Tillage), fertiliser type (FertType), and annual paddock sediment loads losses (Sediment).

Fig. 3. (a) Cumulative urea-N losses (kg ha^{-1}) in paddock runoff water for annual monitoring periods. Note log (x+1) transformation of y-axis values; (b) Relationships between proportionate annual urea-N load losses and time interval (days) between fertiliser application and first paddock runoff event (red line indicates significant logarithmic regression relationship; $R^2 = 0.42$, $P < 0.01$).

453

454

455 **Fig. 4.** Nitrogen event mean concentration dynamics of different dissolved nitrogen forms in runoff
456 events following identical 200 kg N ha⁻¹ urea fertiliser applications in (a) 2010, and (b) 2011 at
457 Mackay Site 1. Arrows indicate fertiliser application dates. Cumulative runoff (mm) is depicted in the
458 grey trace.

Tables

Table 1 Farming system, nutrient application, soil classification (Isbell, 1996), climatic and hydrological properties of the six study sites located across the Wet Tropics (WT), lower Burdekin (LB) and Mackay-Whitsunday (MW) canegrowing regions of the GBR catchment area.

Site	Soil type	Farming system	Annual water application (mm)	Tillage treatment [‡]	Crop residue management [^]	Paddock slope (m/m)	Fertiliser application method	Annual fertiliser application (kg N ha ⁻¹)	Annual runoff (mm)
WT1	Kandosol (brown)	Rainfall	1237-3779	CTMT	GCTB	0.010	Sub-surface (granular)	0 [#] -130	40-465
WT2	Kandosol/Hydrosol	Rainfall	1365-3780	CFS	GCTB	0.030	Sub-surface (granular)	50-138	0.3-200
LB1	Vertosol (grey)	Irrigated	1320-1885*	CTMT	Burnt cane	0.001	Sub-surface (granular)	180-220	460-745
LB2	Dermosol (brown)	Irrigated	1811-2000*	CFS	Burnt cane	0.010	Sub-surface (granular)	180-170	281-921
MW1	Vertosol (black)	Rainfall	2200-3200	CFS	GCTB	0.011	Surface (liquid)	197-200	841-2025
MW2	Vertosol (black)	Rainfall	2200-3200	CTMT	GCTB	0.011	Surface (liquid)	135-139	671-1751

*Includes rainfall + irrigation volumes

[#]monitored fallow period with no fertiliser application

[^]GCTB; green cane trash blanket retained as paddock cover following harvest; burnt cane: signifies crop is burnt prior to harvest to remove harvest residues

[‡]CTMT; controlled traffic-minimum tillage with minimal or targeted zonal tillage through crop cycle, CFS; conventional farming system with multiple tillage and cultivation events occurring on an annual basis through crop cycle.

FIG 1

(a)

(b)

FIG 2

FIG 3

FIG 4