



# Urea contributions to dissolved ‘organic’ nitrogen losses from intensive, fertilised agriculture



Aaron M. Davis<sup>a,\*</sup>, Michelle Tink<sup>a</sup>, Ken Rohde<sup>b</sup>, Jon E. Brodie<sup>a</sup>

<sup>a</sup> Centre of Tropical Water and Aquatic Ecosystem Research (TropWATER), James Cook University, Townsville, Queensland 4811, Australia

<sup>b</sup> Department of Natural Resources and Mines, Mackay, Queensland 4740, Australia

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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.

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## 1. Introduction

Despite a long-standing focus on what are perceived to be more biologically available nitrogen forms (i.e., ammonium (NH<sub>4</sub><sup>+</sup>-N) and nitrate (NO<sub>3</sub><sup>-</sup>-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 (Jørgensen, 2009). Urea (CO(NH<sub>2</sub>)<sub>2</sub>) 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<sup>-1</sup> (Glibert et al., 2006), with a twofold increase in application expected by 2050 (Millennium 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, its 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

\* Corresponding author.

E-mail addresses: [aaron.davis@jcu.edu.au](mailto:aaron.davis@jcu.edu.au) (A.M. Davis), [michelle.tink@jcu.edu.au](mailto:michelle.tink@jcu.edu.au) (M. Tink), [Ken.Rohde@dnrm.qld.gov.au](mailto:Ken.Rohde@dnrm.qld.gov.au) (K. Rohde), [jon.brodie@jcu.edu.au](mailto:jon.brodie@jcu.edu.au) (J.E. Brodie).

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 intensively fertilized crop in 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 the previous harvest. Annual fertiliser applications on all sites (Table 1 and Table A.1) were predominantly surface-applied liquid or sub-surface granular urea treatments (stool split

via coulter 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 to 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, 1987) 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 1.2 µm 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).

**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 <sup>d</sup>	Crop residue management <sup>c</sup>	Paddock slope (m/m)	Fertiliser application method	Annual fertiliser application (kg N ha <sup>-1</sup> )	Annual runoff (mm)
WT1	Kandosol (brown)	Rainfall	1237–3779	CTMT	GCTB	0.010	Sub-surface (granular)	0 <sup>b</sup> –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 <sup>a</sup>	CTMT	Burnt cane	0.001	Sub-surface (granular)	180–220	460–745
LB2	Dermosol (brown)	Irrigated	1811–2000 <sup>a</sup>	CTMT	Burnt cane	0.010	Sub-surface (granular)	180–170	281–921
MW1	Vertosol (black)	Rainfall	2200–3200	CTMT	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

<sup>a</sup> Includes rainfall + irrigation volumes.

<sup>b</sup> monitored fallow period with no fertiliser application.

<sup>c</sup> GCTB; green cane trash blanket retained as paddock cover following harvest; burnt cane: signifies crop is burnt prior to harvest to remove harvest residues.

<sup>d</sup> 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.

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