Tracking nitrogen from the paddock to the reef- a case study from the Great Barrier Reef

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Abstract
The water discharged from rivers draining into the Great Barrier Reef (GBR) lagoon carries land-derived suspended sediments, nutrients and pesticides. Total nitrogen (N) loads have more than doubled since development, with the extensive grazing and intensive sugarcane industries the largest contributors. Runoff and soil erosion are the main sources of riverine particulate nitrogen (PN) while fertilizer application has contributed to the increase in dissolved inorganic nitrogen (DIN). Dissolved organic N (DON) loads have increased less and it is unclear if DON has changed with development. DIN is rapidly taken up by marine plants and cycled through the marine food web, resulting in typically low concentrations of DIN in GBR waters, and an N-pool dominated by DON and PN of marine origin. The productivity of marine plants is sustained by rapid recycling of organic nutrients. Additional available N, as occurs from land runoff, can result in adverse effects on coral reefs by increasing coral vulnerability to temperature stress, and by benefitting coral competitors and predators.
Ambitious targets to reduce N loads from key catchments have been set and a combination of changes to land use and nutrient management practices will be required to achieve the necessary water quality improvement. Prioritization of actions that maximize water quality benefits will require new fertilizer technology for cropping industries and greater certainty around underlying processes contributing to bioavailable N loads from all land uses. Uncertainties include the relative importance of DIN compared to total bioavailable N, and of the contribution of runoff compared to other N loss pathways like subsurface lateral flow and deep drainage.

Key Words
Water quality, erosion, nitrogen fertilizer, extensive grazing, sugarcane, bioavailability

Introduction

The Great Barrier Reef is the world's largest coral reef system, covering an area of 344, 000 square kilometres, extending 2300 km along the Queensland coast and consisting of approximately 3000 reefs. While corals are a prominent feature of the Reef, the listing on the World Heritage Register in 1981 was on the basis of its Outstanding Universal Value, with the importance of the Reef ecosystem as a whole recognized.

Agriculture (grazing and cropping) is the dominant industry in the Reef catchments, employing over 35,000 people and contributing approximately $3.7 billion annually in gross value of production. Land use areas in the GBR catchment are dominated by grazing (75%), followed by nature conservation (13%) and forestry (5.1%) (Figure 1). Dryland and irrigated cropping only occupy 3% of the catchment area, with sugarcane (40% of the cropped area) the most prevalent broadacre crop. Horticultural crops occupy <1% of the total GBR land use, however banana cropping areas are significant in some sub-catchments. Approximately 85% of the sugarcane is grown in the Wet Tropics, Mackay Whitsunday and Burdekin Natural Resource Management (NRM) regions (DSITIA 2012), while the Burdekin and Fitzroy NRM regions contain 78% of the total grazing area.
Large climatic variation occurs across the Reef catchments. In the coastal areas of the Wet Tropics average annual rainfall exceeds 3000 mm, while large areas of the Burdekin, Fitzroy and Burnett Mary regions have average annual rainfall in the 500–750 mm range. The northernmost Cape York and Wet tropics regions experience a typically tropical climate with a distinct wet and dry season. These two regions generate 60% of the average annual runoff for the GBR, primarily arising from major events such as rain depressions, monsoons and cyclones.

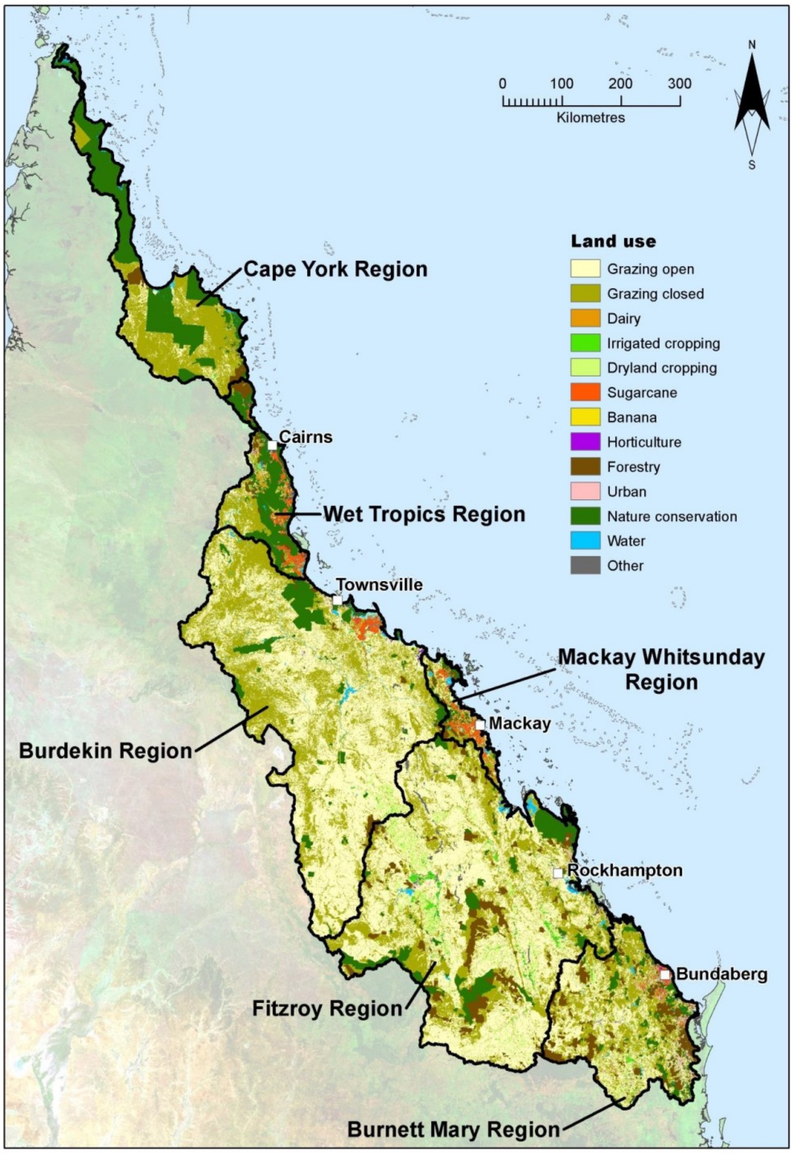

Figure 1. Natural resource management regions and land use in GBR catchments

End of catchment nitrogen (N) loads entering the GBR lagoon

End of catchment N loads entering the GBR lagoon are estimated using a modelling approach informed by an extensive loads-monitoring program, with the effect of climate variability accounted for by using a static climate period (1986–2009) to produce average annual baseline loads (Waters *et al.* 2014). Differentiation between pre-development loads and the current baseline estimates were used to calculate anthropogenic loads. The pre-development loads were based on current hydrology (including dams and weirs) but pre-development land use and ground cover (McKergow *et al.* 2005a, b). The latest estimates of baseline loads suggest that anthropogenic activity has more than doubled total N loads (from 20,000 to 46,500 t N/year), with the greatest proportional increase in particulate N (PN) from runoff (Fig. 2). In relative terms, anthropogenic activity has resulted in the proportion of PN increasing from 27% to 36% of total loads, while the proportions of dissolved organic N (DON) decreased from 47% to 38% and dissolved inorganic N (DIN) remained relatively constant (McCloskey *et al.* 2016).

The contributions to total GBR N loads vary markedly between regions (Fig. 3a) and between land uses. The Wet Tropics region is the main regional contributor of total N load (32%), while Mackay Whitsunday and Burnett Mary regions (each 9%) are the lowest contributors. For the current baseline, the land uses dominating N loads are grazing (37%), nature conservation (24%) and sugarcane (20%), with the relative proportions of constituents markedly different between land uses (Fig. 3b). The predominant loss constituent in both nature conservation and grazing areas is DON (45-49%), but DIN is predominant in sugarcane (48%)

and PN makes a greater relative contribution in grazing lands (37%) than in sugarcane (31%) or nature conservation (29%) areas.

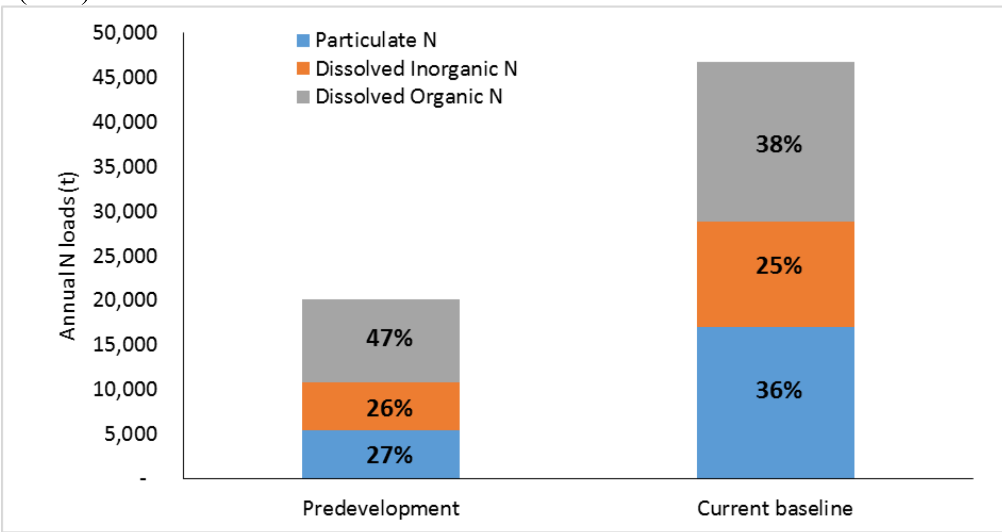

Figure 2. The impact of changing land use (pre- and post-development) on estimated total and constituent N loads entering the GBR lagoon annually (McCloskey *et al.* 2016).

There is still considerable uncertainty about the relationship between constituent N loads measured/modelled at the end of catchment, and the quantities and form of N from various sources and in-stream losses/transformations. The conceptual diagram (Fig. 4) outlines some of the likely contributing factors, highlighting the potential for elevated DIN and depleted PN (mineralization and/or denitrification) and DON (mineralization) loads at end of catchment as a result of in-stream processes that are currently not well quantified. While Thorburn and Wilkinson (2013) concluded that in-catchment N loss processes like denitrification may be minimal for surplus N lost from cropping systems (due to short residence times and rapid flow rates in coastal river systems draining the main crop production centres), that logic may not apply to N losses from the more distant inland grazing areas. The extent of N transformations and their ultimate effects on constituent loads can have immediate impacts in the marine receiving waters, as outlined below, and on the management strategies chosen to minimize the impact of off-site N losses at source (discussed later).

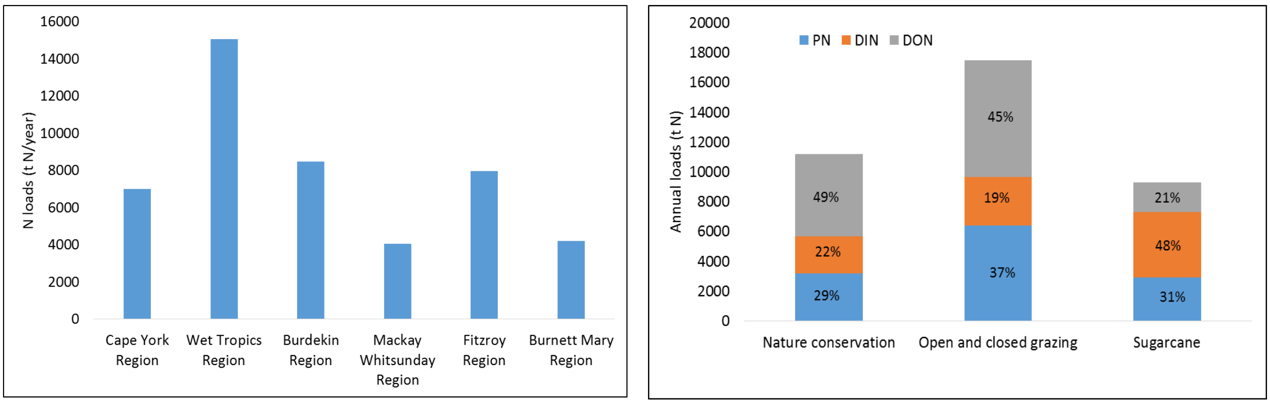

Figure 3. Estimates of total annual baseline N loads from (a) the various GBR regions, and (b) constituent N loads sourced from the land uses contributing the greatest proportions of annual N loads across the entire GBR (McCloskey *et al.* 2016)

Influence of constituent N loads on ecosystem function in the GBR lagoon

Nitrogen is an essential nutrient to sustain the productivity of the coastal and marine food webs. However, there is concern in many parts of the world that excess nutrients from human activity cause eutrophication of receiving waters. Sections of the inner GBR lagoon are considered to be episodically eutrophic (sensu Nixon 1995) during and after river flood events when high levels of nutrients, chlorophyll, pelagic production and organic matter are observed (Schaffelke *et al.* 2012, McKinnon *et al.* 2013, Furnas *et al.* 2014, Thompson *et al.* 2014).

River runoff is the largest external source of "new" nitrogen to the GBR system; other sources are planktonic nitrogen-fixation and upwelling of deep, cold nitrogen-rich water at the edge of the continental shelf (Furnas *et al.* 2011). The majority of riverine nitrogen is transported into the GBR lagoon during the summer wet season, and the transport and fate differs between the constituent N forms. Most of the PN settles out of the water column close to river mouths (Lewis *et al.* 2015), while the finer fraction is incorporated into organic aggregates ("marine snow") which are dispersed more widely in the GBR lagoon (Bainbridge *et al.* 2012). A detailed review of the sources, transport and fate of terrestrial nitrogen transported into the GBR (Brodie *et al.* 2015) concluded that the bioavailability of DON and PN is still largely unknown. It is known that riverine DIN is 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). During major flood events, DIN may be transported further afield because N-uptake by phytoplankton is limited in highly turbid, low salinity flood plumes. This may result in inshore reefs and seagrass meadows being exposed to high DIN concentrations for short periods of time (Devlin *et al.* 2012). The footprint of the riverine influence differs between years, as river discharge varies, and between catchments/regions, and can cover substantial areas of the inner and mid-shelf lagoon of the GBR (Thompson *et al.* 2014, Fabricius *et al.* 2016).

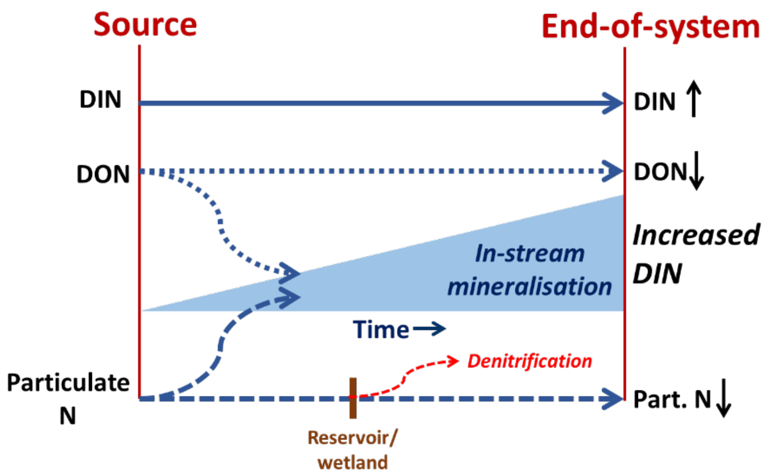

Figure 4. Conceptual model illustrating potential in-stream N transformations influencing end-of-catchment loads.

In the GBR lagoon, about 80% of N in the water column, regardless of location or season, is present as DON (5-10 µM) and about 20% as PN (1-2 µM), predominantly of marine origin due to the dominant recycling processes (Furnas *et al.* 2011). DIN concentrations are usually very low (0.01-0.2 µM), comprising only 1-2 % of the total water column N pool (Schaffelke *et al.* 2012). Nitrogen concentrations change significantly with seasons, especially in the inner lagoon, with higher concentrations during summer reflecting riverine inputs (Schaffelke *et al.* 2012, Thompson *et al.* 2014). During winter, N concentrations are low, except for periods of strong winds leading to re-suspension of seafloor sediments and release of nitrogen adsorbed to fine particles and from sediment pore-waters (Furnas *et al.* 2005, 2011).

Ratios between concentrations of bio-available forms of the major algal nutrients (N, P, Si) in GBR waters indicate that phytoplankton biomass in the GBR lagoon is N-limited (Furnas *et al.* 2005). Inorganic phosphorus is generally present in measureable concentrations and there is always sufficient silicon available to support production of phytoplankton (especially diatom) biomass. Most of the N-demand for marine production is sustained by recycling of organic matter, both in the water column and from seafloor sediments (Furnas *et al.* 2011). Phytoplankton is considered to be a key far-field transport mechanism for nitrogen as it goes through repeated cycles of growth, decay and remineralisation (D'Angelo and Wiedenmann (2014). Decomposing plankton, which are components of "marine snow" particles, are more abundant closer to the coast, especially during summer (Uthicke *et al.*, 2009). These detrital particles are one of the main mechanisms by which nitrogen ultimately affects marine benthic communities, such as coral reefs, and influences their structure, productivity, and health for long periods (reviewed in Fabricius 2005).

There is a large body of literature describing the adverse effects of impaired water quality on coral reefs. However, it is a challenge to separate the effects of nitrogen from other co-occurring and correlated factors

(Fabricius *et al.* 2013). For example, land runoff delivers a complex mixture of nutrients, suspended sediments and other compounds such as agrichemicals. Interactions between these water quality constituents are complex and often additive (Uthicke *et al.* 2016). The responses of coral reef organisms to nutrients may be similar to the response to other water quality pressures, and can often only be separated in complex experiments. In nature, the effects mostly occur simultaneously, so the availability of excess nutrients affects coral reef ecosystems both directly and indirectly.

While excess DIN availability alone has few direct adverse effects on corals (Fabricius *et al.* 2005), in concert with increased temperature, high DIN concentrations and unbalanced N:P ratios can increase the susceptibility of corals to “bleaching” (Vega Thurber *et al.* 2013, D’Angelo and Wiedenmann 2015). Coral bleaching is a response of corals to extreme temperatures involving the loss of their algal symbionts which are essential for the nutrition of corals. The interaction between high temperature, which is a global pressure, and nutrient availability, which is controlled by local or regional processes, is particularly relevant now. In 2016, the third world-wide mass coral bleaching event was recorded (see, e.g., NOAA 2016), leading to significant coral mortality which is still being fully quantified.

Nitrogen is required for the growth of plankton, which, together with particulate organic matter, provide food for filter feeders such as corals. However, the exposure to additional nutrients can be a stress factor for most coral species, in interaction with temperature (as above) or with suspended sediments which leads to light-limitation or smothering by organically and nutrient-enriched sediments (Fabricius *et al.* 2013).

Nitrogen enrichment can promote growth of fleshy macroalgae where light levels are sufficient (Schaffelke *et al.* 2005). Macro-algae have higher abundance on reefs with high concentrations of water column chlorophyll, which is generally considered as a proxy for high nutrient availability (De’ath and Fabricius 2010). High macroalgal biomass on reefs has a number of adverse effects on corals: space competition (e.g. McCook *et al.*, 2001); affecting coral metabolism by altering the corals’ microenvironment (Hauri *et al.*, 2010); reducing coral settlement (Birrell *et al.*, 2008);, and increasing the susceptibility to coral disease (Morrow *et al.*, 2012). Coral disease is a significant cause of coral cover declines on the GBR (Osborne *et al.* 2011) and has been related to environmental factors, especially high temperatures, sedimentation and elevated concentrations of nutrients and organic matter (Bruno *et al.* 2003, Happkylä *et al.* 2011, Vega Thurber *et al.* 2013, Thompson *et al.* 2014).

Perhaps the most important indirect effect of excess N on the corals of the GBR is the assumed link to a native pest, the coral-eating crown-of-thorns starfish (COTS). High N availability after a significant riverine flood increases phytoplankton biomass, which in turn increases survival of the planktonic larvae of the starfish and ultimately increases likelihood of a population outbreak (Fabricius *et al.*, 2010), although other factors may contribute to this (Pratchett *et al.* 2014). Since the 1960s, three major COTS population outbreaks have been recorded and a fourth is now in progress on the northern GBR. When COTS occur in plague proportions they can significantly reduce the coral cover on a reef. COTS were identified, together with cyclones, as a major cause of 50% decline in coral cover on the GBR from 1989 to 2012 (De’ath *et al.* 2012).

The future outlook for coral reefs is poor as global climate change leads to increasing ocean temperatures and acidification. Global warming is also increasing rainfall variability (Lough, 2011). Increased sediment and nutrient losses from agricultural lands are particularly large when floods follow severe droughts as a result of low vegetation cover (Packett *et al.* 2009); this is likely to exacerbate the effects of riverine runoff on the water quality of the GBR lagoon and the ecosystems it sustains.

Opportunities for reducing terrestrial source N loads from the major contributing land uses

The Australian and Queensland Governments have set ambitious targets to reduce the runoff of nitrogen and suspended sediments from key catchments by 2025 (Reef 2050 Long-Term Sustainability Plan 2015). Initial targets were based on models that estimated the end-of-catchment DIN loads which maintained chlorophyll concentrations in the GBR lagoon within the current GBR marine water quality guidelines (Wooldridge *et al.* 2006, subsequently updated in Brodie *et al.* 2014).

Sugarcane
Although the high proportion of DIN leaving sugarcane catchments represents an immediate risk to marine ecosystem health, an analysis of recent Paddock to Reef studies (Armour *et al.* 2013; Nachimuthu *et al.* 2013; Rohde *et al.* 2013) suggests that DIN loads in runoff from fertilized cane fields are often small (1-2 kg N/ha/year), particularly where N is banded below the trash blanket and soil surface, although annual loads can be up to 40 kg N/ha in the worst cases. These direct DIN losses are typically equalled (or in some cases dwarfed) by losses of other N forms (e.g., PN – Fig. 5) that represent labile N sources that will potentially mineralize in-stream (Fig. 4, Fig. 6) or in the GBR lagoon (Fig. 6).

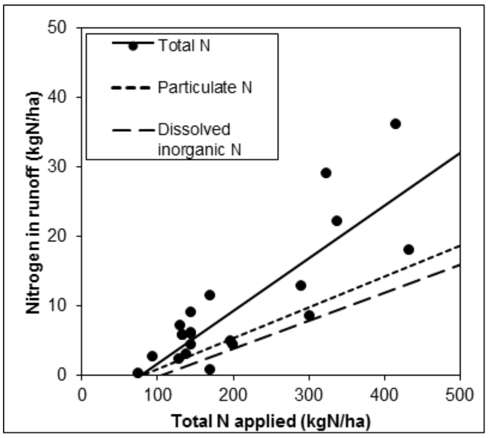

Fig. 5. Relationship between total N input (fertilizer and legumes) and total wet season N in runoff (total N, PN and DIN) from >20 sugarcane sites in GBR catchments. Data points indicate total N losses, while fitted regressions are shown for PN and DIN from the same sites.

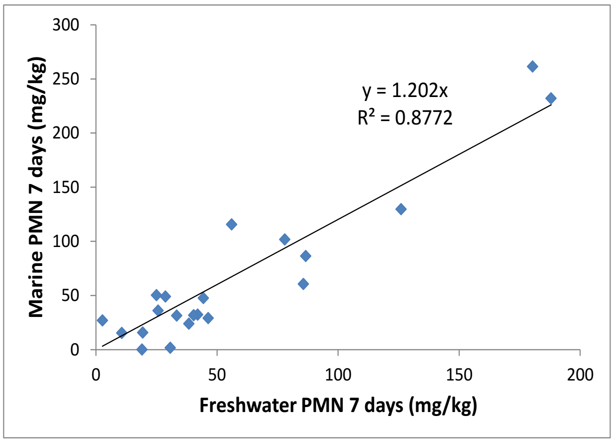

Fig 6. Potentially mineralisable N from <10um sediments after 7 days incubation at 25°C suspended in deionised water (freshwater conditions) and 0.5M NaCl (marine conditions). Data from Burton *et al.* (2015).

While runoff loss of DIN may often be small, this N loss pathway is often greatly exceeded by N losses by lateral or deep drainage of DIN in nitrate form in lighter textured soils, or denitrification in soils where drainage is impeded. For example, J. Palmer (unpublished data) estimated that DIN in runoff from cane fields under contrasting management in Bundaberg (reported in Nachimuthu *et al.*, 2013) ranged from 0.6-1.5 kg N/ha (0.5-1.0% of the applied fertilizer N), with these losses dwarfed by drainage (50-90 kg N/ha) and denitrification (25-45 kg N/ha) under wet seasonal conditions. The importance of drainage losses was consistent with observations of elevated groundwater DIN concentrations in sugarcane regions (e.g. Thorburn *et al.* 2003; Rasiah *et al.* 2013). This DIN can rapidly return to streams in constructed drains, although direct measurement of the delivery ratios of groundwater DIN into stream DIN has not yet been achieved.

Thorburn and Wilkinson (2013) linked the quantum of N losses to the concept of N surplus, with a combination of site and soil characteristics, climate, and management practices ultimately determining the loss pathway. We develop this approach further (Fig. 7) to determine the potential impacts of improved fertilizer management on N losses and cane productivity.

This analysis illustrates the potentially large N surplus arising from recommended N application rates in low loss environments, but as environmental losses increase with conventional fertilizer products, the surplus shrinks and in fact can disappear altogether, leaving the crop N-limited. The deployment of hypothetical enhanced efficiency fertilizer technology (that mitigates fertilizer N losses by maintaining N in the ammonium form, or controls the release of mineral N) would minimize environmental losses and allow reduced N application rates without compromising crop productivity.

Grazing
Within the extensive grazing systems, N loads are dominated by DON and PN. Given the uncertainty with mitigation and management of DON, as discussed earlier, the focus will be directed towards reducing PN through reduction in erosion rates.

To characterise the nitrogen and phosphorus status of sediments for catchment modelling, total elemental concentrations (i.e., quantity) have been measured with little attention given to the bioavailability of nutrients and organics (i.e., quality) associated with fine sediments. Recent work by Bainbridge *et al.* (2012) indicates 80% of the total particulate nitrogen is deposited near the mouth of the Burdekin River as the coarse sediment fraction (>16um). The remaining 20% in the flood plume disperses away from the mouth of the Burdekin River with organic-rich flocs forming around the fine-grained (<16um) suspended sediments. Importantly, these organic-rich suspended sediments in the flood plume impinge on coral reefs and seagrass meadows (Bainbridge *et al.*, 2012), and similar material has been shown to be particularly detrimental to corals under laboratory conditions (Weber *et al.*, 2006, 2012). A review by Brodie *et al.* (2015) suggests that a large proportion of particulate nitrogen is likely to be available for mineralisation.

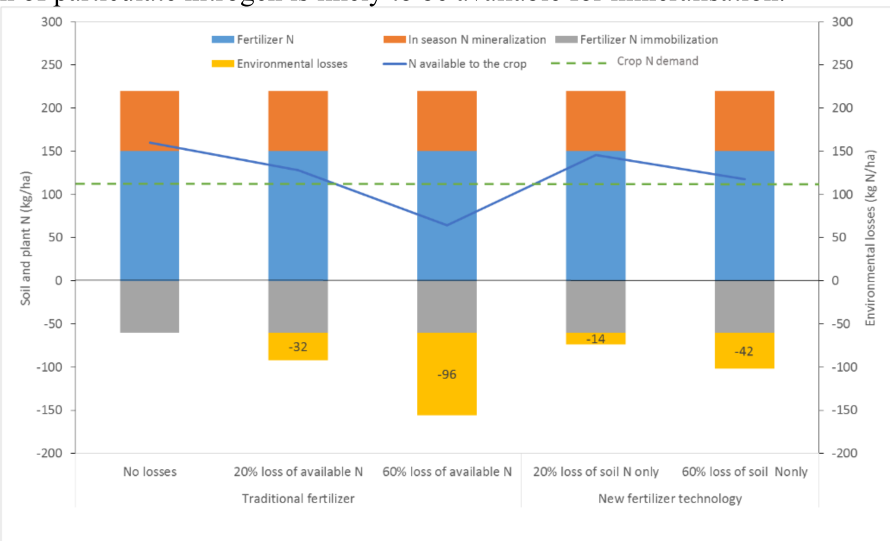

Fig 7. Hypothetical N budgets for sugarcane crops grown in the wet tropics with average yields of 80 t/ha. Fertilizer inputs are based on current N Best Management Practice for the sugar industry (Soil Health and Nutrient Management module https://www.smartcane.com.au) and assumptions about mineral N losses are based on data presented in SRA (2014).

To date much of the catchment-based research has focused on the physical characteristics (i.e., quantity) of sediment and its links to soil erosion processes, and has shown that fine silt and clay fractions of sediment delivered from a number Reef catchments to the Great Barrier Reef lagoon have been predominantly derived from the erosion of sub-surface sources (Bartley *et al.*, 2004; Hughes *et al.*, 2009; Tims *et al.* 2010; Olley *et al.* 2013). As a result, the management of sub-surface erosion features such as gullies, channel banks and hillslope scalds and rills in grazing lands has been recommended to reduce the delivery of fine silts and clays to the GBR. However the relative importance to water quality of the quantity of sediment versus the quantity of bioavailable N in that sediment has recently been highlighted by Burton *et al.* (2015), with a case example reproduced in Table 1 below. These results indicate that further understanding of the bioavailability and release rates of particulate nutrients and how they vary with sediment particle size, soil type, erosion process and land use is critical to informing management strategies and prioritisation of investment to improve the health and resilience of the GBR and to inform sustainable management of agricultural lands.

Table 1. PN concentrations and bioavailability (expressed as Potentially Mineralisable Nitrogen, PMN) in the <10um sediment fraction derived from surface and sub-surface soils in grazing lands of the Burdekin/Bowen catchment. Loads of bioavailable nutrient delivered to end-of-system were calculated assuming 5.99 M tonnes of <10um sediment were delivered to the end of the Burdekin catchment (Bainbridge *et al.*, 2015), with 10% and 90% of the sediment derived from surface and subsurface erosion processes respectively (Wilkinson *et al.*, 2015). Excerpt from Burton *et al.*, 2015

	Concentrations (mg/kg)		Loads (g N/yr)		(%)
	Surface sediment	Sub-surface sediment	Surface sediment	Sub-surface sediment	Surface sediment N in total N load
PN (mg/kg)	2111	1167	1300	6300	17
PMN @ 1 day (mg/kg)	26	1	16	5	74
PMN @ 7 day (mg/kg)	66	26	40	140	22

These data show that while hillslope (surface) erosion may represent a relatively small proportion of the total N load associated with fine sediments (i.e., those likely to reach the outer reef), it represents a significantly greater proportion of the biologically active N that will continue to contribute to generation of DIN in receiving waters. Therefore, even though the quantity of hillslope-derived (i.e., surface) sediment is small compared to that derived from stream bank and gully erosion (i.e., sub-surface), the higher concentration of bioavailable N means that mitigation strategies that reduce hill slope erosion in grazing lands (such as stocking rate control and maintenance of surface cover) need to continue to be addressed. This requirement is recognised in the current Best Management Practices documentation for grazing lands in GBR catchments (Grazing Land Management module https://www.bmpgrazing.com.au).

Conclusion

Nitrogen loads leaving GBR catchments have more than doubled as a result of anthropogenic activity, with significant direct and indirect effects on water quality and environmental health in the GBR lagoon. Significant improvements in system understanding and in development of better industry management practices to reduce the runoff of N have been made in the last decade. However, to ensure that chlorophyll concentrations in the GBR lagoon are maintained within the current GBR marine water quality guidelines, ambitious new targets to reduce runoff of N and suspended sediments from key catchments have been set. While it is recognized that achieving those targets will require a combination of changes to land use and nutrient management practices, the ability to reach these targets and the priority of actions needed to maximize water quality benefits are being constrained by availability of appropriate technology (e.g., appropriate enhanced efficiency fertilizers) and uncertainty around some of the underlying processes that contribute to bioavailable N loads. Examples include the relative importance of DIN compared to total particulate N, and focussing on monitoring and modelling runoff with less attention given to other N loss pathways such as deep drainage.

The focus on grazing and sugarcane industries in this presentation is based on the dominance of those land uses in contributing to total N loads. It is therefore logical to expect the drive for practice change and technological intervention to be focussed on those industries in the near future.

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