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SEDIMENTS, SEC 2 • PHYSICAL AND BIOGEOCHEMICAL PROCESSES • RESEARCH ARTICLE

The bioavailability of particulate nitrogen in eroded sediment: Catchment sources and processes

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Abstract

Purpose Anthropogenic land use change has caused an increase in particulate nutrient loads from catchments draining to the Great Barrier Reef (GBR). The research in GBR catchments has indicated that particulate nutrients are bioavailable to both freshwater and marine phytoplankton, but relative importance of this source of nutrients to the GBR is unknown. We quantified the contribution of this source of bioavailable nitrogen in a dry-tropics grazing and a wet-tropics fertilized mixed land use catchment of the GBR.

Materials and methods The different bioavailable nitrogen pools and associated processes through which dissolved inorganic nitrogen (DIN) is generated from eroded sediment (mass of DIN generated per mass of sediment) were identified. These pools and processes were quantified from a range of representative sediment sources (e.g. surface and subsurface soil and different land uses). We collected 17 sediment source samples in the wet tropics and 41 in the dry tropics. We combined the N pool concentration data with spatial and hydrological fine sediment modelling to estimate the contribution from different sources and processes/pools to the end-of-catchment DIN load.

Results and discussion The modelled load of DIN generated from sediment accounted for all the monitored DIN load in the grazing-dominated catchment but was insignificant in the fertilized mixed land use catchment. Sediment from surface erosion (hillslope erosion) and some soil types contributed disproportionally to the modelled DIN generation. Fast solubilisation of DIN was the main process in the catchments studied. The importance of mineralisation of the organic fraction increased with the time the sediment was in suspension.

Conclusion Particulate nutrients in sediment are a significant source of bioavailable nitrogen in eroding grazing catchments. The processes that drive this bioavailability are complex, vary with sediment source and operate at different timeframes and spatial scales.

Keywords Sediment · Nutrients · Bioavailability · Rivers · Organic matter

1 Introduction

The use of land for agriculture has caused changes in the natural catchment fluxes of sediments and nutrients globally. Eutrophication of receiving waters is a worldwide phenomenon threatening the health and resilience of these ecosystems and ultimately the services they provide to humanity. In Australia, poor water quality induced by land use change is considered a major threat to the Great Barrier Reef (GBR), an ecosystem of global importance (Great Barrier Reef Marine Park Authority 2019). Sediments, nutrients and pesticides have been identified as the major pollutants causing a range of negative impacts to the GBR

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Phil Moody passed away before the publication of this paper.

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(Brodie et al. 2005; Wooldridge 2009; De'ath and Fabricius 2010; Fabricius et al. 2010, 2014, 2016; Lambert et al. 2021) and have been targeted for reduction. Although there is still debate about the nutrient status of the GBR and the relative importance of nitrogen (N) versus phosphorus (P) and their key sources (Brodie et al. 2011; Bell et al. 2014a, b; Furnas et al. 2014; Bell 2021), dissolved inorganic nitrogen (DIN), which is directly bioavailable to phytoplankton, is considered a nutrient fraction of high importance to target for reduction to increase the GBR resilience (Queensland Government 2013).

Historically, particulate nitrogen has received less attention and has had a lower target for reduction when compared to DIN (Queensland Government 2013). It has also been assumed that by targeting the largest sources of sediment, the largest sources of particulate nitrogen would be targeted. Nonetheless, it has previously been recognised that particulate nitrogen may provide an important source of bioavailable nitrogen to the GBR (Furnas et al. 2011; Brodie et al. 2015). Recent research in the GBR catchments has demonstrated that particulate nitrogen associated with sediment is bioavailable to phytoplankton, both in freshwater and marine water (Garzon-Garcia et al. 2018a, b, 2021). For example, previous work showed that during the few days that Burdekin riverine plumes take to enter coastal environments of the GBR, DIN generated from organic and particulate inorganic nitrogen associated with eroded sediment contributed an additional 9–30% to the end-of-catchment DIN load. These findings demonstrated that particulate nitrogen associated with eroded sediment generates bioavailable nitrogen (measured as generated DIN) as the sediments are eroded and transported through the catchment.

The bioavailability of particulate nutrients sourced from erosion in catchments depends on (a) source characteristics such as its parent soil, land use and erosion process (e.g. surface versus subsurface erosion) (Garzon-Garcia et al. 2018b) and (b) biogeochemical processes that operate on the sediment as it moves from its source to the end of catchment. These biogeochemical processes include solubilisation, desorption and mineralisation/immobilisation, which convert particulate N to forms that are readily available to primary producers [ammonium-N (NH_4-N), oxidized-N (NO_X-N) and some bioavailable fractions of dissolved organic N)].

Riverine-suspended sediment is a natural hotspot for microbial mediated N transformations and plays a crucial role in N transformations from the catchment source to the coastal environment (Xia et al. 2021; Huang et al. 2021). N transformation process rates have been shown to increase with a decrease in sediment particle size and an increase in the sediment carbon content (Wu et al. 2021; Xia et al. 2021).

In this research, we combined empirical data (laboratory generation of bioavailable N measured as DIN) with predictions from GBR Dynamic SedNet models (McCloskey et al. 2021a) representing a dry tropics catchment with land use dominated by grazing and a wet tropics catchment containing significant areas of fertiliser dependent cropping (primarily sugarcane) to quantify DIN generation from sediments as they are eroded and transported to the end-of-catchment monitoring site. We demonstrate that sediment is an important contributor to end-of-catchment DIN in dryland grazing catchments and that targeting the main sources of sediment does not necessarily target the main sources of 'DIN from sediment'.

2 Methods

2.1 Definition of bioavailable nitrogen pools generated from eroded sediment

A conceptual model was developed to define the main biogeochemical processes that produce dissolved inorganic nitrogen (DIN) when soil is eroded, fractionated into fine sediment and transported through catchments in rivers and into riverine plumes in estuaries and the coastal zone (DIN from sediment) (Fig. 1). To develop this model, we used our current understanding of the main bioavailable nitrogen (BAN) pools. These pools are differentiated by the timeframe in which the biogeochemical process that converts the particulate N into a bioavailable form operates, which also determines its spatial scale of importance.

The following processes were identified:

1. Solubilisation of DIN and dissolved organic N (DON) from eroded soil: This is a fast-occurring process at source in which the DIN (all the NO_3-N and the fraction of the NH_4-N not adsorbed onto sediment) and DON in the eroded soil pore water and/or leached from soil organic matter (i.e. vegetation litter) enter the aquatic environment via runoff. These fractions will be transported to the stream system irrespective of the bulk soil being delivered. This is why these parameters were measured on the parent soil sample (see Section 2).
2. Particulate organic N (PON) mineralisation: This is a slow-occurring process with a timeframe of days to weeks (e.g. varies depending on catchment size or length of time sediment is in suspension in a riverine plume) in which the particulate organic N fraction of eroded sediment (after fractionation to fines) is mineralised to DIN during stream transport by the action of micro-organisms (bacteria and fungi). This process would continue to occur in sediment plumes as they enter the estuarine and coastal environment (Garzon-Garcia et al. 2021).
3. DON mineralisation: This is a slow-occurring process with a timeframe of days to weeks in which the organic fraction of dissolved N that has been solubilised or

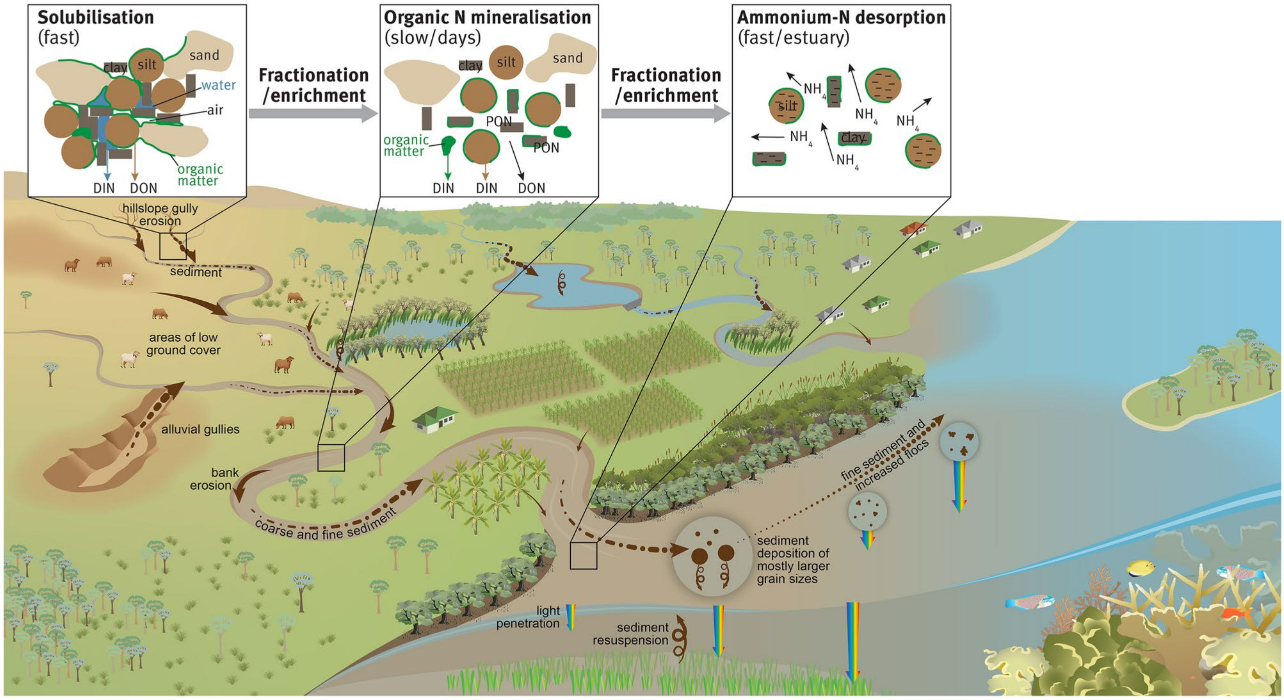


Fig. 1 Conceptual diagram depicting the key processes underlying the generation of dissolved inorganic nitrogen from eroded soil in water. (Baseline map courtesy of NESP sediment synthesis project 6.4)

leached from eroded soil is mineralised to DIN during stream transport by the action of micro-organisms. This process would continue to occur in sediment plumes as they enter the estuarine and coastal environment.

4. Particulate inorganic N (PIN) desorption: This is a physico-chemical process in which the ammonium (NH_4^+-N) adsorbed to the negatively charged silt and clay particles in eroded fine sediment is desorbed (release into solution) through cation exchange processes (e.g. exchange of ammonium with dissolved cations present) in water. This process would tend to occur when terrestrial sediment enters saline water in the estuaries. PIN would be measured as a component of particulate N at end-of-catchment sites if these are upstream from the estuary.

2.2 Catchment study sites

The study was undertaken in two GBR catchments: one in the wet tropics, viz. Johnstone River catchment; and one in the dry tropics, the Bowen River catchment (Supplementary material S1). The Johnstone River catchment has the following dominant land uses: conservation (55%), cattle grazing (23%), sugar cane (12%) and banana (2.5%) (Department of Environment and Science 2016). The Johnstone River catchment was selected as it is a representative wet tropics catchment with high levels of fertiliser use for agriculture. The Bowen River catchment is predominantly cattle grazing land (87%) with some area in conservation (9%) (Department of Environment and Science 2016). The Bowen River catchment was selected as it is the subcatchment of the Burdekin River that delivers the most sediment to the GBR, delivering around 45% of the annual fine (< 63 µm) total suspended solid load from the Burdekin River (Bainbridge et al. 2014).

Parent soil sampling (58 soils) was carried out to cover a range of major soil types, geologies, the predominant catchment land uses and various erodibilities as part of a previous study (Garzon-Garcia et al. 2018b). A total of 17 soil samples were collected during the first week of March 2016 from the Johnstone River catchment, and a total of 41 samples were collected during the third week of April 2016 from the Bowen River subcatchment. This resulted in nine combinations of soil type, land use and erodibility for the Bowen River catchment and six combinations of soil type and land use for the Johnstone River catchment (Table 1). Erodibility was rated from the major soil attributes that contribute to a soil being vulnerable to erosion (Zund and Payne 2014). Surface soil samples (0–10 cm) were collected at all sampling points after removing vegetation, loose leaves and woody litter from the surface. Subsurface soil samples were taken at sampling points of high erodibility (Bowen River catchment only) by sampling all vertical strata differentiated by soil colour on an exposed gully bank. Samples from each stratum were integrated. Each combination was sampled

Table 1 Parent soil sampling site characteristics in the Johnstone River and Bowen River catchments

Catchment	Soil types[a]	Erodibility class	Land use	Geology	Number of samples[b]
Johnstone	Ferrosol (FE)	High	Dairy	Basalt	3
		Moderate	Sugar cane	Basalt	3
		High	Native forest	Basalt	3
		Low-moderate	Banana plantations	Basalt	3
	Dermosol (DE)	Low	Sugar cane	Alluvium	3
		Low-moderate	Banana plantations	Alluvium	2
Bowen sub-catchment	Vertosol (VE)	High	Grazing native	Alluvium, arenite-mudrock, sandstone	6
		Low	Grazing native	Basalt, colluvium	4
	Sodosol (SO)	High	Grazing native	Sedimentary (sandstone/mudstone)-labile mudstone	7
		Low	Grazing native	Granitoid, sedimentary (sandstone)	3
	Chromosol (CH)	High	Grazing native	Alluvium	6
		Low	Grazing native	Granitoid-metamorphic	2
	Dermosol (DE)	High	Grazing native	Arenite-mudrock	7
		Low	Grazing native	Arenite-mudrock	3
		Low	Native forest	Granitoid	3

[a]The Australian Soil Classification (Isbell 2016)

[b]Samples for high erodibility soils in the Bowen subcatchment include both surface and subsurface soils

across each catchment in triplicate, except in a few cases where circumstances prevented this collection. Streambank samples were not collected in the Johnstone River catchment due to operational difficulties in obtaining samples from this source of sediment. For details on parent soil sample collection methods, see Garzon-Garcia et al. (2018b). See Supplementary material (S1) for the location of sampling sites. Additionally, fine sediments were generated from each soil sample by fractionation to < 10 µm using settling columns. This size fraction (clays and fine silt) was selected as it is the dominant fraction transported to the GBR lagoon in large events (Bainbridge et al. 2012). For details on the fractionation method, see Garzon-Garcia et al. (2018b).

2.3 Quantification of BAN pools

BAN pools associated with the identified processes (Fig. 1, Table 2) were quantified in the laboratory. Pools relevant to catchment processes and PIN desorption were quantified for each relevant soil × land use combination for each of the two catchments (Bowen River catchment and Johnstone River catchment) on either parent soil or both the parent soil and < 10 µm corresponding sediment depending on the pool being quantified (Table 2). In addition to BAN pools, total nitrogen (TN) was also quantified on the < 10 µm sediment samples. All BAN pools are reported as mg DIN per kg of sediment. Average BAN pools for all soil/sediment types can be seen in Supplementary material (S2).

2.3.1 DIN solubilisation (catchment)

Parent soils were sieved to < 2 mm, dried at 40 °C in the oven and then extracted with deionised (DI) water using a 1:10 soil-to-water ratio (for 1 h at 25 °C and 15 rpm in an end-over-end shaker). The suspension was centrifuged at 4300 rpm for 20 min and then filtered (0.45 µm) to quantify oxidized-N (NO_x-N) and water-soluble ammonium (NH_4^+-Nsol) which added together are referred to as 'DIN

Table 2 BAN pools and the processes that produce them

Process[a]	BAN pool/method
DIN solubilisation (catchment, parent soil)	Oxidized N + soluble ammonium (NOx-N + NH_4-Nsol)
PON mineralisation (catchment, all fractions)	Potential mineralisable N in 1, 3 and 7 days (PMN1, PMN3, PMN7)
DON mineralisation (catchment, parent soil)	Bioavailable DON (DONb)
PIN desorption (estuary, all fractions)	Adsorbed ammonium (NH_4-Nad)

[a]In parenthesis, it is specified where the process generates BAN (measured as DIN) and the fractions (parent soil or fine sediment) for which the process was quantified

solubilisation'. This method was adapted from the Potential Mineralisable Nitrogen in soils method (Bremner 1965).

2.3.2 PON mineralisation (catchment)

PON catchment mineralisation potential was quantified on the < 10 µm sediment types for all sediment samples (58) by quantifying the potentially mineralisable N as follows:

Oven-dried (40 °C) sediment samples were incubated using a 3:10 sediment to DI water ratio under aerobic conditions at 25 °C for 0, 1, 3 and 7 days, respectively. This sediment-to-water ratio generates thick slurries that would simulate the order of magnitude of fine sediment concentration in the Johnstone and Bowen rivers (Garzon-Garcia et al. 2018b). The amounts of mineral-N (NO_x-N + NH_4-N) formed at different times were measured by adding an aliquot of 3 M KCl solution to give a 1:10 sediment/solution ratio in a 2 M KCl solution. Potentially mineralisable-N at any time during the incubation is calculated as the difference between the mineral-N before and after the incubation. Considering that the water travel time in the Johnstone and Bowen River catchments during typical high-flow events is of the order of 1 day; the potential mineralisable-N (PMN) used in our analysis was that produced after 1 day of incubation (PMN1). This method is an adaptation to sediment of the method described by Bremner (1965), to provide an index of plant-available soil N.

PMN results were negative in fine sediments containing high concentrations of NO_x-N at day 0 of the incubation (20 of the 58 sediments analysed) (Supplementary material S3). This indicates that when there are readily bioavailable sources of N, there is no net mineralisation of organic N. Considering that the NO_x-N would be diluted out during transport, to obtain the true mineralisation potential of sediment, it was necessary to wash the NOx-N out of these sediments (20 sediments) and carry out the PMN incubations once again. The procedure to remove the NO_x-N was to shake 3 g of the sediment with high initial NO_3-N content in a tube with 30 mL of DI water for 20 s by hand. The suspension was then centrifuged at 4300 rpm for 20 min, and the supernatant was poured off. The wet recovered sediment weight was recorded to quantify the weight of water present and considered for the PMN incubation procedure which followed.

2.3.3 DON mineralisation (catchment)

Twenty soils were selected, one from each of the 15 combinations of soil type and land use in each of the Bowen and Johnstone River catchments (Table 1) with both surface and subsurface soils included for the high erodibility soils. To generate the DON sample from each soil, 100 g of < 2 mm oven-dried (40 °C) soil was suspended in 1.8 L of DI water in settling columns by agitating for 1 min after a 2-min sonication bath. The suspension was allowed to settle for 48 min after which the supernatant was recovered, centrifuged for 20 min at 4300 rpm and filtered to < 0.45 µm. The filtrate from each soil type (in duplicate) was recovered and incubated for 7 days at 25 °C in the dark. Destructive sampling was used to recover a sample for laboratory analysis of all carbon, nitrogen and phosphorus fractions at 0, 1, 3 and 7 days. The data were analysed to quantify the amount of the DON present at day 0 that was lost to net mineralisation in 1 day (difference between the mineral-N at day 1 and mineral-N at day 0), assuming this is the order of magnitude of the typical travel time of water in the Johnstone and Bowen River catchments. This was considered the labile fraction of DON (DON_b) available to microbial mineralisation.

2.3.4 PIN desorption (estuary)

PIN desorption is the adsorbed ammonium that would be displaced, by exchange, into solution by the high Na^+ ion concentration of sea water. Adsorbed ammonium (NH_4-Nad) was quantified on the < 10 µm sediment types (oven-dried (40 °C) sediment) by extracting with a 2 M KCl solution using a 1:10 soil to extractant solution ratio (for 1 h at 25 °C and 15 rpm in an end over end shaker) (Rayment and Lyons 2011) (method 7C2). The suspension was centrifuged at 4300 rpm for 20 min and then filtered (0.45 µm). The extracted NH_4^+-N was directly measured on the filtrate using the APHA/AWWA/WPCF (2012) method 4500-NH_3G. The adsorbed NH_4^+-N (NH_4^+-Nad) was calculated by subtracting the water-soluble NH_4^+-N measured on the < 10 µm sediment from the extracted NH_4^+-N. The former was measured after an extraction with deionised (DI) water using a 1:10 soil-to-water ratio (for 1 h at 25 °C and 15 rpm in an end-over-end shaker). The suspension was centrifuged at 4300 rpm for 20 min and then filtered (0.45 µm) to quantify water-soluble ammonium (NH_4^+-Nsol).

2.4 Analytical methods

Total nitrogen in the < 10 µm sediment was analysed using an automated segmented-flow colorimetric procedure following a Kjeldahl digestion (Rayment and Lyons 2011) (method 7A2). Analytical methods used for water samples were as follows (APHA/AWWA/WPCF 2012): total organic carbon (TOC) and dissolved organic carbon (DOC) determined using an automated carbon analyser by combustion at 680 °C over a platinum catalyst in accordance with method 5310 D (uncertainty = ± 8%); total Kjeldahl nitrogen (TKN), total Kjeldahl phosphorus (TKP), dissolved Kjeldahl nitrogen (DKN) and dissolved Kjeldahl phosphorus (DKP) determined according to methods 4500-Norg D and 4500-P B (using a catalysed acidic block digestion with colorimetric segmented flow analyser finish) (uncertainty = ± 12%); ammonium nitrogen (NH_4-N), nitrogen oxides (NO_x-N) and phosphate phosphorus (PO_4-P) determined colorimetrically by segmented flow analyser according to methods 4500-NH3, 4500-NO3 and 4500-P (uncertainty = ± 8%), respectively.

2.5 Data analysis and assumptions

2.5.1 Enrichment ratios

Enrichment ratios for TN and the BAN pools associated with all soil fractions (adsorbed ammonium, PMN1, PMN3 and PMN7) were calculated by dividing the pool value present in the < 10 µm sediment by the pool value present in the corresponding parent soil.

2.5.2 PON mineralisation rates

Net PON mineralisation rates were obtained for each sediment type (from PON mineralisation incubations) by iteratively fitting a linear first-order decay model with one pool or an exponential first-order decay model with two pools [a labile and a recalcitrant pool (N mineralisation rate of 0 for the timeframes considered)], which ever had a better fit to the DIN concentrations generated during the incubations (Qualls and Haines 1992; Kalbitz et al. 2003; McDowell et al. 2006). The models were fitted using the growth rate package in R (Petzoldt 2018).

$$\mathrm{DIN}_t = \mathrm{DIN}_o + \mathrm{PON}_o \times k_m \times t \tag{1}$$

$$\mathrm{DIN}_t = \mathrm{DIN}_o + a \times \mathrm{PON}_o \times \left[1 - e^{-k_m \times t}\right] \tag{2}$$

where t = time (days), a is the fraction of organic N in the labile fraction, k_m is the net DIN generation rate (day^{-1}), DIN_t is the DIN present at any time (mg l^{-1}), DIN_0 is the DIN present at the start of the incubation (mg l^{-1}) and PON_0 is the particulate organic N at the start of the incubation (mg l^{-1}).

2.5.3 Catchment sediment DIN generation loads

The average particulate nitrogen (PN) and BAN pools for all sediment types (Supplementary material S2) were used to generate a spatial layer for each of the PN and the BAN pools (mass content per unit mass of sediment). The BAN pools added together account for the total BAN from sediment. The map calculator conditional function in ArcMap was used to apply the corresponding value depending on soil type and land use. For the Bowen catchment, a layer for PN and each BAN pool was generated for each of surface and subsurface sediment. For the Johnstone catchment, which is not affected by subsurface erosion processes, only contributions from surface (hillslope) erosion were quantified. The generated layers (PN, DIN solubilisation, PON mineralisation, DON mineralisation and PIN desorption) interacted with the GBR Dynamic SedNet (McCloskey et al. 2021a) fine sediment generation model (P2R sediment model) (< 20 µm) to generate a load of PN and a load of each of the BAN pools (Table 1) from each modelled subcatchment and erosion process (i.e. surface and subsurface) in the catchments (BAN model). The GBR Dynamic SedNet catchment models are built on eWater Source—Australia's National Hydrological modelling platform (McCloskey et al. 2021a). This framework allows to simulate how catchment and climate variables (i.e. rainfall, land use and cover) can affect runoff, constituent generation and transport (McCloskey et al. 2021a). The model operates on a daily time-step; catchment area delineation is of ~ 65 km^2 and is spatially distributed. The model is run for a fixed 28-year climate period (1986–2014) to normalise the effects of climate variability on constituent loads being exported to the GBR for each catchment. This period also aligns with the availability of remote sensing data relating to ground cover, which is an important data input for calculating hillslope erosion.

We acknowledge that the PN and BAN pools were measured on < 10 µm sediment, a slightly smaller fine fraction than the modelled fraction. The PN and BAN pools were measured on sediment obtained from soil samples taken during a below-average rainfall year in the Johnstone River catchment and an average to below average rainfall year in the Bowen River catchment. We acknowledge the role that antecedent soil moisture conditions have on bioavailable nutrient pools in soils but believe that our samples represent a near average condition, also considering that they were taken towards the end of the wet season when the soils are at their highest moisture content and that all the samples were oven-dried (40 °C) before analysis. Using legacy data from a previous study (Garzon-Garcia et al. 2018b) presented a great opportunity to estimate the order of magnitude of the DIN from sediment contribution, and results from this study should be considered as such. The modelled BAN pool loads were added together, except for PIN desorption which would occur in the estuary, to account for the catchment DIN from sediment load. The output from this model was compared with the contemporary DIN GBR Dynamic SedNet (McCloskey et al. 2021b).

The following parameters, specifications and assumptions were used to run the models:

- Delivery ratios of sediment to the stream network were 100% from gully erosion and streambank erosion, 10% from hillslope erosion in the Bowen River catchment, 15% from sugarcane in the Johnstone River catchment and 20% from other land uses in the Johnstone River catchment.

- Delivery ratios of soluble N were 100%.
- The model was run for 28 years (1986–2014), a range representing average, dry and wet periods.
- Specific settings used for parameter generation, delivery to stream and instream transport can be seen in Supplementary material S3.
- In the absence of BAN pool data for certain soil types in the Bowen catchment (a very small fraction), considering similarities in granulometry (texture) or soil forming processes: Calcarosols were assumed to have similar contents to Vertosols; Kandosols with heavy granulometry (SL, SCL, LS) as Sodosols; Kandosols with light granulometry (CL) and Ferrosols as Ferrosols from cane and banana in the Johnstone; and Kurosols as Sodosols. For Rudosols, Tenosols, subsurface Kandosols with light granulometry (CL) and subsurface Ferrosols, an average of the other soil types was used.[1]
- In the absence of BAN pool data for certain soil types or land uses in the Johnstone catchment: It was assumed that all land use classified as 'grazing modified pastures' had similar content to dairy soils in Ferrosols; land use classified as 'nature conservation' + 'managed resource protection' + 'other minimal use' had similar content to forest soils. It was also assumed that Dermosols and Kandosols in forests have similar content to Dermosols in forests of the Bowen catchment. For the rest of the soil types × land uses with no data, it was decided not to model the BAN contribution due to large uncertainty in the assumptions (11% of catchment area). The outputs from the Johnstone model were only analysed for the catchment areas with information.

Previous sediment tracing studies in the Bowen River catchment have reported significantly different source contributions compared to modelling studies (Wilkinson et al. 2015). Therefore, in addition to modelling long-term average sediment source contribution to the total DIN from sediment load in the Bowen River catchment, sediment contributions from radioisotope tracing studies (Wilkinson et al. 2015) were also used to calculate the DIN from sediment load generated from the catchment. To do so, the average DIN from sediment generated per kg of sediment was calculated from the BAN model outputs for gully, riverbank and hillslope sources in the catchment. BAN contributions generated from subsurface erosion sources (gully and riverbank) were allocated based on sediment tracing studies showing 83% and 93% subsurface erosion contribution reported after a period of below and above average rainfall for the Bowen River catchment, respectively (Wilkinson et al. 2015).

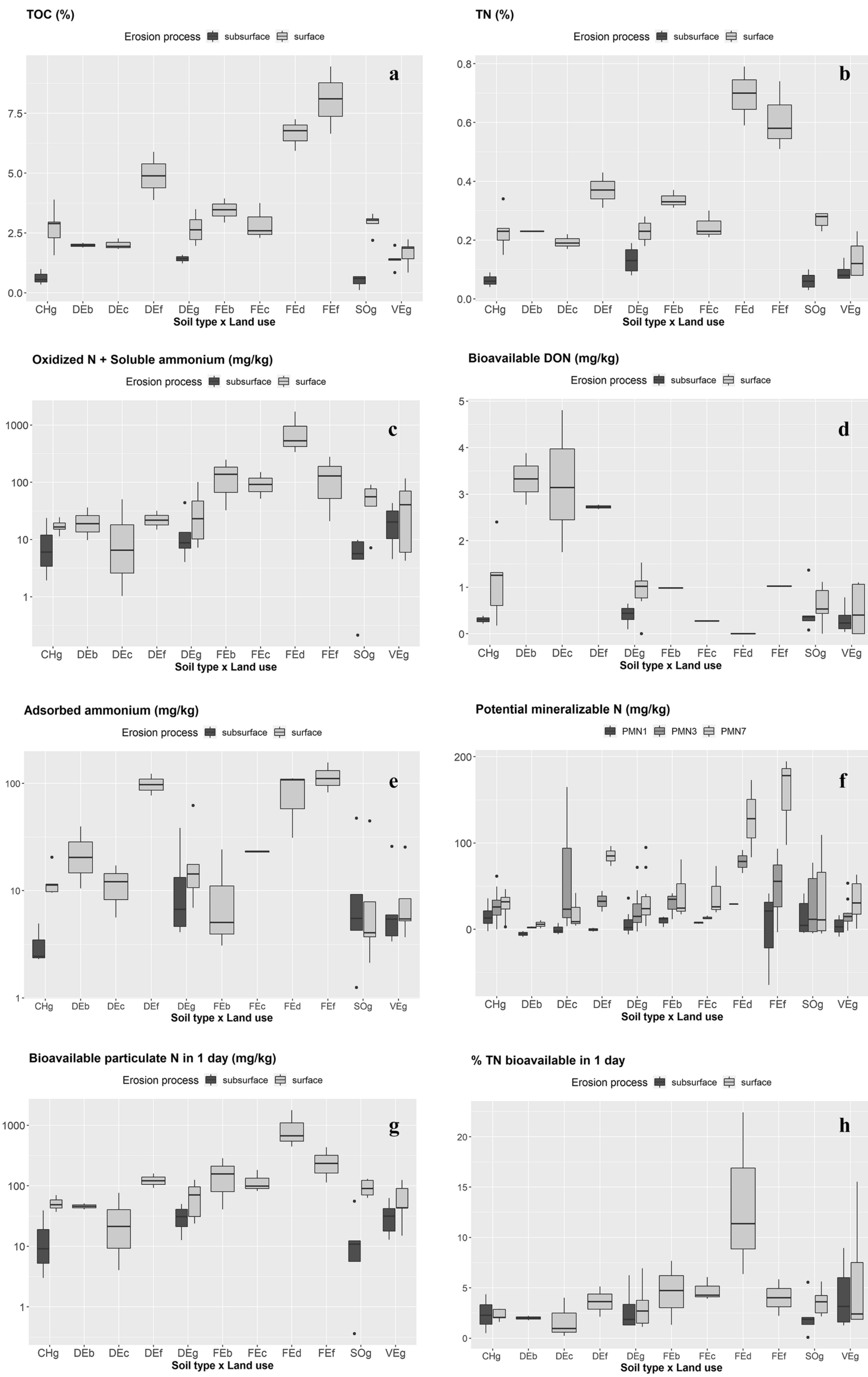
[1] SL: sandy loam, SCL: sandy clay loam, LS: loamy sand; CL: clay loam.

3 Results

3.1 BAN distribution in soils and sediments

The TN and bioavailable particulate nitrogen (BAN) pool content of eroded sediment varied widely between different sediment types (e.g. soil types, land uses and erosion processes) (Fig. 2). Surface sediments generally had higher BAN content (Fig. 2g) than their corresponding subsurface sediments, though for some specific BAN pools and soil types, there was no significant difference (i.e. adsorbed ammonium in Sodosols). There was clearly higher BAN content in sediments from some land uses/soil types. Overall, BAN was higher in Ferrosols and in forest sediments (Rashti et al. 2023). Ferrosols used for dairy production in the 'wet tropics' catchment had the highest BAN content of all. Interestingly, Chromosol and Sodosol subsurface sediments, which are highly erodible and dispersive, had the lowest BAN content. DIN solubilisation (oxidized N + soluble ammonium N) and adsorbed ammonium-N were important pools contributing to total BAN from soils/sediments. Potential mineralisable-N tended to increase its contribution with timeframe for mineralisation (Fig. 2f). An exponential first-order decay model with two pools (a labile and a recalcitrant pool) was the best model describing net mineralised DIN in lab incubation experiments for most sediment types. This means that DIN generation tended to slow down and stabilise towards the end of the 7-day incubation. The mineralisation rates and organic N labile fraction for each sediment type can be observed in Fig. 3 and Supplementary material S4 (see also significance of slope and linear/exponential model fit). The generated DIN depended not only on the mineralisation rate, but also on the size of the organic N labile fraction. The total BAN generated in 1 day as a percent of the TN content of the sediment varied between soil types and land uses from 1 to 25% (Fig. 2h). This proportion increases with timeframe for bioavailability.

TN and BAN pools in the < 10 µm fine sediment fraction tended to be enriched relative to its parent soil (Fig. 4). Surface soils (Bowen and Johnstone catchments) tended to have larger TN enrichment ratios (1.0–3.8) than subsurface soils (Bowen catchment only) (1.0–2.0), and enrichment ratios varied between soil types. Adsorbed ammonium-N was on average 4.3 and 5.5 times higher in the < 10 µm surface sediment compared to its parent soil in the Johnstone and Bowen River catchments, respectively (Garzon-Garcia et al. 2018b). It was on average 7 times higher in the < 10 µm subsurface sediment compared to its parent soil in the Bowen River catchment. The potential mineralisable N in the < 10 µm did not have a clear trend towards enrichment relative to its parent soil. In some cases, there was enrichment, but in other cases, the parent soil had higher potential mineralisable N.


TOC (%)
Erosion process subsurface surface
a
0.0 2.5 5.0 7.5
CHg DEb DEc DEf DEg FEb FEc FEd FEf SOg VEg
Soil type x Land use
TN (%)
Erosion process subsurface surface
b
0.0 0.2 0.4 0.6 0.8
CHg DEb DEc DEf DEg FEb FEc FEd FEf SOg VEg
Soil type x Land use
Oxidized N + Soluble ammonium (mg/kg)
Erosion process subsurface surface
c
1 10 100 1000
CHg DEb DEc DEf DEg FEb FEc FEd FEf SOg VEg
Soil type x Land use
Bioavailable DON (mg/kg)
Erosion process subsurface surface
d
0 1 2 3 4 5
CHg DEb DEc DEf DEg FEb FEc FEd FEf SOg VEg
Soil type x Land use
Adsorbed ammonium (mg/kg)
Erosion process subsurface surface
e
1 10 100
CHg DEb DEc DEf DEg FEb FEc FEd FEf SOg VEg
Soil type x Land use
Potential mineralizable N (mg/kg)
PMN1 PMN3 PMN7
f
0 100 200
CHg DEb DEc DEf DEg FEb FEc FEd FEf SOg VEg
Soil type x Land use
Bioavailable particulate N in 1 day (mg/kg)
Erosion process subsurface surface
g
1 10 100 1000
CHg DEb DEc DEf DEg FEb FEc FEd FEf SOg VEg
Soil type x Land use
% TN bioavailable in 1 day
Erosion process subsurface surface
h
0 5 10 15 20
CHg DEb DEc DEf DEg FEb FEc FEd FEf SOg VEg
Soil type x Land use

◂**Fig. 2** **a** Total organic carbon, **b** total nitrogen, **c**–**f** BAN pools, **g** total BAN in 1 day, and **h** percent TN bioavailable in 1 day, in surface and subsurface < 10 µm sediment from different land use × soil type combinations in the Bowen River and Johnstone River catchments. First two letters stand for soil type: CH (chromosols), DE (dermosols), FE (ferrosols), SO (sodosols) and VE (vertosols) (see Table 1), and lowercase letter to land use: g (grazing), b (banana), f (forest), c (sugar cane) and d (dairy). See Table 1 for number of samples in each category. High and low erodibility soil samples are included in each soil type and land use combination

3.2 DIN load generated from eroded sediment in a dry grazing catchment (Bowen River catchment)

In the next sections, we generally refer to this paper's new BAN modelled results, and when comparing to previously modelled results without BAN data, we refer to the 'currently modelled' outcomes. Modelled DIN from sediment at the Bowen River end-of-catchment was 130 t N year^{-1} on average for the 28-year modelled period (1986–2014). The load was generated from the three identified DIN generating processes associated with erosion that occur in the catchment (DIN solubilisation + PON mineralisation + DON mineralisation). This was approximately 1.6 times the currently monitored DIN load of 85 t N year^{-1} [2012–2021 (Wallace et al. 2014, 2015; Garzon-Garcia et al. 2015; Queensland Government 2018)] and 1.3 times the currently modelled DIN load of 100 t N year^{-1} (Bartley et al. 2017). The DIN from sediment contributed to coastal waters (beyond end-of-catchment) includes an added 25.8 t N year^{-1} from PIN desorption on average. The GBR Dynamic SedNet model indicates that gully erosion is on average the main source of sediment (62% contribution) followed by hillslope erosion (33% contribution) (Fig. 5a). Modelling results for the 28-year modelled period based on this distribution of sediment sources indicated that the main source of PN is hillslope erosion (56% contribution) and that the main source of DIN producing sediment is also hillslope erosion (87%) (Fig. 5b, c).

DIN solubilisation is the main process contributing to the generation of the end-of-catchment DIN load from sediment. This process makes up more than 70% of the DIN load from sediment contributed by hillslope erosion and a little over 50% of the load contributed by gully erosion (Fig. 5d). PIN desorption is an important process contributing more than 30% of the DIN generation load from gully erosion and more than 10% of the load from hillslope erosion, where the mineralisation of DON was of similar importance. PIN desorption will occur when the sediment enters a high salinity environment in the river estuary (Garzon-Garcia et al. 2021). PON mineralisation was not such a significant contributor to the end-of-catchment Bowen River DIN load.

Sediment tracing studies carried out in the Bowen River catchment have indicated that the contribution of subsurface erosion (gully and streambank erosion) to sediment export may be larger than the average P2R model estimates of 68% (Fig. 5a) (Wilkinson et al. 2015). When we adjusted our results using the tracing data scenarios (83% and 93% subsurface erosion contribution), the total catchment exported DIN from sediment drastically reduced in both scenarios, to 96 t year^{-1} in the former and 58 t year^{-1} in the latter. The 83% and 93% subsurface erosion contributions were reported after a period of below and above average rainfall, respectively (Wilkinson et al. 2015). The main DIN generation source would continue to be surface erosion (hillslope) for the 83% subsurface contribution scenario but would change to be equivalent between surface and subsurface erosion (gully and streambank) sources for the 93% subsurface contribution scenario (Fig. 5e).

3.3 DIN load generated from eroded sediment in a fertilised cropping catchment (Johnstone River catchment)

In contrast to the Bowen River catchment results, the BAN model outputs indicate that DIN generation associated with sediment erosion and transport is not significant in the Johnstone River catchment. Modelled DIN at end-of-catchment from the three identified DIN generating processes associated with erosion that occur in the catchment (DIN solubilisation + PON mineralisation + DON mineralisation) was 35 t year^{-1} on average for the 28-year modelled period (1986–2014). This is approximately 9% of the currently monitored DIN load at the end-of-catchment of 390 t year^{-1} (Wallace et al. 2014, 2015; Garzon-Garcia et al. 2015; Queensland Government 2018) and 4% of the currently modelled DIN load at the end-of-catchment of 857 t year^{-1} (McCloskey et al. 2021b). The DIN from sediment contributed to coastal waters (beyond end-of-catchment) includes an added 1.8 t N year^{-1} from PIN desorption on average. The GBR Dynamic SedNet model indicates that for the 28-year modelled period, streambank erosion is on average the main source of sediment at the end-of-catchment (72% contribution) followed by hillslope erosion (27% contribution). The main source of PN at the end-of-catchment was hillslope erosion (66% contribution), with minor contributions from other sources of erosion.

Although streambank erosion is an important source of sediment in this catchment, for this case study, we concentrated on understanding the contributions of the main land uses in the catchment (bananas, conservation, dairy and sugarcane) to hillslope erosion DIN from sediment export. This erosion process is the main source of PN in the catchment (contributing 66% of the PN) (Bartley et al. 2017). The P2R sediment model estimated that on average 71% of the sediment and 48% of the PN in the catchment are sourced from these land uses and erosion process. Conservation was the main source of hillslope

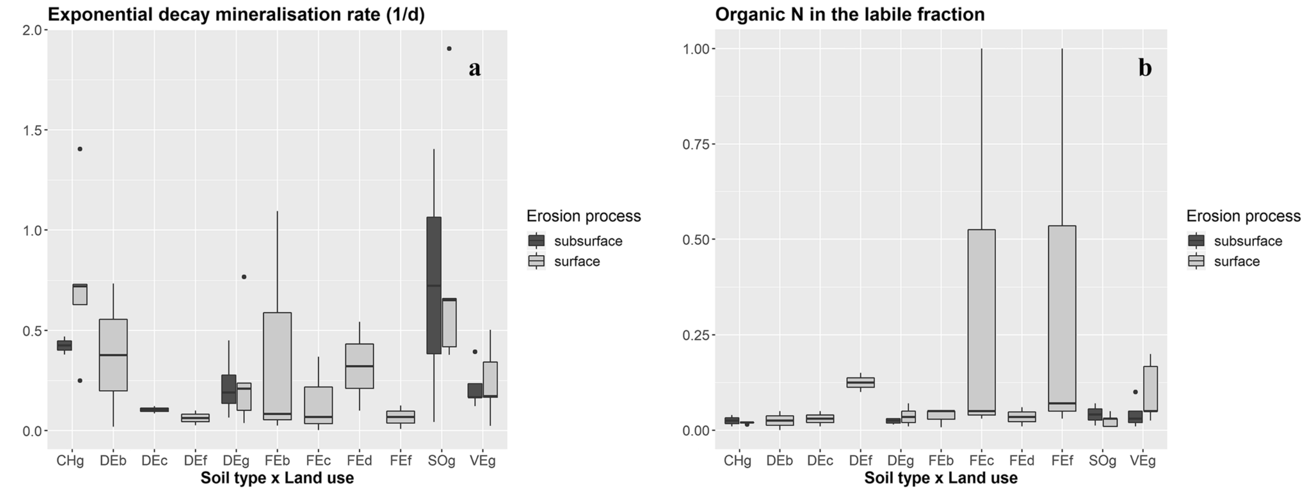


Fig. 3 Exponential first-order decay model with two pools (a labile and a recalcitrant pool) fitted parameters: **a** mineralisation rate k_d and **b** organic N fraction a, in surface and subsurface < 10 µm sediment from different land use × soil type combinations in the Bowen River and Johnstone River catchments. First two letters stand for soil type: CH (chromosols), DE (dermosols), FE (ferrosols), SO (sodosols) and VE (vertosols) (see Table 1) and lowercase letter to land use: g (grazing), b (banana), f (forest), c (sugar cane) and d (dairy)

erosion sediment at end-of-catchment (46% contribution) followed by sugarcane (35%) (Fig. 6a). The modelling results based on this distribution of sediment sources indicated that the main source of PN at the end-of-catchment among the considered land uses is sugarcane (66%) (Fig. 6b). Although conservation and sugarcane dominated sediment export, and sugarcane alone dominated PN export, BAN modelling results for the 28-year modelled period indicated that dairy may be an important source of DIN from sediment at the end-of catchment (39% contribution) together with sugarcane (44% contribution) (Fig. 6c). Previous research using tracing methods has identified rainforest as the main contributor of PN to the bed sediment of the upper Johnstone River (Bahadori et al. 2020). On the other hand, they found the largest contributor of PN to be banana land use followed by sugarcane for the lower Johnstone riverbed sediment. These discrepancies may relate to the fact that our modelling exercise considers only the fine fraction contribution (< 20 µm), which would be in suspension at the end of catchment, and it also estimates a long-term average (30 years). Additionally, Bahadori et al. (2020) sampled riverbed sediment, which would be representative of what settles at that point in the catchment (dependent on suspended sediment particle size distribution) and of shorter-term sediment accumulation and sourcing (according to sediment sampling methods used). In addition to this, the tracing paper does not produce estimates of contributions to load export, but this paper does.

DIN from sediment yields (kg DIN generated from eroded sediment per hectare per year) in the Johnstone River catchment were much higher than in the Bowen River catchment, which indicates higher bioavailability of N in these sediments (Figs. 5f and 6d). The higher bioavailability of this sediment could be due to the quality of this sediment, which sourced from the A horizon and not subsurface horizons like in the Bowen River catchment, has higher organic matter, bacterial biomass and nutrients in excess (also from fertilisation).

Similar to the findings for the Bowen River catchment (Fig. 5d), DIN solubilisation is the main process contributing to DIN generation from eroded soils. In the Johnstone River catchment, this contribution is even more striking with more than 80% of the DIN from sediment coming from this process in bananas, dairy and sugarcane land uses (Fig. 6e). PIN desorption was not as important relative to other processes generating DIN from sediment in the Johnstone catchment, except for conservation areas where around 25% of the DIN from sediment would be generated from this process. DON mineralisation contributed around 10% of the DIN from sediment coming from conservation and sugarcane land uses.

4 Discussion

4.1 Catchment sources of sediment, PN and DIN from sediment

Using a combination of empirical data and modelling, we have demonstrated that the main sources of sediment contributing to catchment export are not necessarily the main sources of DIN from sediment. The main reason for this is the interaction between soil type, land use and erosion process in controlling sediment quantity (Hunter and Walton 2008; Porto et al. 2009) and sediment quality (Bartley et al. 2017; Garzon-Garcia et al. 2018b; O'Mara et al. 2019). Differences in enrichment of PN and BAN in

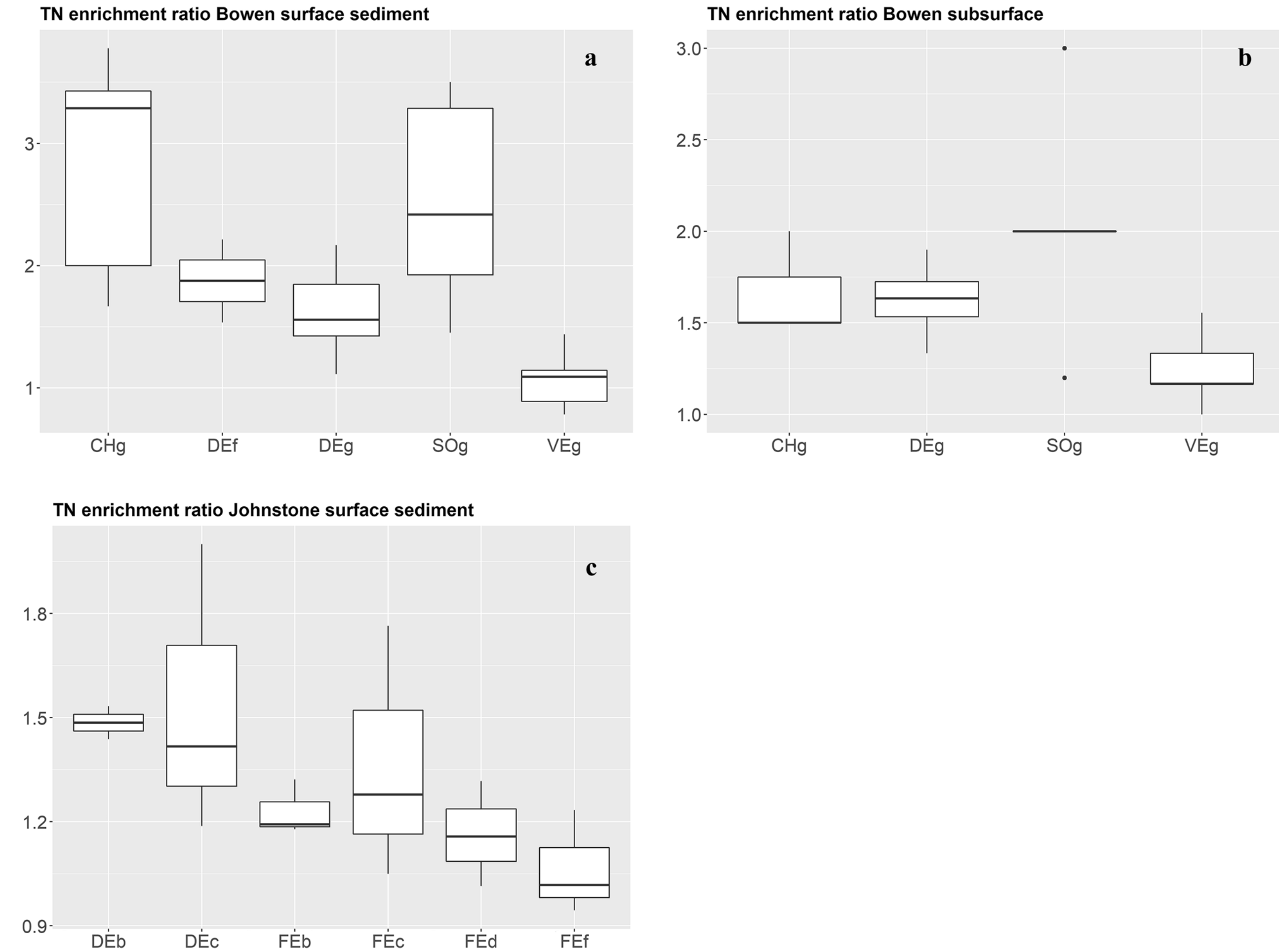


Fig. 4 Enrichment ratios between parent soil and < 10 µm sediment for different **a** surface and **b** subsurface soil types in the Bowen River catchment and **c** surface soil types in the Johnstone River catchment. First two letters stand for soil type: CH (chromosols), DE (dermosols), FE (ferrosols), SO (sodosols) and VE (vertosols) (see Table 1) and lowercase letter to land use: g (grazing), b (banana), f (forest), c (sugar cane) and d (dairy)

the fine fraction of sediment between different soil types and between sediments sourced from different erosion processes (e.g. surface versus subsurface erosion) would also have a significant role in determining the areas of the catchments that export more PN and BAN (Horowitz and Elrick 1987; Mayer et al. 1998). When evaluating and prioritising contributions to PN and BAN from erosion, the content of PN and BAN in different sediment types (soil type × land use × erosion process) and quantity of eroded sediment from each type should be considered.

The BAN model outputs indicate that DIN generation associated with sediment erosion and transport is significant in the Bowen River catchment and that all the currently modelled end-of-catchment exported DIN (Bartley et al. 2017) can be accounted for by the DIN generated from sediment. It is worth noting here that the current DIN model for this catchment uses a simple event mean concentration/dry weather concentration approach that does not allocate DIN generation to any process (McCloskey et al. 2021b). DIN generation from the BAN model is larger than the DIN modelled value at end-of-catchment (1.3 times the currently modelled DIN load, 1.6 times the monitored DIN load). This may be explained by the fact that stream processing and system losses are not explicitly represented in the models (e.g. denitrification), but the current DIN GBR Dynamic SedNet model is adjusted to match monitoring data, which was not done for our BAN model. It has been estimated that from 30 to 70% of the N input to rivers is emitted as N_2 to the atmosphere (Galloway et al. 2004) and that in many cases, these estimates may have been underestimated (Liu et al. 2013; Xia et al. 2018). Additionally, some of the BAN model assumptions need to be further revised including if fine

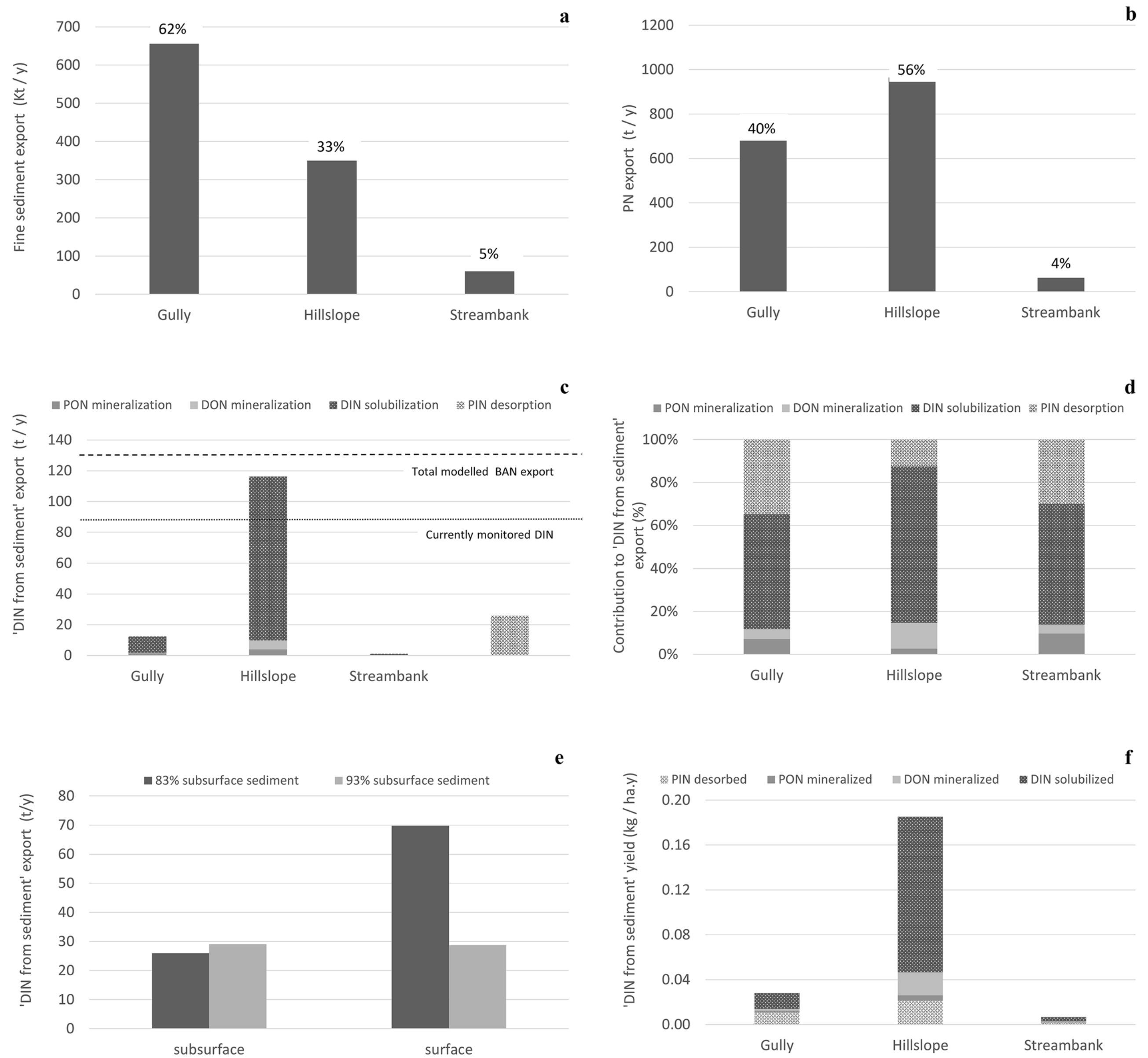


Fig. 5 Bowen River end-of-catchment average modelled main sources of **a** fine sediment (<20 μm), **b** PN and **c** 'DIN from sediment' by DIN generation process; **d** average modelled percent contribution to DIN from sediment by DIN generation process, **e** 'DIN from surface and subsurface sediment' for two subsurface sediment contribution scenarios (83% and 93%) based on tracing studies (Wilkinson et al. 2015) and **f** DIN from sediment yields by DIN generation process. Presented results are the average for the 1986–2014 modelling period carried out in this study. Total modelled BAN export adds results from gully, hillslope and streambank and does not include PIN desorption (**c**). Currently monitored DIN (**c**) is the average for the period 2012–2021 (Wallace et al. 2014, 2015; Garzon-Garcia et al. 2015; Queensland Government 2018)

sediment that settles in-stream mineralises at different rates compared to suspended sediment. Recent research has found that suspended sediment in rivers is a hotspot for microbially mediated N transformations including ammonification, nitrification and denitrification with suspended sediment concentration increasing the rates of all these processes (Liu et al. 2013; Xia et al. 2013, 2018). Rates of sediment mineralisation are controlled by sediment characteristics like sediment particle size, organic matter and nutrient content (Stelzer et al. 2014; Huang et al. 2021), as well as by the physico-chemical environment surrounding the sediment (e.g. redox conditions, temperature, rates of sediment accretion) (Skoulikidis and Amaxidis 2009; Gomez et al. 2012). The role of other input sources of DIN to catchment runoff like rainfall may also be of importance and need to be accounted for in future improved models including the P2R model. It has been

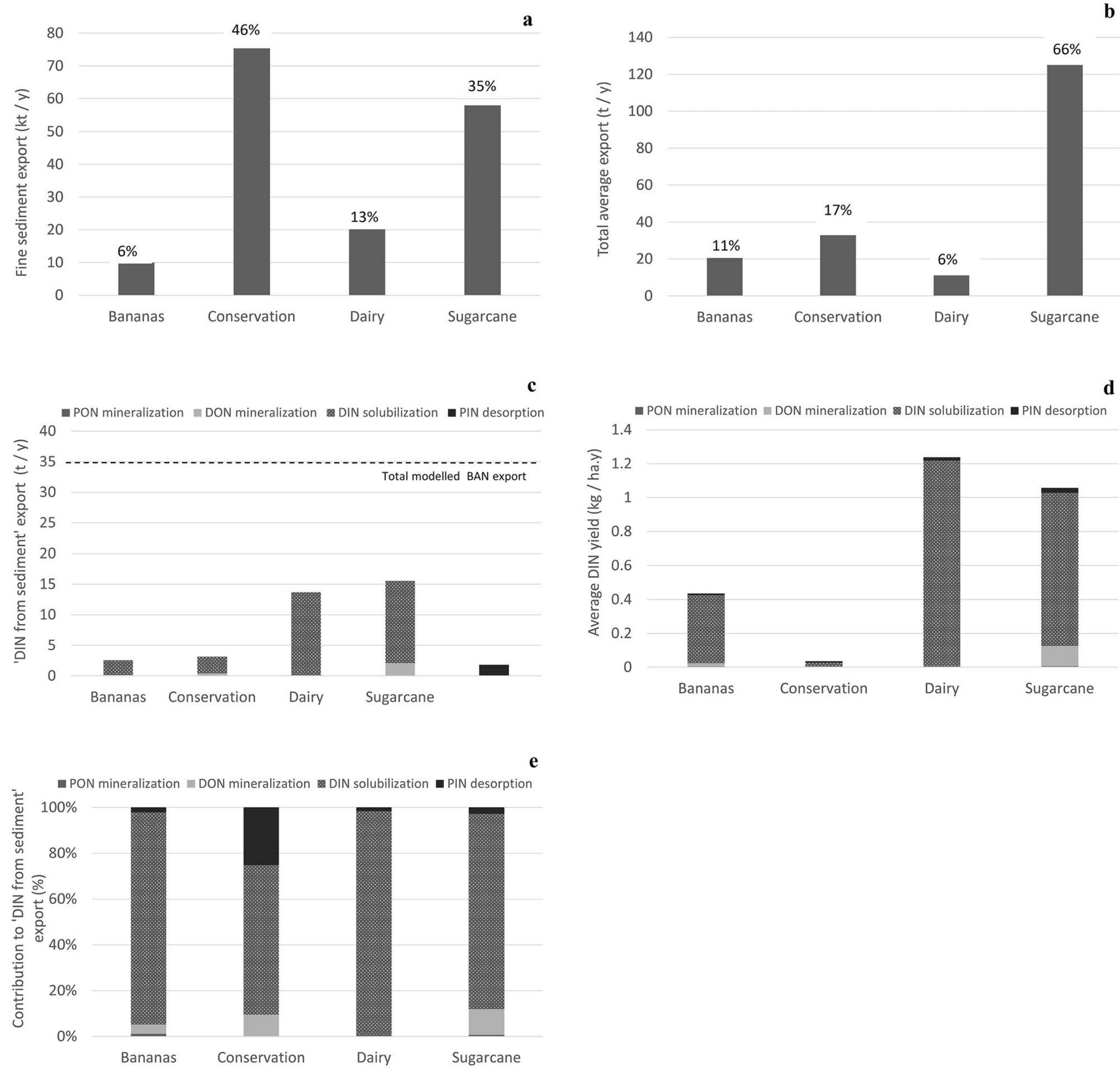


Fig. 6 Johnstone River end-of-catchment average modelled main sources of **a** fine sediment (< 20 μm), **b** PN and **c** 'DIN from sediment' by DIN generation process; **d** DIN from sediment yields by DIN generation process and **e** percent contribution to DIN from sediment by DIN generation process. Presented results are the average for the 1986–2014 modelling period carried out in this study. Total modelled BAN export adds results from all land uses and does not include PIN desorption (**c**)

estimated that a conservative contribution of rainfall to DIN in runoff could be on average 28% of the long-term average catchment export for GBR catchments (Packett 2017). This unaccounted source could explain the gap in the estimated DIN generation from sediment in the BAN model relative to the monitored data, when using the tracing data scenario of 93% subsurface erosion contribution. Considering 84% of the sediment generated in the Bowen Bogie catchment is attributed to erosion induced by humans (Bartley et al. 2017), a large part of the DIN generation associated with sediment erosion and transport modelled in this study would be of anthropogenic origin (110 t year^{-1} on average, assuming all sources of sediment have increased equally). Currently, it is assumed that the modelled DIN from grazing catchments of the GBR is not of anthropogenic origin (Bartley et al. 2017), and our findings for the first time demonstrate that DIN generation from sediment can explain an important fraction of the exported DIN in these catchments.

DIN generated from sediment was significant in the grazing, but not the cropping catchment. The low relative contribution of sediment to DIN export at the Johnstone River end-of-catchment compared to the large relative contribution at the Bowen River end-of-catchment is a result of the very high DIN yields from fertilizer use in the Johnstone (Bartley et al. 2017) and not by a lower generation of DIN from sediment in this catchment. In fact, DIN from sediment hillslope yields in the Johnstone River catchment were higher than in the Bowen River catchment (1.4 times higher on average), which indicates much higher bioavailability of these surface sediments. Basaltic soils make up 10–40% of the terrigenous sediment component deposited in the GBR from the Johnstone River catchment (McCulloch et al. 2003). These are some of the most fertile soils in the GBR with some of the highest phosphorus contents and bioavailability (McCulloch et al. 2003). This confirms previous research findings of higher bioavailability in sediments from the Johnstone River catchment using phytoplankton activity as an indicator (Garzon-Garcia et al. 2018b). As mentioned in the PON mineralisation methods section, we observed that in the presence of large DIN concentrations in the surrounding water, microorganisms do not generate additional DIN from sediment but immobilise DIN from the water, which is the case in the Johnstone River catchment. A similar outcome was found in riverine sediment plumes entering coastal environments off the Tully River, where DIN in the plume was immobilised in sediment incubations in the lab, a river of similar characteristics with a similar catchment, also located in the wet tropics of Australia (Garzon-Garcia et al. 2021). Nonetheless, there is potential for this PON to be mineralised later in the marine environment after settling on the marine floor. Given this, a significant contribution from Johnstone River sediment to DIN in the marine environment cannot be discounted at this stage.

In conclusion, the larger sources of DIN from sediment in grazed catchments may not necessarily match the larger sources of sediment (sources include soil type, land use and erosion process). The contribution to DIN from sediment was significant in a grazed eroding catchment, but not in a fertilized catchment where the availability of DIN from fertilizer was enough to drive bacterial mineralisation processes. Other processes like DIN instream losses and rainfall DIN contributions may be important in catchment DIN budgets and ideally should be included in future models.

4.2 What determines the main sources of DIN from sediment erosion in a catchment?

DIN from sediment source contribution in a catchment is a product of the mass of sediment eroded from each source and the corresponding mass of DIN per unit of sediment. The latter is determined by sediment biogeochemical characteristics that change with the parent soil order, land use and the erosion process (surface versus subsurface erosion). Surface soils from hillslope erosion make a disproportionately higher contribution to PN and DIN from sediment export compared to subsurface soils from gully and streambank erosion (50–73% contribution versus 27–50%) in the Bowen River catchment (see Fig. 5e). As a result, while subsurface erosion is the main source of sediment in this catchment (from 83 to 93% contribution) (Wilkinson et al. 2015), the dominant source of PN and DIN from sediment may be surface soil when the percentage of subsurface soil is lower than approximately 93%. This can be explained by the higher content of PN in surface sediment compared to subsurface sediment (on average 3.1 times higher in the Bowen, SD = 2), as well as its higher bioavailability (Garzon-Garcia et al. 2018b) (on average, a mass unit of surface < 10 µm sediment has the potential to produce 13 times more DIN than a subsurface < 10 µm sediment from source to end-of-catchment in the Bowen). Our findings highlight the importance of hillslope erosion in supplying particulate and bioavailable nutrients to receiving waters.

These findings also highlight the importance of accurately modelling the distribution of surface and subsurface erosion to accurately model 'DIN generation from sediment' and PN loads. Considering the important relative contribution of hillslopes to PN and DIN from sediment and the large sensitivity of PN and BAN loads at end-of-catchment to this contribution, it is crucial to accurately model these fractions to have a better understanding of the contemporary spatial and temporal contribution of hillslope erosion in catchments. Similar modelling accounting and BAN techniques could be applied to estimate the pre-European loads of DIN, a gap in current knowledge.

4.3 Processes that generate DIN from sediment operate at different timeframes and positions in the catchment

The three main biogeochemical processes that generate DIN from sediment differ in the timeframe and spatial scale of occurrence (Fig. 1). Solubilisation of DIN from sediment was an important process in generating DIN in catchments relative to the other processes (e.g. PIN desorption, organic N mineralisation), irrespective of the erosion process generating sediment. This source of DIN contributes bioavailable nitrogen from the erosion source directly. It is interesting to note that DIN from solubilisation contributes a lesser proportion to the total DIN from sediment in conservation areas (65% in the Johnstone River catchment and 40% in the Bowen River catchment) compared to other land uses (80–90% in the Johnstone River catchment and 65–80% in the Bowen River catchment). The fact that the DIN from solubilisation pool, which is immediately available, is smaller in conservation areas than it is in all other land uses indicates that anthropogenic land uses have increased the size of the immediately available pool. It is also important to note that solubilisation/leaching of DIN from the soil would occur irrespective of if the soil is eroded and transported in runoff. This process can occur in situ and the solubilized DIN move either in runoff or infiltrate to groundwater. More research is needed to understand the difference in the contribution of this source of DIN depending on the hydrological process taking place.

The magnitude of DIN solubilisation from an eroded soil would depend on soil antecedent conditions including previous frequency of drying-wetting cycles and organic matter content, but also on fertiliser inputs, crop cycle and time after fertilisation (Austin et al. 2004; Manzoni and Porporato 2011; Gomez et al. 2012). For this project, DIN solubilisation was quantified for samples taken at one point in time in the catchment (See Section 2). Considering the important contribution from this process to the DIN from sediment budget, it is recommended that further work is carried out to understand how to better account for antecedent soil conditions and the scale of the temporal variations within a soil in the quantification of this process for different soil types.

PIN desorption was an important process in generating DIN from subsurface sediments (gully and streambank erosion), contributing an important fraction of the DIN from sediment exported from the grazing-dominated Bowen catchment. It was not an important process in the fertilised Johnstone catchment. This source of DIN becomes bioavailable in estuaries where high concentrations of cations in sea water can displace the ammonium-N from the sediment by cation exchange (Rosenfeld 1979; Boatman and Murray 1982; Mackin and Aller 1984). PIN desorption has been identified as an important source of bioavailable N in riverine sediment plumes of the Burdekin River (contributing between 25 and 100% of the DIN generated in the plume) (Garzon-Garcia et al. 2021), and the Bowen River subcatchment contributes around 45% of the annual fine (< 63 µm) total suspended solids load of the Burdekin River (Bainbridge et al. 2014).

The mineralisation of organic N associated with sediment is slow (occurring at days to weeks), and although it was not such a significant contributor to the end-of-catchment Bowen River DIN load, it is important to consider that sediment may continue to generate DIN from PON mineralisation as it is further transported in the Burdekin River, in the Burdekin River plume entering the coastal marine environment and after sediment settles or resuspends from the marine floor (Alongi et al. 2007; Lønborg et al. 2018; Garzon-Garcia et al. 2021). Recent research has demonstrated that riverine sediment plumes of the Burdekin River have the potential to be considerable sources of bioavailable nitrogen to coastal environments of the GBR, adding an additional 9 to 30% to the load of DIN exported at end-of-catchment (Garzon-Garcia et al. 2021). Our research indicates that it is likely that in grazing catchments, a large proportion of the observed end-of-catchment DIN loads are generated by erosion and processing of N associated with eroded sediment in transport. It is important to note here that part of the DIN measured at end-of-catchment would be colloidal (associated with particles < 0.45 µm) (Judy et al. 2018). Although in this research we did not discriminate between colloidal N and dissolved N, doing so would not alter the estimated mineralisation of organic N into DIN, because this is calculated from the change in DIN during the experiment. Although in the studied catchments mineralisation was not the main process contributing to DIN from sediment and DIN generation tended to stabilise at the end of a 7-day incubation period for most sediment types, this was not the case in riverine plumes of the Burdekin catchment entering coastal environments of the GBR. In incubated sediment from these plumes, there were no signs of mineralisation slowing down after the 7-day incubation period (Garzon-Garcia et al. 2021). Riverine plumes across the estuarine mixing zone are highly dynamic places of transformation for sediments and nutrients that favour fast turnover rates of organic matter, which would explain additional mineralisation of sediment in riverine plumes when entering coastal environments. The availability of labile carbon for N mineralisation from sediment has been postulated as a limiting factor and would explain differences in DIN generation rates for the same sediment types at different positions in the landscape (Garzon-Garcia et al. 2018a, b, 2021).

4.4 Key contribution, study limitations and areas of further research

Eroded sediment generates bioavailable nitrogen (including DIN) from source to Reef in a continuous process controlled by the source of the sediment, the erosion process and the physico-chemical environment. This paper not only explains how these processes operate from source to Reef, but also accounts for them using a dataset obtained from extensive field and lab work going beyond many previous modelling exercises. We have also importantly demonstrated that DIN from sediment in grazing Great Barrier Reef catchments, which is currently not considered of anthropogenic origin and reported as zero (Bartley et al. 2017), has an important fraction that is actually anthropogenic and is generated from increased erosion (surface and subsurface) in these catchments. We estimate that an important fraction of at least 1780 t year^{-1} of DIN not attributed to anthropogenic processes in grazing GBR catchments would be from that origin (note the currently modelled anthropogenic DIN exported to the Reef is estimated to be around 7570 t year^{-1}).

The generation of bioavailable nutrients from sediment is complex and is mediated by microorganisms and other physico-chemical processes like cation exchange. Our research indicates that the quantity of DIN generated by sediment may be significant in grazing catchments like the Bowen River catchment. In addition, it suggests that targeting the largest sources of sediment in a catchment in an effort to achieve the TSS, PN and DIN targets set for the GBR will not necessarily target the largest sources of DIN generated by sediment. This applies both for spatial sources (e.g. soil type or land use) and process sources (e.g. surface versus subsurface erosion). Modelling of the source of DIN from sediment is feasible by combining sediment source modelling and its DIN generation potential (from representative sampling in catchments) and would provide better understanding of the main sources of DIN from sediment in an eroding catchment. Surface soil erosion contributes disproportionally to DIN from sediment export (primarily because of high N concentrations and high bioavailability) and may be the main source of DIN from sediment even if subsurface soil erosion dominates sediment export. These findings indicate that prioritisation of management actions and locations within grazing catchments, such as selection of gully sites for remediation or hillslopes to protect from erosion should include not only their potential to generate sediment, but also DIN. This would allow to protect and rehabilitate the catchment soils that provide a higher productivity value for agriculture and reduce the impact of their erosion on aquatic ecosystems downstream.

Limitations of this study include the difficulty in obtaining representative soil/sediment samples of the highly variable weather conditions in Australia (dry/wet decadal periods). Further research is needed on the implications of antecedent moisture conditions on the BAN from sediment. Additionally, channel bank contribution to DIN generated by sediment was not analysed in the Johnstone River catchment due to operational difficulties in obtaining soil samples from this source. We do not expect this to be such an important source in this catchment, considering stream banks contribute only 34% of the end-of-catchment PN load, which would imply an even lesser contribution to DIN from sediment due to lower bioavailability of subsurface sources. Lastly, other DIN sources like rainfall input and other DIN sinks like instream denitrification were not accounted for in the model. These may explain differences between monitored and modelled data and should be explored further as part of the GBR Dynamic SedNet model and future research.

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Data availability Data are contained within the article and Supplementary Materials, further inquiries can be directed to the corresponding author.

Declarations

Conflict of interest The authors declare no competing interests.

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