

# **RP178a Transitional work program for bioavailable nutrients**

Sediment particle size and contribution of eroded soils  
to dissolved inorganic nitrogen export in Great Barrier  
Reef catchments

Prepared by: Chemistry Centre - Landscape Sciences, Department of Environment and Science

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## Executive summary

The Great Barrier Reef (GBR) is threatened not only by climate change (i.e., global warming and acidification), but also by an excess of sediment, nutrients and pesticides delivered to the Reef in catchment runoff. The extent of the impact of nutrient loads on the GBR is dependent on their bioavailability (a measure of how available nutrients are to biota). The emphasis of GBR water quality management has been on reducing sediment and dissolved inorganic forms of nitrogen (DIN) (Queensland Government, 2013), under the assumption that by targeting sediment, particulate nutrients would be targeted too. The role of particulate nutrients and organics associated with sediment in generating bioavailable nutrients, in particular DIN, at the end of GBR catchments and in the GBR has been largely overlooked (Bartley et al., 2017).

Recent research has shown that particulate nutrients exported from the GBR catchments are an important source of bioavailable nutrients to the reef system (Garzon-Garcia et al; 2017; Franklin et al., 2018; Garzon-Garcia et al., 2018). Although there has been significant advances in the understanding of the bioavailability of particulate nutrients in the GBR, the relative contribution of this source of DIN to marine eutrophication when compared to other catchment sources like fertilised agriculture, is unknown. In addition, whilst it is known that fine (<16 µm) organic rich sediment is the fraction most likely to be transported long distances into the Great Barrier Reef lagoon and also influences water clarity on the inshore and mid-shelf of the Great Barrier Reef (Lewis et al., 2015a; Lewis et al., 2015b; Lewis et al., 2014a, Bainbridge et al., 2012), to understand the contribution of particulate sources to DIN in the marine environment it needs to be recognised that all particle size ranges have the potential to produce bioavailable nutrients. As a result it is important to understand not just the particle size being transported into the marine environment, but also the range of particle sizes reaching the end-of-catchments. The need to improve understanding of particle size and bioavailable nutrients was highlighted in the 2017 Scientific Consensus Statement (Bartley et al., 2017).

The objectives of this project were therefore to:

1. Improve understanding of the sediment particle size exported during high-flow events from end-of-catchments and subcatchments of the GBR using monitoring data from the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP).
2. Develop a method to estimate the proportion of end-of-catchment DIN generated from eroded soils and a framework/process to report on Particulate Nitrogen (PN) and DIN reductions associated with erosion management. This task was carried out in collaboration with Paddock to Reef (P2R) modellers. The method to estimate DIN generation from eroded soils was applied in two pilot catchments, the Bowen River catchment and the Johnstone River catchment.

### Improving our understanding of sediment particle size exported from GBR catchments during high flow

The existing sediment particle size GBRCLMP monitoring data (2005-2017) was analysed. To do this 1) the dataset was collated; 2) spatial and temporal representivity was analysed and 3) the range and dominant particle size classes at each end-of-system and subcatchment sites was examined. In addition the current methods used to measure and report on fraction sizes were assessed.

Findings with respect to sediment particle size include:

- The majority of the sediment monitored at end-of-system sites in the GBR catchments is in the <63 µm particle size range (silt and clay) (>90%).
- Greater than 90% of sediment exported from the larger, predominately grazed dry catchments (Normanby, Burdekin, Burnett and Fitzroy) is <16 µm (clay and fine silt), although there is large variability between samples.

This may be related to the timing of sampling during events, the variability of sampled flows and sediment source. In contrast, suspended sediment samples collected in the coastal wet catchments (Barron, Herbert, Tully, Houghton, Pioneer and Plane) have a lower fine silt (<16 µm) and clay (<2 µm) content and higher coarse fraction content (≥63µm).

- A considerable fraction of the fine sediment (i.e. <63 µm) leaving the GBR catchments at end-of-system is larger than 16 µm (from 5 to 29%), particularly in the Wet Tropics and Mackay-Whitsunday regions.

This is important to note as it has implications for the validation of the suspended sediment modelling which currently only models the <20 µm fraction.

The fractions of fine sediment larger than 16 µm will have water quality effects (e.g. DIN generation) in the river estuaries that need to be assessed (see section on the contribution of eroded soils to DIN export).

To ensure continued and improved confidence in particle size data analysis it is recommended that:

#### *Immediate action*

- Continue to undertake particle size analysis by laser size diffraction using the three methods of dispersion (pre-dispersed, mechanical and ultra-dispersion) used previously. Particle size distribution should be reported as a percent volume basis using the results from the ultra-dispersion method (that measures absolute particle size distribution).
- Monitoring of particle size should be included as a standard parameter in the GBRCLMP at least for the catchments where sediment and particulate nutrient management is prioritised (e.g., grazing catchments).

#### *Further clarification*

- Further and broader discussions are necessary to define the particle size methods and classes to report particle size distribution. Particle size datasets are currently being collected and analysed at paddock, sub-catchment, end-of-system and in marine plumes. To ensure data sets from different scales can be integrated it would be useful to do a full source to sink assessment of the particle size methods and data before finalising recommendations for reporting methods and size classes.
- An understanding of the true representativeness of the existing data is necessary, including how representative the flow conditions sampled are with respect to historical flow, and inter and intra annual variability. This is necessary to ensure the findings are representative of all flow conditions and not biased by the characteristics of sampled flow and flow events.
- Organic content appears to be higher in marine plumes in wet smaller coastal catchments. Given this, it is important to understand the influence of organic content on sediment particle size determination. This may play a role in the binding of smaller particle sizes, consequently shifting the particle size towards coarser fractions if the organics are not removed (Lewis et al., 2018).

### **Modelling the generation of DIN from eroded soils and improved PN modelling**

In this project a new method for modelling DIN generation from eroded soil as it is fractionated into fine sediment and transported in rivers was developed and successfully tested using the P2R model. Using bioavailable nutrient datasets for the Bowen and Johnstone River catchments collected in RP128 G phases 1 and 2 (Burton et al., 2015, Garzon-Garcia et al., 2017a) and as part of this project and knowledge of nitrogen pools and transformations we adapted the Paddock to Reef (P2R) Source Catchments model to quantify the amount of DIN generated from eroded soils.

Additionally, we ran the P2R model for PN using spatial layers developed from the bioavailable nutrient datasets and compared the results with the PN estimates from the existing P2R platform. The key difference between the two is that the proposed new PN modelling method uses measured data to account for the variability in enrichment between the bulk soil and the <20 µm fine sediment for different soil types, land uses and erosion processes, whereas the existing model uses soils data and assumes an enrichment factor with no variation in enrichment across different soil types, land uses or erosion processes.

The key outcomes of this work were:

- PN modelling can be improved to account for the variability in fine sediment (<20 µm) characteristics in the catchments particularly the variability in enrichment ratios of particulate nutrients in sediment from that of their parent soils.
- In the Bowen River catchment pilot study we found that all of the end of catchment DIN that is currently modelled can be accounted for by the DIN generated from eroded sediment that was modelled using the new method.
- The DIN generated from eroded sediment modelled using the new method was not significant in the Johnstone River catchment (around 3% the currently modelled DIN load at the Johnstone River end-of-catchment).
- Although 'DIN generated from sediment' yields (kg DIN generated per kg of eroded sediment per hectare per year) were much higher in the Johnstone than in the Bowen River catchment, the very large modelled

yields of 'DIN from fertilizer' dominated the DIN source to end of catchment in the Johnstone. However, sediment will likely continue to generate DIN from PON mineralisation as it is transported further in the estuary and the marine environment which may increase the importance of DIN generation from eroded soils in the Johnstone Catchment.

- A large part of the DIN generation associated with sediment erosion and transport is of anthropogenic origin and it is not targeted as such in current reporting. Considering the significant quantity of DIN that can be generated from eroded soils in grazing catchments it is important to identify, model and target this fraction.
- The main sources of sediment in a catchment are not necessarily the main sources of PN or DIN-producing sediment. For example, modelling in the Bowen River catchment indicated that although gully erosion is the main source of sediment, hillslope erosion is the main source of PN and 'DIN generation from sediment'. Our findings highlight the disproportionate contribution of hillslope erosion to particulate and bioavailable nutrient catchment export per unit mass of eroded sediment, when compared to subsurface erosion (gully and streambank). Conversely, in the Johnstone River catchment, although conservation and sugarcane dominated sediment export, and sugarcane alone dominated PN export, the new modelling results indicated that dairy may be an important source of DIN generated from eroded sediment at the end-of catchment (39% contribution) together with sugarcane (44% contribution).
- Sediment source contribution (surface versus subsurface erosion) is an important determinant of the total DIN load generated from sediment in the catchment and of the source contributions to these loads. Calculations using tracing data as a second line of evidence for the Bowen River catchment indicated large variability in surface versus subsurface source contributions to 'DIN generation from sediment' with changes in the proportion of sediment sourced from subsurface sources. Under a scenario with subsurface sediment contribution >93%, subsurface sediment would be an equally important source to the DIN generated from sediment as surface erosion. These findings highlight the importance of accurately modelling the distribution between surface and subsurface sediment sources in catchments to accurately model DIN generation from eroded sediment and also PN loads.

## Implications

In summary, this study has demonstrated that:

- Modelled DIN generated from sediments eroded from grazing catchments account for a significant proportion of the end-of-system DIN measured and modelled in these catchments. This source of DIN is therefore likely to pose a significant risk to water quality and ecosystem health in the GBR. As reductions in end-of-system DIN associated with erosion management are not currently being accounted for they are not included in progress towards the DIN reduction target. Therefore there is a need to specifically address bioavailable particulate nutrients for grazing catchments when the targets are revised for the WQIP update in 2022.
- PN and bioavailable nutrients from eroded soil need to be prioritised separately from sediment in all catchments. Including the potential for DIN generation in the prioritisation of areas for erosion management will multiply the benefit to water quality of these investments. Erosion management practices that target different erosion sources should be considered in the context of generation of both sediment and 'DIN from sediment' yields per unit area. In order to reduce DIN from eroded sediment there is a need to develop and promote land management practices that reduce nutrient-rich fine sediments (i.e., mitigate surface soil erosion).
- DIN generation from erosion should be included when undertaking cost-benefit analysis of various management options for reducing DIN.
- Trading for nitrogen forms as part of nutrient markets/offsets should take into account the bioavailability of the different pools of bioavailable nitrogen, which directly relate to the identified DIN generation processes in this project.
- Reinforces the need for monitoring of particle size to be included as a standard parameter in the GBRCLMP. This would enable the GBRCLMP to capture comparable datasets and would facilitate the validation of sediment and PN modelling data against monitored data.

- The main bioavailable particulate nutrient parameters (at least POC, DOC, adsorbed ammonium, and particle size distribution in addition to DON, soluble ammonium and nitrate) should be included in routine loads monitoring or in strategic catchments (e.g., grazing catchments) and paddock monitoring to validate the modelling of bioavailable particulate nutrients ('DIN from sediment') and to estimate bioavailability to phytoplankton.

In addition, this project linked the analysis of the GBRCLMP sediment particle size dataset with the modelling of PN and DIN generation from eroded sediment. Given that there is a significant proportion of  $>16\ \mu\text{m}$  particles reaching the end of system which will generate DIN, an assessment of the full contribution of eroded sediment to DIN loads in the marine environment will require an understanding of how much DIN is being generated during transport from particle sizes greater than  $16\ \mu\text{m}$ . If the contribution from the  $>16\ \mu\text{m}$  particles is significant then the modelling may need to include multiple size classes.

The framework developed in this project for modelling DIN generation from sediment and reporting on DIN reductions from sediment management is recommended for grazing catchments where this process generates significant DIN loads. It requires additional input information, including further understanding of DIN contribution from particle sizes  $>16\ \mu\text{m}$  and the coupled improvement of sediment modelling (see 'Further work').

The method developed in this project for modelling PN in catchments could be implemented so that PN modelling is more accurate and supported by the most recent process-based knowledge.

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## Introduction

An excess of sediment and bioavailable nutrients, in particular nitrogen (N) in the form of dissolved inorganic nitrogen (DIN), have been associated with a range of damaging impacts to the Great Barrier Reef (GBR). These impacts include: an increase in the frequency of Crown of Thorns Starfish (COTS) outbreaks (Brodie et al., 2005; Fabricius et al., 2010); loss of seagrass and coral through reduced photic depth (Fabricius et al., 2014); an increase in the susceptibility to coral bleaching (Wooldridge, 2009); reef degradation and reduced coral biodiversity (DeVantier et al., 2006; Fabricius, 2005); an increase in macroalgae and subsequent competition with coral (De'ath and Fabricius, 2010); and possible links to coral disease (Haapkyla et al., 2011). Management to improve water quality in the GBR has historically focused on reducing these 'pollutants' from catchments (Queensland Government, 2013) under the assumption that by targeting the largest sources of sediment, the largest sources of particulate nutrients would also be targeted. The contribution of particulate nutrients and organics associated with sediment to bioavailable nutrients, in particular to DIN at the end of GBR catchments and in the GBR have been largely overlooked. DIN is of importance because it includes ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ), two of the most bioavailable forms of N, which is considered the limiting nutrient in the GBR (Furnas et al., 2005). This knowledge gap has been identified as a priority in the 2017 Scientific Consensus Statement for the GBR together with sediment particle size distributions at the end of catchments (Bartley et al., 2017). Addressing these knowledge gaps would allow for more robust targeting of the ecologically threatening sediment sources.

Recent research has contributed to an increased understanding of the importance of the bioavailability of particulate nutrients (Franklin et al., 2018; Garzon-Garcia et al., 2018). These are some of the main findings:

- Particulate nutrients associated with fine sediment are bioavailable to both fresh and marine phytoplankton of the GBR and its catchments. This implies that eroded sediment is contributing to GBR eutrophication.
- The magnitude of this bioavailability depends not only on the sediment load, but on sediment characteristics associated with its parent soil. These characteristics vary with soil type, land use and erosion process (surface versus subsurface erosion).
- The bioavailability of particulate nutrients to phytoplankton is mediated by microorganisms (e.g., bacteria) and the type of carbon (e.g., vegetation type) present is of importance.
- It is possible to assess how bioavailable is sediment of different provenance to phytoplankton using indicator equations composed of various particulate nutrient bioavailability parameters.

Although this research has significantly advanced our understanding of the bioavailability of particulate nutrients, the relative contribution of this source of DIN to marine eutrophication when compared to other catchment sources like fertilised agriculture is unknown. This project aims to address this gap in knowledge.

Here we report on the following objectives:

1. Improve our understanding of the sediment particle size exported during high-flow events from end-of-catchments and subcatchments of the GBR using monitoring data from the Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP).
2. Develop a method to estimate the proportion of end-of-catchment DIN generated from eroded soils and a framework/process to report on PN and DIN reductions associated with erosion management. This outcome was carried out in collaboration with P2R modellers. The method to estimate DIN generation from eroded soils was applied in two pilot catchments, the Bowen River catchment and the Johnstone river catchment.

# Suspended sediment particle size distributions in GBR catchments

## Methods

An analysis of the range and dominant particle size classes of sediment collected from the GBR end of system and subcatchment sites by the GBRCLMP was conducted. The data analysis only included the existing data set (i.e. no further lab work was conducted) which was extracted from the Chemistry Centre Laboratory Information Management System (LIMS) by SQL query. To carry out the analysis it was considered necessary to collate the existing information and determine how representative the samples are. The representivity was assessed in terms of spatial coverage and temporal coverage (inter-annual and intra-annual).

The Great Barrier Reef Catchment Loads Monitoring Program (GBRCLMP) has included opportunistic sampling (Dr. Ryan Turner *pers. com*) to quantify particle sizes during high flow events as part of their Program since (2005). Water samples were collected according to the methods outlined in the Environmental Protection (Water) Policy Monitoring and Sampling Manual (DEHP, 2009). In short, samples were either collected with manual grab sampling or automatic grab sampling using refrigerated pump samplers. Samples were then refrigerated and transported to the lab for analysis as fast as practically possible to minimise issues regarding the aggregation or disaggregation of sediments during storage. Particle Size Distribution (PSD) analysis was undertaken by the Science Division Chemistry Centre (Department of Environment and Science) by laser diffraction using either a Malvern Mastersizer 2000 or 3000 (in 2017 the instrument was updated). Laser diffraction is a technique that estimates the particle size distribution of sediment in suspension based on the intensity and directional pattern by which particles scatter light. The Malvern Mastersizer provides PSD for size ranges from 0.24 to 2000  $\mu\text{m}$ . The particle size distributions results obtained are based on a spherical model, while in reality most particles are non-spherical or irregular. The laser light obscuration (the degree of laser obstructed by the particles) used is between 5 and 15% to obtain optimal results and the refractive index used is 1.52. Particle size distribution results are reported on a % distribution by volume basis.

Particle size distribution was measured using three dispersion methods:

- Pre dispersion (PRED) – PSD when no external dispersant is placed in the water sample. Measured as the initial reading. Results will represent the natural aggregation or disaggregation of the water sample during storage and transportation.
- Mechanical dispersion (MECD) – PSD measured on the 5<sup>th</sup> reading after mechanical dispersion with the laser sizer commences.
- Ultra-dispersion (ULTD) – PSD measured after sediments are broken down to their absolute particle sizes using ultrasound (3.2 min). After the ultrasound unit is activated and a further nine readings are taken, if the relative standard deviation for the 11<sup>th</sup> to 15<sup>th</sup> reading is less than 5 percent, the 15<sup>th</sup> reading is adopted as the ultrasound dispersed measurement. If this is not the case, further groups of five readings are made until the relative standard deviation is less than 5 percent.

A comparison between results from the different dispersion methods was carried out as part of this study.

The uncertainty of the PSD laser diffraction method is presented in Table 1.

Table 1 Uncertainty of the method to obtain particle size distribution by laser diffraction

% of particles in size range	Uncertainty estimate. ( $\pm\%$ )
1 to 5	25
5 to 10	20
10 to 15	16
15 to 20	11
20 to 25	7
25 to 30	6
Above 30	6

Particle size distribution by volume was aggregated for the following classes: <2  $\mu\text{m}$  (clay), <16  $\mu\text{m}$  (clay + fine silt), <63  $\mu\text{m}$  (clay + fine silt + coarse silt) and  $\geq 63 \mu\text{m}$  (sand). These ranges combine the international system, for clay,

and the Udden-Wentworth sediment grain size scale for the other fractions (Leeder, 1982) Table 2.

Table 2 Sediment size classes and classification systems used in this study

	Udden-Wentworth	International system	This study
sand	$\geq 63 \mu\text{m}$	$\geq 20 \mu\text{m}$	$\geq 63 \mu\text{m}$
silt	4-63 $\mu\text{m}$	2-20 $\mu\text{m}$	2-63 $\mu\text{m}$
fine silt	4-16 $\mu\text{m}$		2-16 $\mu\text{m}$
clay	$< 4 \mu\text{m}$	$< 2 \mu\text{m}$	$< 2 \mu\text{m}$

Particle size distribution was analysed to understand variability by region and catchment for all end of system and subcatchment sites.

Additionally, an analysis to understand if particle size distributions by weight (% mass) is significantly different from particle size distributions by volume was carried out. Using specific gravity values from literature for the selected particle size classes (coarse sand:  $> 250 \mu\text{m}$ , fine sand: 63 – 250  $\mu\text{m}$ , silt: 16 – 63  $\mu\text{m}$ , clay:  $< 2 \mu\text{m}$ ) and the corresponding total suspended solids concentration, the distribution of sediment in the different classes was calculated on a per mass basis. The assumed specific gravity values were: 2.66 for coarse sand, 2.66 for fine sand, 2.8 for silt and 2.8 for clay. It was also assumed that sediment is predominantly composed of mineral sediment particles with a minimal presence of organic matter particles (which would have much lower specific gravities).

## Results and Discussion

### Representivity of sampling for particle size analysis

The GBRCLMP has included opportunistic sampling to quantify the distribution of sediment particle size during high flow events as part of their Program. The existing dataset contains a total of 960 samples with particle size distribution (PSD) from ten end-of-system (EoS) catchment monitoring locations, 13 subcatchment (SC) monitoring locations and 9 other monitoring locations in Queensland. This report predominantly focuses on the particle size distribution from EoS and SC monitoring stations.

A spatial distribution of the sampled sites can be seen in Figure 1. Table 3 provides the number of EoS, SC and other monitoring sites with particle size data in each of the NRM regions. EoS monitoring sites with PSD data are evenly distributed across the Great Barrier Reef catchments, with more than half of the major river systems having information (10 of 17 EoS sites). GBRCLMP monitored rivers (based on the 2015-2016 monitoring period) without particle size information at the EoS include the Mulgrave, the Russell, the Haughton, the O'Connell, the Mary and Tinana creek. The Johnstone River has information at the end of each of its main subcatchments. Only two of the nine currently monitored SC sites (based on the 2015-2016 monitoring period) do not have particle size information: Tully River at Tully Gorge National Park and Bowen River at Myuna. Four of the subcatchment sites with particle size information have been decommissioned by the GBRCLMP.

Table 3 Number of EoS, SC and other monitoring sites with particle size distribution information per NRM region

Region	No. of EoS	No. of SC	No. of other monitoring locations
Burnett Mary	1	3	0
Fitzroy	1	3	2
Mackay/ Whitsundays	2	0	2
Burdekin	2	3	0
Wet Tropics	3	4	0
Cape York	1	0	5

Particle size data collection started in 2005/2006 and has been extremely varied with only a small amount of samples collected from 2005 to 2010 (only 96 samples across 10 EoS and 11 SC sites). This variability seems to correspond to annual rainfall with more intensive sampling generally corresponding to wetter years. Particle size monitoring efforts have generally increased since 2010, with 2010/2011 (258 samples) and 2016/2017 (263 samples) being the two highest sampled years for all monitoring sites (Figure 2). These years were relatively wet years when compared to other years. However, 2013/2014 and 2014/2015 are poorly represented in terms of data, though these years had below average rainfall in the Mackay Whitsunday, Burdekin, Fitzroy and Burnett Mary regions. The majority of the sampling occurred in the wet season (November to April) in order to capture periods of high flows, with 826 out of 960 samples (86%) conducted during this time.

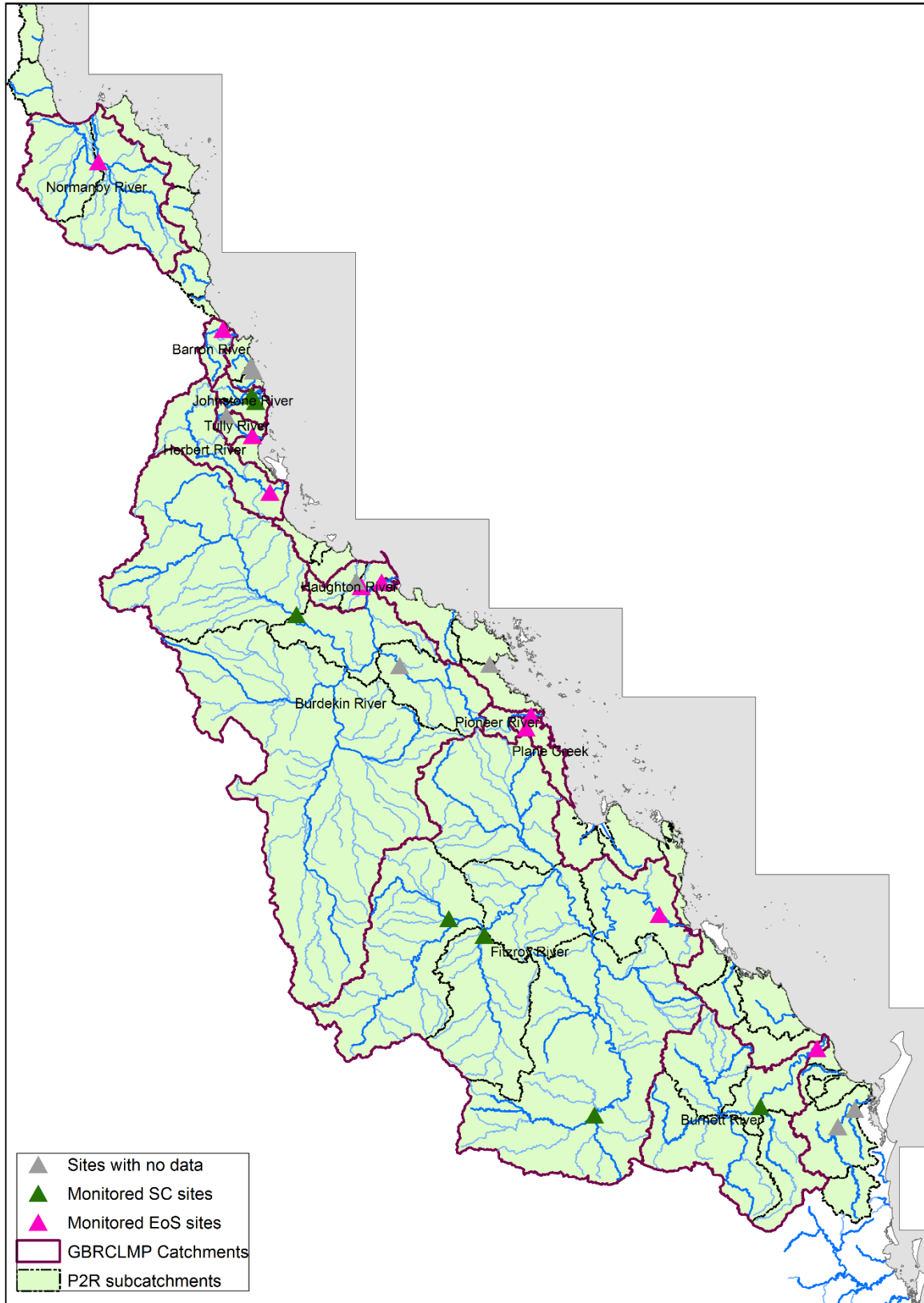


Figure 1 Location of EoS and SC GBRCLMP monitoring sites with and without particle size distribution information

The continuity of sampling is not homogenous between sites, with five of the 10 sampled EoS sites (at Barratta Creek, Barron River, Tully River, Pioneer River and Sandy Creek) not having any data in the last five years of sampling (Figure 3). For example, Barratta Creek in the Haughton catchment only has a total of five samples from 2011 and the Normanby River has only been sampled on two occasions approximately 10 years apart (2006 and 2016) with 29 samples in total. The remaining five EoS sites (at the Burdekin, Burnett, Fitzroy, Herbert and Normanby Rivers) have been sampled somewhat regularly since 2015 (Figure 3). However, the number of samples per year per EoS site varies widely, which may be associated with the frequency of high-flow events. The Burnett River has been sampled the most regularly since 2012. The increased sampling during 2016-2017 in the Burdekin and Fitzroy corresponds to Cyclone Debbie and the resulting flood plume (in March and April a combined 46 out of 79 samples were taken during this time in both the Burdekin and Fitzroy catchments). This very uneven coverage across all years and sampling sites makes it very difficult to deduce the representativeness of particle size data. To understand true representativeness of the data it is necessary to carry out an analysis of how representative the flow conditions sampled are with respect to historical flow for each of the sampled sites. This analysis was not a part of the current project.

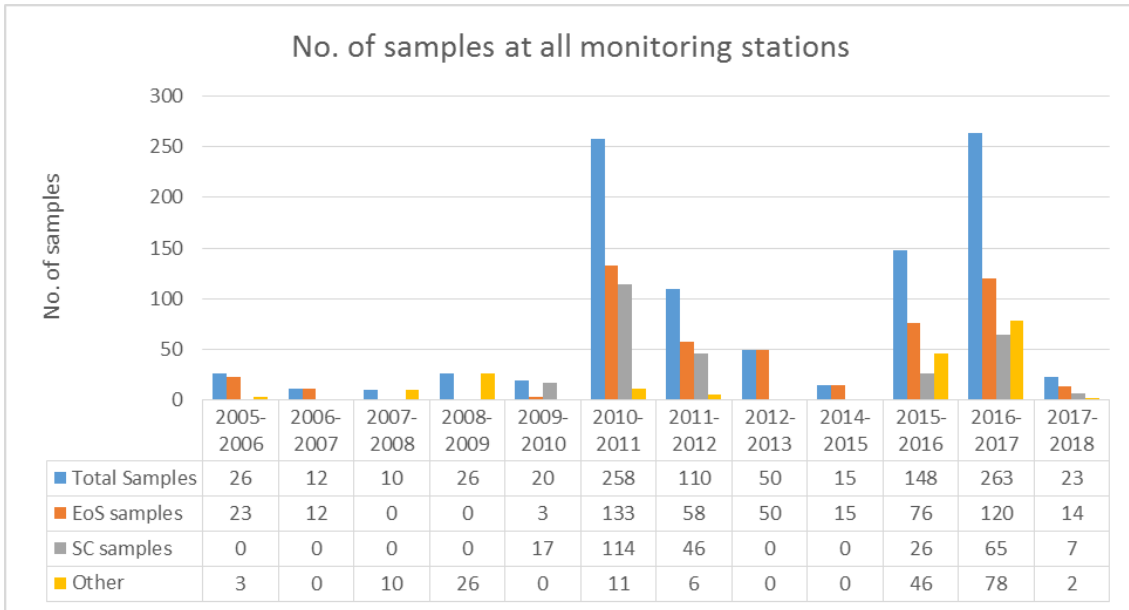


Figure 2 Number of particle size distribution (PSD) samples across the monitoring period

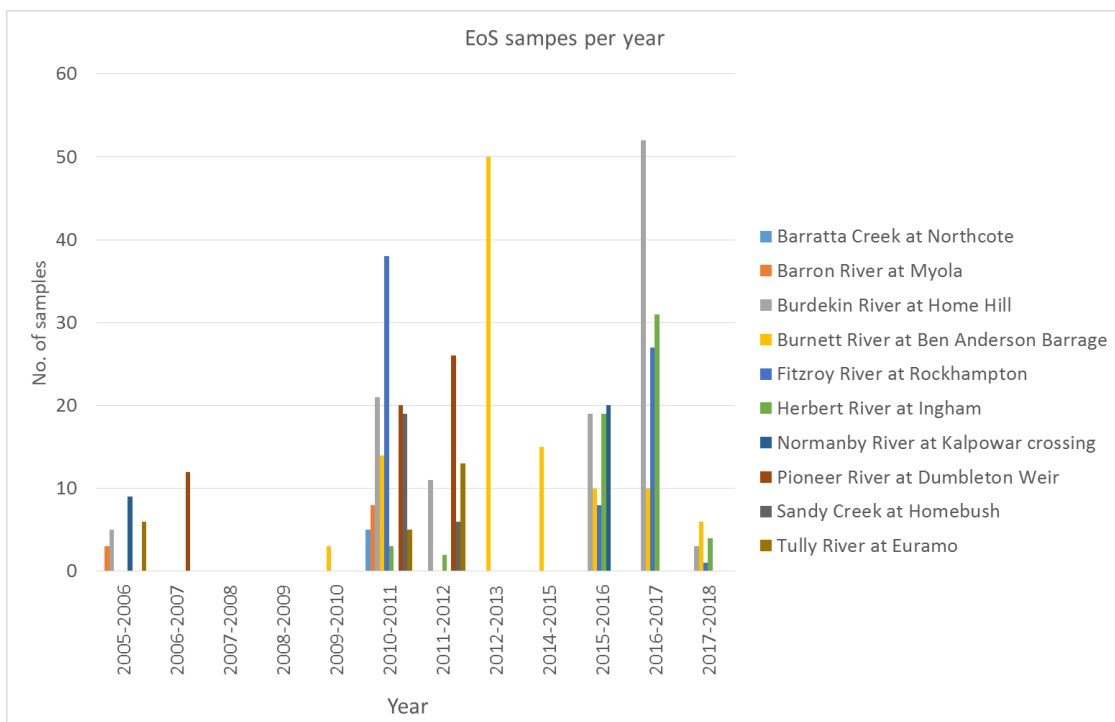


Figure 3 Number of particle size distribution (PSD) samples for each monitored year per EoS sampling site

## Comparison between particle size analysis for different dispersion methods and distributions by volume and weight

Differences in particle size distribution are larger between the ultra-dispersion (ULTD) method and the mechanical dispersion (MECD) method than between the pre-dispersion (PRED) and the MECD. The ULTD method has around 50% lower  $\geq 63 \mu\text{m}$  fraction size volumes and two times higher  $< 2 \mu\text{m}$  fraction size volumes than the MECD. The standard deviations for the latter fraction tend to be larger for the ULTD method. These differences in distributions between the MECD and ULTD method are important and can be mostly attributed to the disaggregation of sediment after dispersion using sonication.

Aggregation of riverine transported sediment is an important determinant of settling velocity and surface area, which controls important biogeochemical process rates like the mineralisation of organic matter and adsorption/desorption, all of which directly affect the physico-chemical characteristics of the sediment. The natural aggregation of sediment particles in the environment (river transported sediment) is affected by storage, transport and refrigeration of the samples. Aggregates may be broken into smaller aggregates or primary particles by oxidation and physical impact processes (Matthews, 1991) and hence the PRED or MECD measurements may not accurately represent field conditions. Whilst the ULTD method is also unlikely to accurately reflect in situ field conditions it does provide the distribution of the absolute particle size composition of the sediment irrespective of aggregation. Because of this, the ULTD method is the only method available that we can comfortably assume the results are comparable across all samples and as such the PSD analysis in this report will generally refer to the ultra-dispersion technique. Understanding sediment aggregation in the environment would give additional insight into the true behaviour of sediment as it is transported in the rivers of the GBR (Bainbridge et al., *Accepted*).

No significant differences were found when comparing the particle size distribution by volume and by weight in the GBR monitored catchments. We are presenting for reference the comparison for the  $< 63 \mu\text{m}$  particle size range only (silt distribution) (Figure 4). It is important to take into account that it was assumed that the presence of organic matter particles in the sediment, which have a much lower specific gravity than mineral particles, is insignificant. The contribution of vegetation litter to fine sediment has been shown to be as high as 20% at the initiation of a high flow event in the Logan River catchment (Garzon-Garcia et al., 2017b). Preliminary results for organic matter sediment content at end of river has been quantified to be 10-15% in the Burdekin River (Bainbridge et al., 2012; Lewis et al., 2018) and 18% in the Tully River, and 29% in the Johnstone River estuary (Lewis et al., 2018). The composition/origin (litter versus organic matter attached to fine sediment through chemical bonds) of this organic matter is still unknown. When litter contribution to sediment is of importance, larger differences between sediment distribution by weight and by volume would be expected.

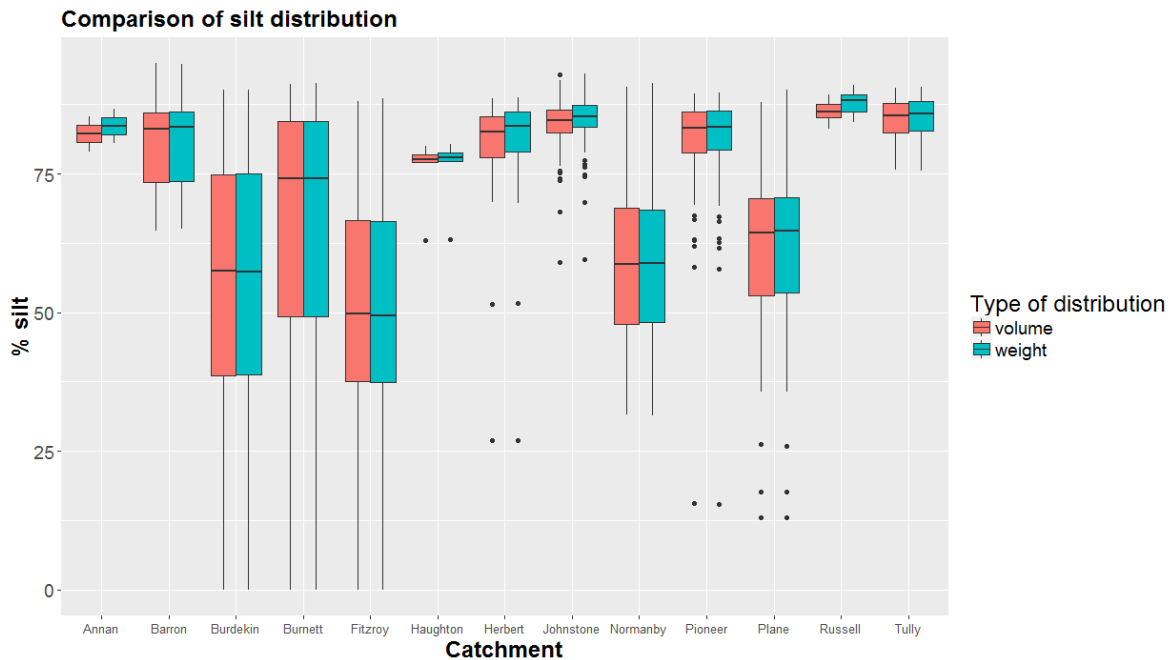


Figure 4 Comparison of the PSD for silt ( $< 63 \mu\text{m}$ ) by weight and volume in GBR catchments

## Particle size distribution in the Great Barrier Reef catchments at end of system

In EoS sites of the GBR, the mean volume of the sediment with a particle size greater than or equal to 63  $\mu\text{m}$  (sand sized fraction) for all the sampling period is small with the Burdekin (3.0%), Fitzroy (1.0%), Normanby (0.7%) and Burnett (1.8%) rivers having less than 3% of the sediment in this fraction size class on average (Figure 5, Table 4). The Wet Tropics and Mackay-Whitsunday rivers [Tully 6.6%, Pioneer 6.3%, Sandy creek (Plane catchment) 6.1%, Herbert 7.7%] have a slightly larger volume in this fraction size class at around 6% and larger variation in the data (Figure 5, Table 4). Barratta Creek in the Haughton catchment has the largest volume of particles  $\geq 63\mu\text{m}$  with 11.1% on average. A higher content of coarser fractions seems to be associated with smaller and wetter coastal catchments in which there is less opportunity for the coarser sediment to settle. The dry tropics catchments (Normanby, Burdekin, Burnett and Fitzroy) and the coastal wet catchments have significant differences in climate, geology and land use with the former being larger and dominated predominantly by grazed exposed lands and the latter being smaller and having their headwaters covered in protected rainforest and cultivated floodplains.

Fine sediment particles ( $<16\ \mu\text{m}$ ) are the fraction of sediment most likely to reach furthest into the GBR lagoon (Bainbridge et al., 2012) and  $<20\ \mu\text{m}$  is the fraction modelled in the Paddock to Reef Source catchments (P2R). In this report we analysed the  $<16\ \mu\text{m}$  fraction rather than the  $<20\ \mu\text{m}$  fraction due the breaking points for particle sizes available in the GBRCLM dataset. This fraction corresponds to the fine silt and clay fraction of the Udden-Wentworth sediment grain size scale (Leeder, 1982). We assume for the purposes of this report that the distribution for this particle size class would not be very different to that of the  $<20\mu\text{m}$ . The Normanby, Fitzroy, Burdekin and Burnett rivers (means of 93.3%, 93.8%, 87.1% and 87.7%, respectively) have the highest % volume of sediment in the  $<16\ \mu\text{m}$  range (Figure 6, Table 4). Rivers located in the Wet Tropics and Mackay-Whitsunday regions have generally a lower % volume of sediment in the  $<16\ \mu\text{m}$  range with the Barron, Pioneer, Sandy Creek (Plane catchment), Herbert and Tully having means of 73.5%, 66.9%, 76.5%, 65.1% and 64.6%, respectively (Figure 6, Table 4). Barratta Creek in the Haughton catchment has the lowest volume of sediment in the  $<16\mu\text{m}$  fraction (mean 59.4%). We note there is large variability between samples collected at each end of system site. Further analysis is required to determine the source of this variability, as discussed below.

For the clay fraction ( $<2\mu\text{m}$ ), the Burdekin, Burnett, Normanby and Fitzroy rivers have the highest % of clay with means of 42.1%, 35.4%, 41.0% and 45.8% (Figure 7, Table 4). A large variation (measured as standard deviation) of clay % between samples is observed for each of these catchments. It is anticipated that this variation is associated with the timing of sampling during events and the variability of sampled flows. It is also possible that the sampled sediment has been sourced from different areas and soil types in the catchment. The Wet Tropics and Mackay-Whitsundays catchments (Tully 8.4%, Pioneer 13.9%, Herbert 11.2%, Barron 7.7%) generally have a lower average % of clay (Figure 7, Table 4). Variability in the data for these catchment tends to be smaller, likely reflecting smaller catchment size and potential source areas. The exception to this is Sandy Creek in the Plane catchment with an average clay fraction of 26.5%.



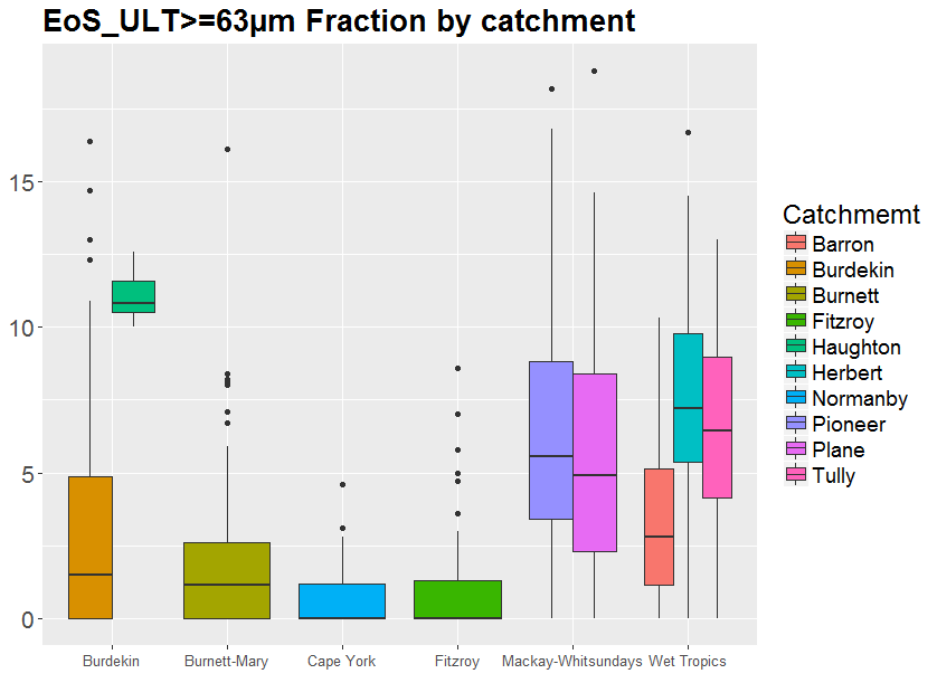


Figure 5 Percent of sediment in the  $\geq 63 \mu\text{m}$  particle size class by catchment and NRM region in the GBR

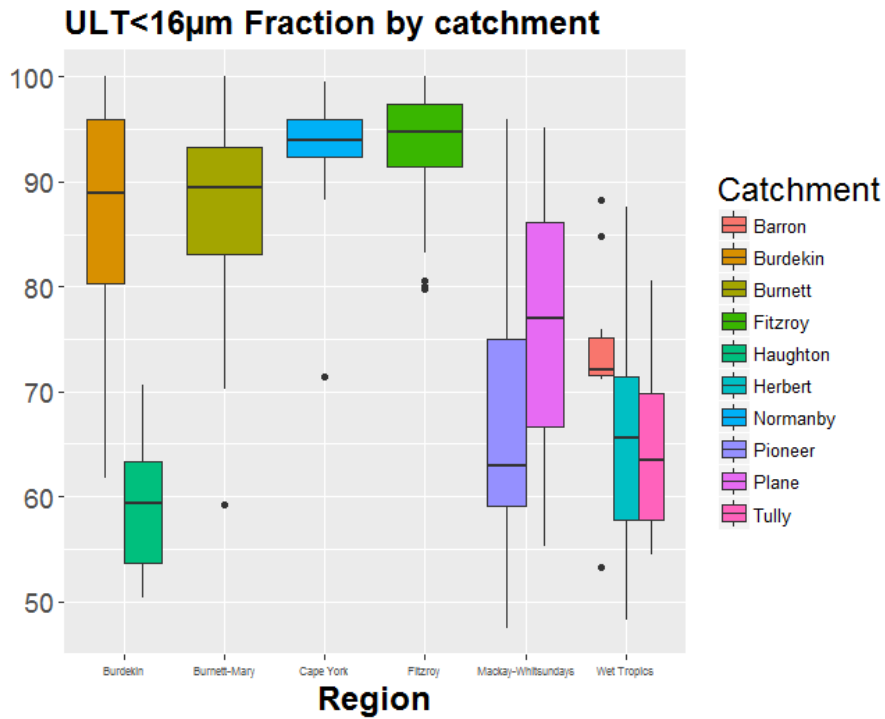


Figure 6 Percent of sediment in the  $< 16 \mu\text{m}$  particle size class by catchment and NRM region in the GBR

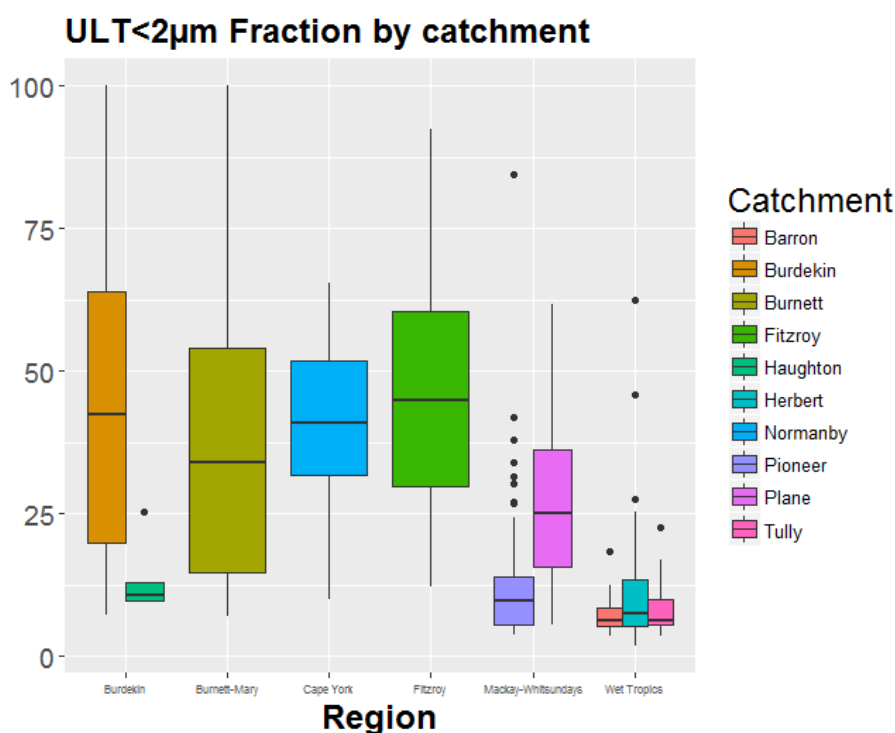


Figure 7 Percent of sediment in the <2  $\mu$ m particle size class by catchment and NRM region in the GBR

Table 4 Average percent of sediment in different fraction size classes for all end of system sites by catchment in the GBR. Standard deviation in parenthesis.

Catchment	EoS sampling site	$\geq 63\mu\text{m}$	$< 63\mu\text{m}$	$< 16\mu\text{m}$	$< 2\mu\text{m}$
<b>Barron</b>	Barron River at Myola	3.5 (3.2)	96.5 (3.2)	73.5 (8.8)	7.7 (4.3)
<b>Burdekin</b>	Burdekin River at Home Hill	3.0 (3.8)	96.5 (3.6)	87.1 (9.9)	42.1 (23.6)
<b>Burnett</b>	Burnett River at Ben Anderson Barrage HW	1.8 (2.5)	98.1 (2.6)	87.7 (7.4)	35.4 (21.7)
<b>Fitzroy</b>	Fitzroy River at Rockhampton	1.0 (1.7)	98.7 (1.9)	93.8 (4.8)	45.8 (21.2)
<b>Haughton (Barratta creek)</b>	Barratta Creek at Northcote	11.1 (1.0)	88.9 (1.0)	59.4 (7.9)	13.7 (6.6)
<b>Herbert</b>	Herbert River at Ingham	7.7 (3.5)	91.7 (3.6)	65.1 (8.7)	11.2 (10.2)
<b>Normanby</b>	Normanby River at Kalpowar Crossing	0.7 (1.2)	98.3 (1.5)	93.3 (5.0)	41.0 (13.5)
<b>Pioneer</b>	Pioneer River at Dumbleton Weir HW	6.3 (4.2)	93.7 (4.1)	66.9 (11.9)	13.9 (13.1)
<b>Plane (Sandy creek)</b>	Sandy Creek at Homebush	6.1 (5.0)	93.9 (4.9)	76.5 (11.5)	26.5 (13.7)
<b>Tully</b>	Tully River at Euramo	6.6 (3.5)	93.4 (3.4)	64.6 (7.5)	8.4 (4.8)

The main conclusions from these analyses are:

- The majority of the sediment monitored at EoS sites in the GBR catchments is in the <63  $\mu\text{m}$  particle size range (silt and clay).
- Greater than 90% of sediment exported from the larger, predominately grazed dry catchments (Normanby, Burdekin, Burnett and Fitzroy) is <16  $\mu\text{m}$  (fine silt and clay), although there is large variability between samples that may be related to the timing of sampling during events, the variability of sampled flows and sediment source. In contrast, suspended sediment samples collected in the coastal wet catchments have a lower fine silt and clay content (<16  $\mu\text{m}$ , <2  $\mu\text{m}$ ) and higher coarse fraction content ( $\geq 63\mu\text{m}$ ). Differences in climate, geology and land use are driving the following reasons for differences in particle size distribution between the two types of catchments:
  - The larger drier catchments with longer transit times would provide more opportunity for the coarser sediment to settle.
  - A larger amount of vegetation cover in the wet coastal catchments would reduce the chance for hillslope erosion.
  - Increased cohesiveness (aggregate stability) and less vulnerability to erosion in wet coastal catchment soils. These soils are generally highly weathered and likely to be less erodible due to low sodicity, moderate organic matter content and often high free iron contents that increase micro-aggregation and aggregate stability.
- There is an appreciable fraction of the fine sediment (i.e. <63  $\mu\text{m}$ ) leaving the GBR catchments at EoS that is larger than 16  $\mu\text{m}$  (from 5 to 29%), particularly in the Wet Tropics and Mackay-Whitsunday regions (see differences between the <63  $\mu\text{m}$  fraction and the <16  $\mu\text{m}$  fraction in Table 4). This is important to note considering that the size range that is modelled in P2R Dynamic SedNet (within Source) is the <20  $\mu\text{m}$  fraction and should be taken into account as part of the validation of suspended sediment models with monitored data. Additionally, it is important to take into account that fractions of fine sediment larger than 16  $\mu\text{m}$  would have water quality effects in the river estuaries that need to be assessed, including the generation of DIN (see section on the contribution of eroded soils to DIN export).
- To be conclusive about these findings an understanding of the true representativeness of the data is necessary, including how representative the flow conditions sampled are with respect to historical flow, and inter and intra annual variability. Additionally, it is important to demonstrate the influence of organic content in sediment particle size determination. Organic content appears to be higher in wet smaller coastal catchments marine plumes and this may be having a role in the binding of smaller particle sizes and consequently affecting particle size determination (Lewis et al., 2018).

## Particle size distribution in the Great Barrier Reef monitored subcatchments

Particle size distributions for the subcatchment monitored sites can be observed in Figure 8, Figure 9 and Figure 10. For the  $\geq 63\ \mu\text{m}$  fraction size (sand-sized fraction) there is some variability in the volume of sediment in this size fraction between subcatchments of the same river. For example, the Cape River tends to have larger volumes of sediment in this coarse fraction compared to other monitored rivers in the Burdekin catchment like the Belyando River. Additionally, there tend to be more outliers towards larger volumes of sediment in this size fraction for the Burdekin subcatchments, which indicates an occasional larger presence of coarse sediment in the subcatchments of the Burdekin River compared to EoS. The North and South Johnstone Rivers have a slightly larger volume in this size fraction on average compared to other rivers in the Wet Tropics or the Mackay-Whitsundays regions.

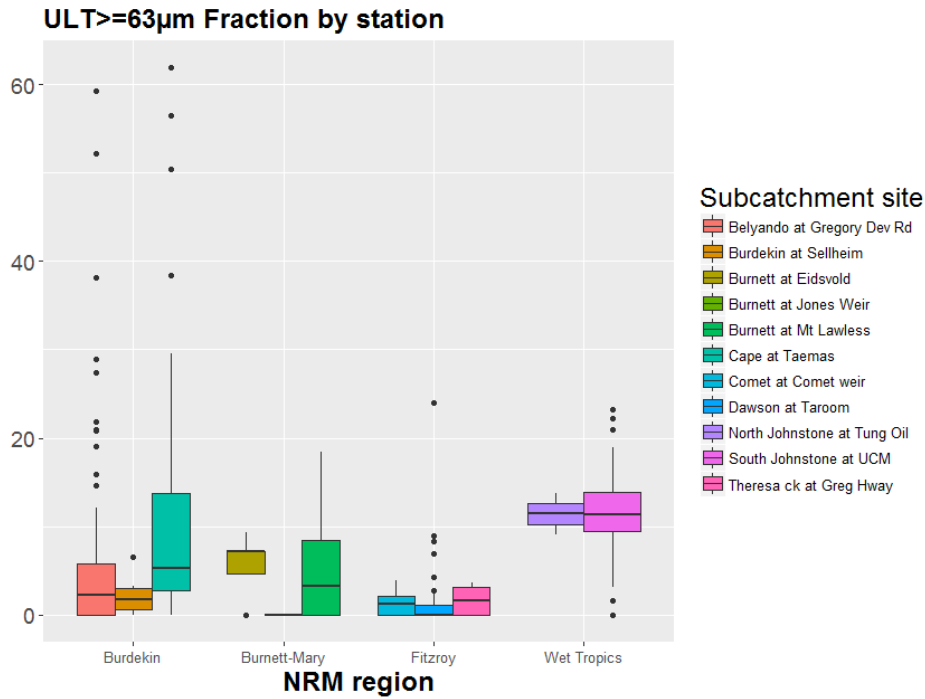


Figure 8 Percent of sediment in the  $\geq 63\ \mu\text{m}$  particle size class by NRM region in the GBR subcatchment sites

There is also large variability in the (very fine) sediment volume for the  $<16\ \mu\text{m}$  and  $<2\ \mu\text{m}$  ranges between subcatchments of the same river. For example in the Burdekin catchment, the Cape River at Taemas tends to have the lowest volume of sediment in both ranges, followed by the Burdekin river at Sellheim and then by the Belyando River with the highest volume. The variability in the sediment content between subcatchments is less in the Fitzroy River for the  $<16\ \mu\text{m}$ . The North and South Johnstone Rivers have the lowest content of sediment in the  $<16\ \mu\text{m}$  and  $<2\ \mu\text{m}$  ranges of all monitored rivers.

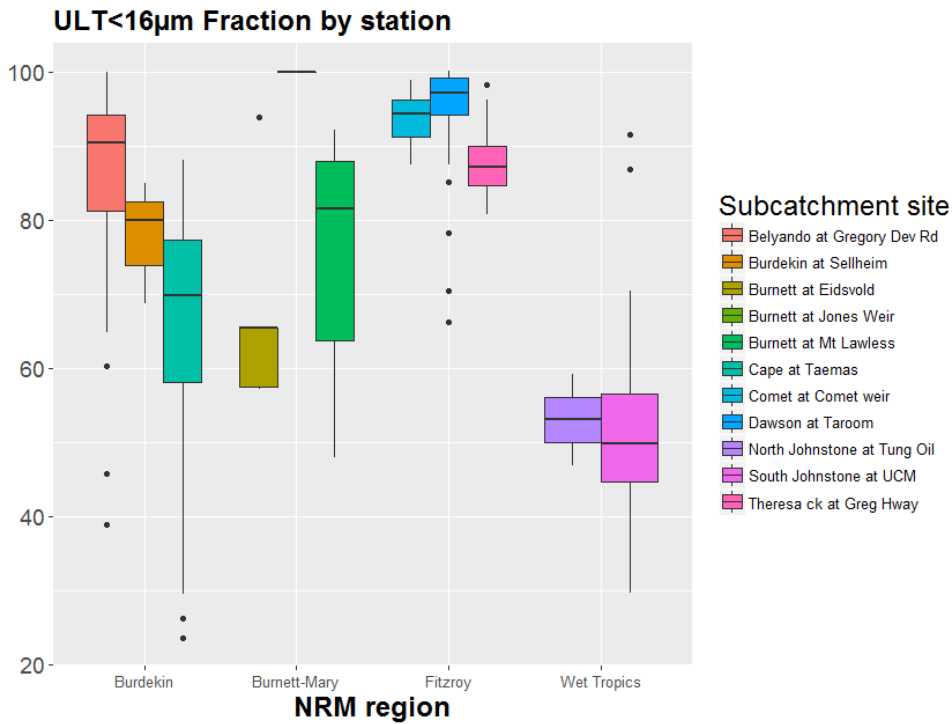


Figure 9 Percent of sediment in the  $< 16\ \mu\text{m}$  particle size class by NRM region in the GBR subcatchment sites

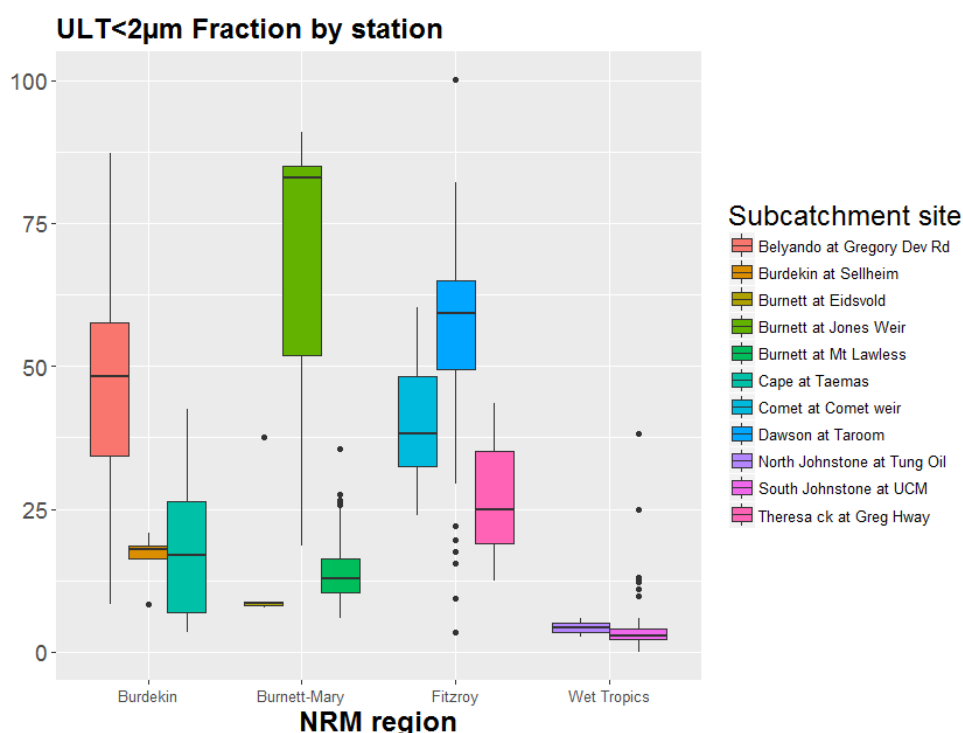


Figure 10 Percent of sediment in the <2 µm particle size class by NRM region in the GBR subcatchment sites

## Recommendations for future particle size distribution monitoring and research in GBR catchments

An appropriate choice of the degree of chemical and physical treatment to which a suspended sediment sample is exposed for analysis in the laboratory depends on the aim of the study. The choice lies between either retention of the aggregates in their natural sizes or disaggregation into individual grains. ***Ideally, the study of sediment particle sizes in streams and rivers would include the role of aggregation*** because this property determines the hydrodynamic properties of the sediment as well as its surface area related biological and chemical exchange properties. In the first instance it would be useful to compare in-situ measurements of particle size with laboratory measurements using the three methods.

Considering that the effect of transporting, storing and refrigerating water samples on the aggregation of GBR suspended sediment particles is unknown, ***it is recommended that the particle size distribution reported continues to use the ultra-dispersion method*** (absolute particle size distribution). ***Further consideration of the role of aggregation and organic matter in GBR sediment transport dynamics and sediment impact on water quality (e.g., DIN generation from sediment) are necessary*** to improve our understanding and modelling of this processes.

The ***particle size distribution of sediment can continue to be reported in a percent volume basis*** considering there were no significant differences found when using a percent weight basis.

***Further and broader discussions are necessary to define the particle size classes to report particle size distribution.*** Things to take into account for this discussion include the need for consistency between the particle size distribution method used for parent soils in SALI (hydrometer), which are an input to the P2R model platform for sediment generation, and the laser sizer particle size distribution method used for river sediment sampled by the GBRCLMP. Importantly, there is also a need for consistency between the particle size range used to generate the fine sediment load from catchments in the P2R Dynamic SedNet (within Source) modelling platform and the monitored sediment fractions. ***Particle size data is currently being collected at paddock, sub-catchment and EoS sites as well as in marine plumes (NESP 2.1.5). It would be useful to do a full source-to-sink assessment of the particle size methods and data before finalising recommendations for reporting and modelling size classes.***

***Monitoring of particle size should be included as a standard parameter in the GBRCLMP*** at least for the catchments where sediment and particulate nutrient management is prioritised (e.g., grazing catchments). This would enable the GBRCLMP to capture comparable datasets and would facilitate the validation of sediment and PN modelling data against monitored data.

## Conclusions - Particle Size Analysis

The key outcomes and conclusions for the contribution of eroded soils to particle size export:

- **The majority of the sediment monitored at EoS sites in the GBR catchments is in the <63  $\mu\text{m}$  particle size range** (silt and clay) (~ >90%).
- **Greater than 90% of sediment exported from the larger, predominately grazed dry catchments** (Normanby, Burdekin, Burnett and Fitzroy) **is <16  $\mu\text{m}$  (clay and fine silt)**, although there is large variability between samples that may be related to the timing of sampling during events, the variability of sampled flows and sediment source. **In contrast, suspended sediment samples collected in the coastal wet catchments have a lower fine silt and clay content (<16  $\mu\text{m}$ , <2  $\mu\text{m}$ ) and higher coarse fraction content ( $\geq 63\mu\text{m}$ ).**
- **There is an appreciable fraction of the fine sediment (i.e. <63  $\mu\text{m}$ ) leaving the GBR catchments at EoS that is larger than 16  $\mu\text{m}$  (from 5 to 29%),** particularly in the Wet Tropics and Mackay-Whitsunday regions. This is important to note considering that the size range that is modelled in P2R Dynamic SedNet (within Source) is the <20  $\mu\text{m}$  fraction and **should be taken into account as part of the validation of suspended sediment models with monitored data.** Additionally, it is important to take into account that **fractions of fine sediment larger than 16  $\mu\text{m}$  would have water quality effects in the river estuaries that need to be assessed,** including the generation of DIN (see section on the contribution of eroded soils to DIN export).
- To be conclusive about these findings **an understanding of the true representativeness of the data is necessary,** including how representative the flow conditions sampled are with respect to historical flow, and inter and intra annual variability. Additionally, it is important to **demonstrate the influence of organic content in sediment particle size determination.** Organic content appears to be higher in wet smaller coastal catchments marine plumes and this may be having a role in the binding of smaller particle sizes and consequently affecting particle size determination (Lewis et al., 2018).
- **At this time it is recommended that the reported particle size distribution continues to use a percent volume basis and the ultra-dispersion method** (that measures absolute particle size distribution).
- **Further and broader discussions are necessary to define the particle size methods and classes to report particle size distribution.** Particle size datasets are currently being collected and analysed at paddock, sub-catchment, EoS and in marine plumes using a variety of methods. It would be useful to do a full source to sink assessment of the particle size methods and data before finalising recommendations for methods and reporting size classes.
- **Monitoring of particle size should be included as a standard parameter in the GBRCLMP** at least for the catchments where sediment and particulate nutrient management is prioritised (e.g., grazing catchments).

# Contribution of eroded soils to dissolved inorganic nitrogen export

## Methods

Using our current understanding of the bioavailability of particulate nitrogen (PN), 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 ( $<20\ \mu\text{m}$ ) and transported in rivers (Figure 11).

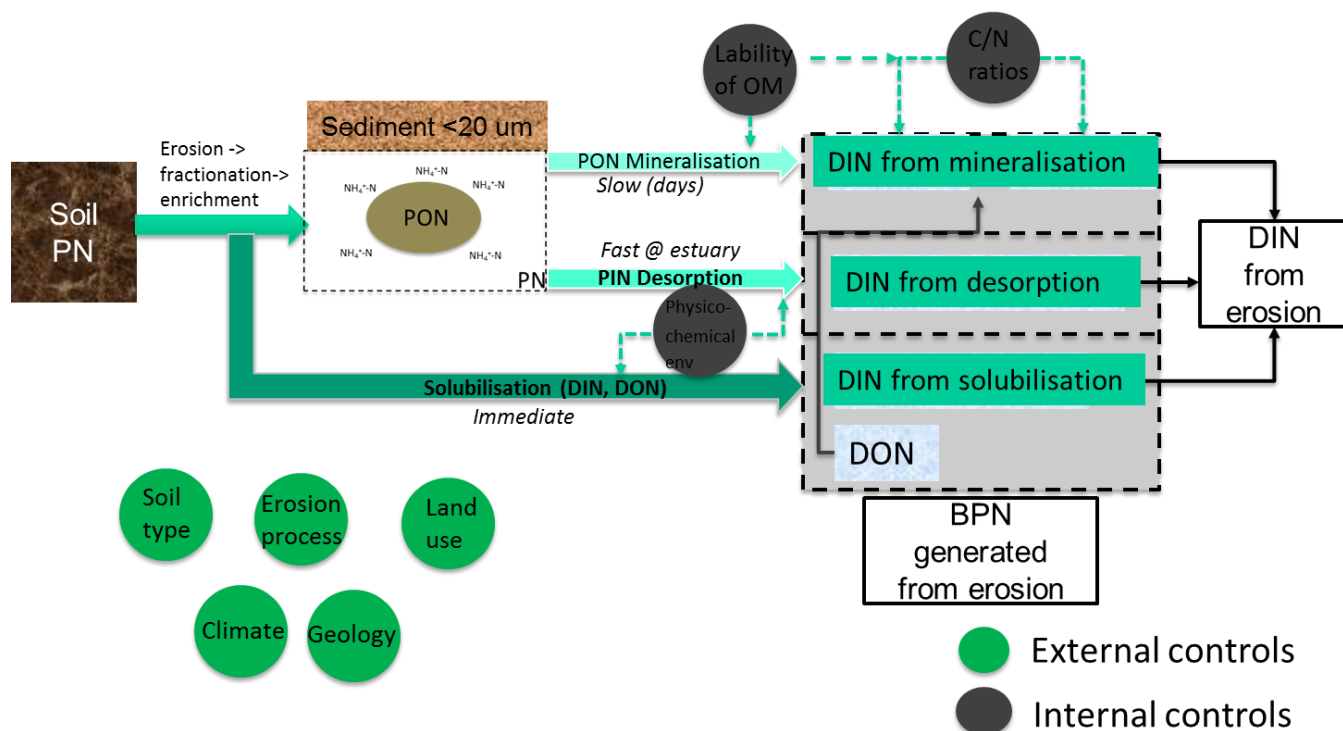


Figure 11 Conceptual diagram depicting the processes and controls underlying the generation of dissolved inorganic nitrogen (DIN) from eroded soil in water. \*BPN – Bioavailable particulate N

The following processes were identified:

1. **Solubilisation of DIN and DON from eroded soil**: This is a fast occurring process at source in which the DIN (all the  $\text{NO}_3^-$ -N and the fraction of the  $\text{NH}_4^+$ -N not adsorbed onto sediment) and DON in the eroded soil pore water enter the aquatic environment via runoff or groundwater. These fractions will be transported to the stream system irrespective of the bulk soil being delivered.
2. **Particulate organic N (PON) mineralisation**: This is a slow occurring process with a timeframe of days (varies depending on catchment size) in which the organic fraction of particulate N associated with the eroded sediment is mineralised to DIN during stream transport by the action of micro-organisms (bacteria and fungi).
3. **DON mineralisation**: This is a slow occurring process with a timeframe of days in which the organic fraction of dissolved N that has been solubilised from eroded soil is mineralised to DIN during stream transport by the action of micro-organisms.
4. **Particulate inorganic N (PIN) desorption**: This is a physico-chemical process in which the ammonium ( $\text{NH}_4^+$ -N) adsorbed to the negatively charged silt and clay particles in eroded sediment is desorbed (becomes soluble) through cation exchange processes (e.g. exchange of ammonium with sodium or magnesium) in water. This tends to occur when terrestrial sediment enters saline water in the estuaries.

The DIN generation processes differ in the timeframe of occurrence and in the position in the catchment where they occur and hence it is important to quantify them separately. Additionally, from previous research we know that DIN produced from these different processes varies with soil type, land use and erosion process (hillslope erosion

versus gully and channel erosion) (Burton et al., 2015; Garzon-Garcia et al., 2018; Garzon-Garcia et al., 2017a).

The Paddock to Reef (P2R) Source Catchments-based modelling framework (Ellis and Searle, 2014) was selected as the modelling platform to quantify the DIN produced from eroded soils from these different processes. Considering the extensive bioavailable nutrient dataset that has been produced for the Johnstone and Bowen river catchments in previous projects (Burton et al., 2015; Garzon-Garcia et al., 2017a), these two catchments were selected as pilot studies.

Additionally, we ran the PN model using the bioavailable nutrient dataset to compare the results with the results for PN using the current method. Currently, the models use PN soil data from the ASRIS data base multiplied by the hillslope fine sediment load (<20 µm), a constant enrichment factor (for hillslope erosion) and a delivery ratio to derive the PN load (See Figure 12).

$$\text{Hillslope PN Supply (kg)} = \text{Hill Sed. Load (kg)} * \text{Surface Soil Conc.} * \text{Enrich. Factor} * \text{Del. Ratio}$$

$$\text{Gully PN Supply (kg)} = \underbrace{\text{Gully Sed. Load (kg)}}_{\text{Fine + Coarse}} * \underbrace{\text{Sub-Surface Soil Conc.}}_{\text{ASRIS}} * \text{Del. Ratio}$$

Figure 12 Source catchments particulate nutrient generation algorithm for Great Barrier Reef catchment modelling

Because The bioavailable nutrient database includes measured soil:fine sediment enrichment ratios, the new method accounts for the variability in enrichment between the bulk soil and the <20 µm fine sediment for different soil types, land uses and erosion processes (Figure 13).

$$\text{Hillslope PN Supply (kg)} = \text{Hill Sed. Load (kg)} * \text{Surface Sediment Conc.} * \text{Del. Ratio}$$

$$\text{Gully PN Supply (kg)} = \underbrace{\text{Gully Sed. Load (kg)}}_{\text{Fine (<20 µm)}} * \underbrace{\text{Sub-Surface Sediment Conc.}}_{\text{Pedo-transfer function (soil N, soil type, land use)}} * \text{Del. Ratio}$$

Figure 13 Proposed particulate nutrient generation algorithm that uses pedo-transfer functions to estimate the concentration of PN in fine sediment

The new modelling approach for PN and DIN from sediment (**BPN models**) was as follows (see conceptual diagram in Figure 14):

- Develop linear equations (pedo-transfer functions) to estimate PN in the <20 µm sediment from PN in the soil at source. (Note that in the existing dataset bioavailable nutrient fractions were measured on the <10 µm sediment, but because the P2R platform models the <20 µm, for practical purposes it was assumed these are equivalent). The equations used for each catchment are presented in Appendix 1.
- Using the pedo-transfer functions, the PN in the <20 µm sediment was calculated for each of the catchments. To do this the pedo-transfer functions were applied to the PN source soil spatial layer currently used in the P2R models (sourced from ASRIS) to generate a spatial layer with PN content in the <20 µm sediment (mass content per unit mass of sediment). The map calculator conditional function in ArcMap was used to apply the corresponding function depending on soil type and land use for each grid (30 x 30 m)<sup>1</sup>. For the Bowen catchment a layer was generated for each of surface and subsurface sediment<sup>2</sup>. For the Johnstone catchment only contributions from hillslope erosion were quantified.
- The spatial distribution of enrichment factors between the PN content in parent soil and the PN content in

<sup>1</sup> This resolution was based on the resolution of the input soil PN data layers from ASRIS

<sup>2</sup> Surface sediment data was obtained from soil samples taken at 0-10 cm depth and subsurface sediment data was obtained from soil samples taken at all vertical strata differentiated by soil colour on exposed gully banks. For detailed methods see Garzon-Garcia et al 2017a.



the <20  $\mu\text{m}$  sediment were calculated in ArcMap for surface and subsurface soils of the Bowen catchment and surface soils of the Johnstone catchment.

- The N pools associated with DIN generation (Table 5) from the identified processes were quantified for the <20  $\mu\text{m}$  sediment in each relevant soil x land use combination for each of the two catchments using the existing bioavailable particulate nutrient (BPN) dataset (Burton et al., 2015; Garzon-Garcia et al., 2017a) and new data generated as part of this project to quantify DIN and DON solubilisation. For detailed methods used to generate the BPN dataset pools see Garzon-Garcia et al., 2017. The average values from three soil type x land use field replicates were used to generate a spatial layer for each of the N pools in the <20  $\mu\text{m}$  sediment (mass content per unit mass of 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 each N pool was generated for each of surface and subsurface sediment. For the Johnstone catchment only contributions from hillslope erosion were quantified.
- The generated layers for the <20  $\mu\text{m}$  sediment (PN, DIN from solubilisation, PON mineralisation, DON mineralisation, PIN desorption) were supplied to the P2R modellers. The 'SedNet Particulate Nutrient Generation Model' was replaced with a new model that allows for the fine sediment generation model (unmodified) to interact with the supplied layers to generate a load of each of the N pools from each hydrounit and erosion process (i.e., surface and subsurface) in the catchments. We refer to these set of models as Bioavailable Particulate Nitrogen models (**BPN models**).
- The P2R models were also run without modifications to estimate PN and DIN export from the catchments as a baseline for comparing the BPN models.

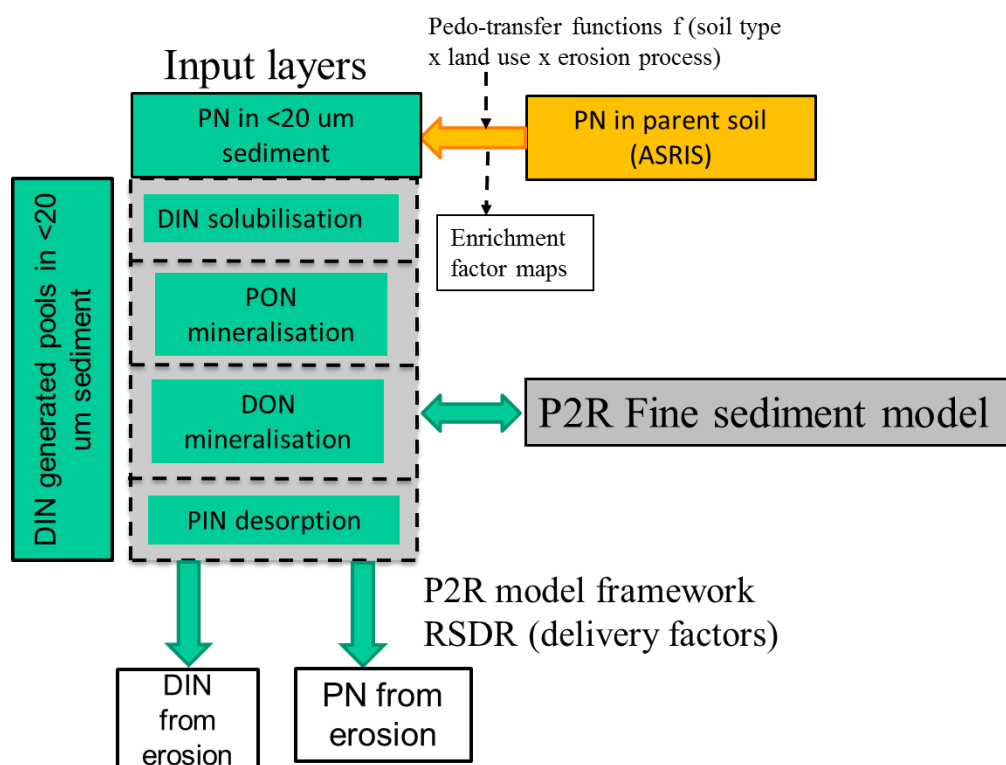


Figure 14 New modelling approach to estimate PN and DIN generated from soil erosion in Reef catchments using the P2R Dynamic SedNet (within Source) platform

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

- Delivery ratios were not modified from the current way the models are run (100% for gully erosion and streambank erosion, 10% from hillslope erosion in the Bowen River catchment, 15% for sugarcane in the Johnstone River catchment and 20% for other land uses in the Johnstone River catchment)
- The model was run for 28 years (1986-2014) as P2R models are.
- Specific settings used for parameter generation, delivery to stream and instream transport can be seen in Table 6.

The following assumptions were made for the BPN models:

- The travel time of water during average high-flow events from the top to the bottom of both the Bowen and Johnstone catchments is around 1 day and hence this was the time applied for instream PON mineralisation.
- DON mineralisation (DONb) was assumed to be 14% of the solubilised DON from parent soils. This is a conservative value when compared to values found from incubation experiments of the solubilised DON from 14 Bowen catchment soils (mean = 18.2%, SD= 14.8%) and 6 Johnstone catchment soils (mean = 23.5%, SD= 21%) carried out as part of this project (see Appendix 2). Note that there is large variability in how bioavailable (mineralisable) the DON fraction from different soil types x land uses is. It was also assumed that only 33% of the bioavailable DON would mineralise in 1 day. This proportion is the average value found for PON mineralisation in 1 day relative to PON mineralisation in 7 days.
- For the soil types in the Bowen catchment with no data in the BPN dataset (a very small fraction of the total area): Considering similarities in granulometry (texture) or soil forming processes, Calcarosols were assumed to have similar BPN content 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.
- For the Johnstone catchment: It was assumed that all land use classified as 'grazing modified pastures' had similar BPN content to dairy soils in the BPN dataset; land use classified as 'nature conservation' + 'managed resource protection' + 'other minimal use' had similar BPN content to forest soils. It was also assumed that Dermosols and Kandosols in forests have similar BPN content to Dermosols in forests of the Bowen catchment. For the rest of the soil types x land uses with no data, it was decided not to model the BPN contribution due to large uncertainty in the assumptions. The outputs from the Johnstone model were only analysed for the catchment areas with information.

Table 5 DIN generation processes and corresponding N pools contributed by soil erosion to downstream aquatic environments

Process	N pool*
DIN Solubilisation	Nitrate + Soluble ammonium ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}_{\text{sol}}$ )
PON mineralisation	Potential mineralisable N in 1 day (PMN1)
DON mineralisation	Bioavailable DON (DONb)
PIN desorption	Adsorbed ammonium ( $\text{NH}_4\text{-N}_{\text{ad}}$ )

\*All of these pools are measured as generated DIN (mass content per unit mass of sediment)

Table 6 Specific model settings for parameter generation, stream delivery and instream transport for BPN models

Parameter	Generation	Stream delivery	Instream transport
PN	Function of eroded fine soil (<20 $\mu\text{m}$ )	as per PN (10%)	as per PN (potential deposition)
DIN solubilisation	Function of eroded fine soil (<20 $\mu\text{m}$ )	as per dissolved, 100%	as per dissolved (no deposition)
PON mineralisation	Function of eroded fine soil (<20 $\mu\text{m}$ )	as per PN (10%)	as per dissolved (no deposition)
DON mineralisation	Function of eroded fine soil (<20 $\mu\text{m}$ )	as per dissolved, 100%	as per dissolved (no deposition)

PIN desorption	Function of eroded fine soil (<20 $\mu\text{m}$ )	as per PN (10%)	as per PN (potential deposition)
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## Results and Discussion

### Modelling the erosion of particulate nitrogen in the Bowen and Johnstone river catchments

Enrichment ratios between the PN content in parent soil and the PN content in the fine (<20  $\mu\text{m}$ ) sediment vary widely in the Bowen and Johnstone River catchments as expected (Figure 15 and Figure 16). Surface soils (Bowen and Johnstone catchments) tended to have larger enrichment ratios (1-17.4) than subsurface soils (Bowen catchment only) (1.3-2.1). This is an important factor to include in the modelling of PN in catchments because it would have an effect on the estimated PN load. Additionally these differences in enrichment would have a significant role in determining the areas of the catchments that export more PN in association with fine sediment. The reason for the difference in enrichment ratios between the catchments needs to be further explored.

The proposed new method for modelling particulate nitrogen (**BPN PN model**) was tested on the P2R model platform for the two case studies. We consider it an improvement to the current way PN is modelled because it includes the variability of sediment enrichment factors in the catchments and the role of soil type and land use in determining this enrichment. Linear regressions between the PN annual loads estimated by the BPN PN model and the loads estimated with the current model were very good (Bowen catchment:  $R^2 \sim 1$ , Johnstone catchment:  $R^2 \sim 0.96$ ) (Figure 17), but the loads estimated with the BPN PN model accounted for only 79% and 44% of the currently estimated average PN annual load for the Bowen and Johnstone river catchments, respectively. The current P2R model would be overestimating the PN load from the <20  $\mu\text{m}$  sediment if it was not for the use of a 10% delivery ratio, because it assumes all the PN in the bulk soil is transferred and transported in the stream system although only the finer fractions reach the end-of-catchments. In reality, not only the <20  $\mu\text{m}$  sediment fraction reaches the end-of-catchments (see results section on sediment particle size), hence the BPN PN model is likely to be underestimating the PN loads associated with sediment. Additionally, the delivery ratio of 10% is inappropriate for the BPN PN model. We need to improve our understanding of delivery ratios.

A first step in improving the PN modelling in the P2R platform is to account for the variability in fine sediment characteristics (e.g. enrichment factors) in the catchment, which was successfully carried out in this pilot case study. Further to this, the role of particle size would have to be included either to model PN loads more accurately or to be able to compare model outputs for the <20  $\mu\text{m}$  sediment fraction with PN monitoring data associated with larger fractions. Additionally, a better understanding of fine sediment delivery ratios is necessary to improve the modelling of PN.

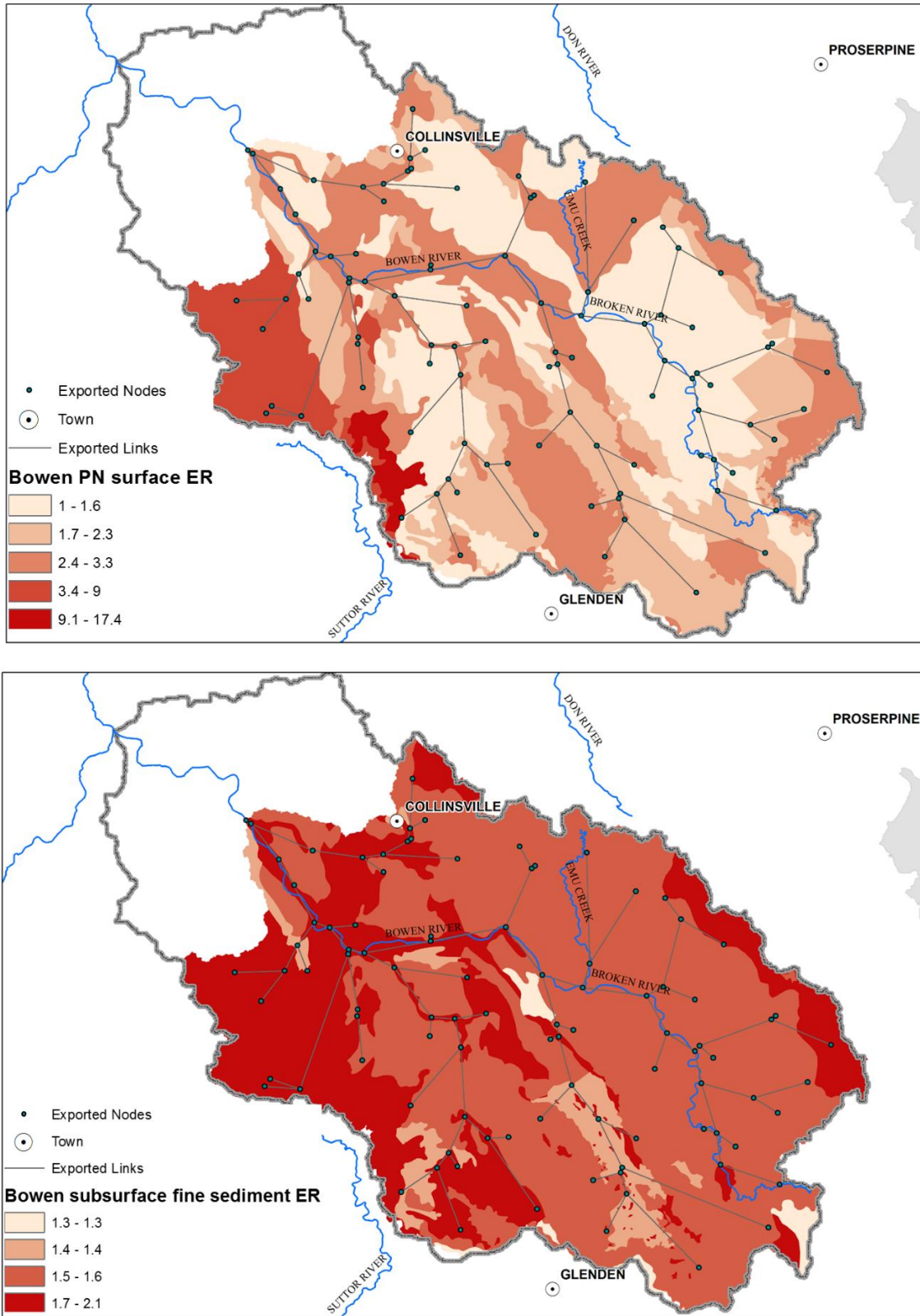


Figure 15 Particulate nitrogen enrichment ratios of fine surface and subsurface sediment (<20  $\mu\text{m}$ ) at source in the Bowen River catchment. Note that the end-of-Bowen-catchment modelling node does not correspond to end-of-Bowen-catchment outlet.

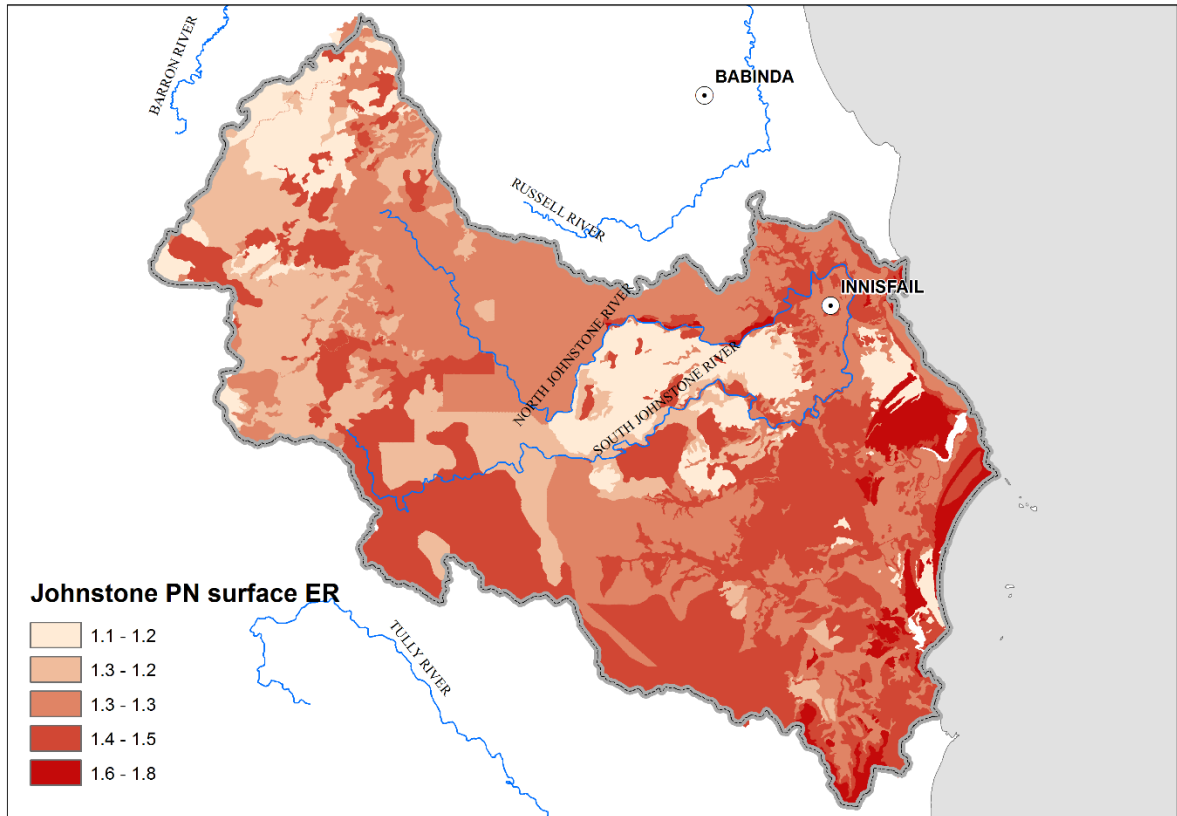
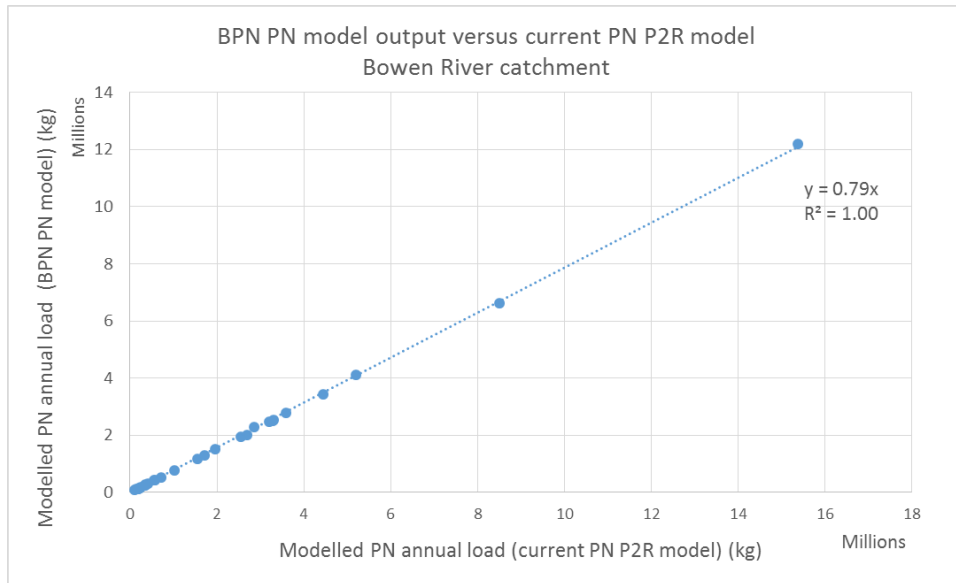


Figure 16 Particulate nitrogen enrichment ratios of fine surface sediment (<20 um) at source in the Johnstone River catchment



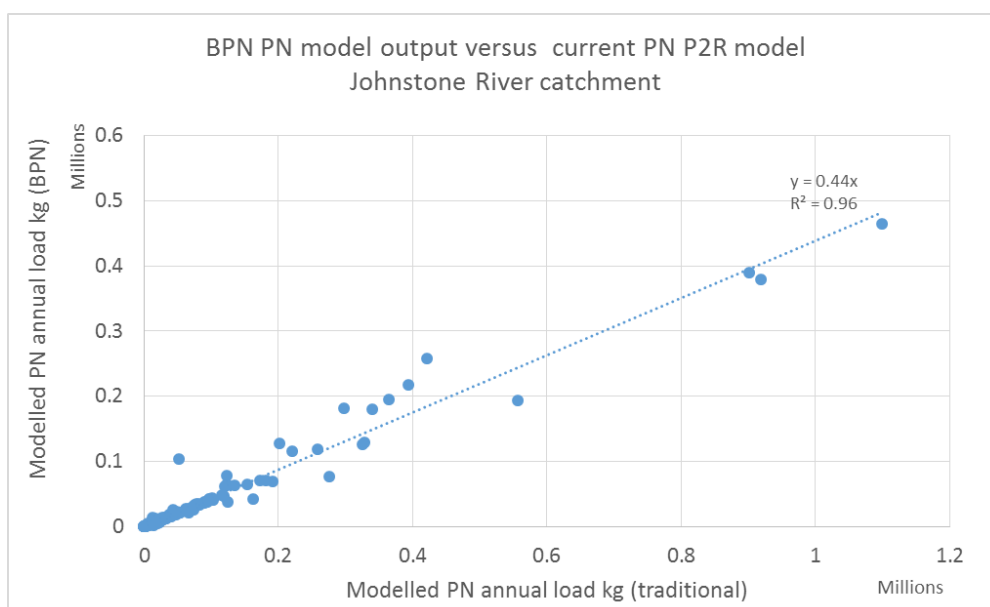


Figure 17 Modelled PN annual loads using BPN model versus modelled PN annual loads using current P2R model for the Bowen and Johnstone River catchments

## The contribution of eroded soils to dissolved inorganic nitrogen export

### Bowen River catchment

The BPN model outputs indicate that DIN generation associated with sediment erosion and transport is significant in the Bowen River catchment and that all of the end-of-catchment exported DIN currently modelled in the Bowen River catchment can be accounted for by the DIN generated from sediment (Figure 18). 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 130 tonnes  $y^{-1}$  on average for the 28 year modelled period (1986-2014) (Figure 18). This is approximately 1.3 times the currently modelled DIN load at the end-of-catchment of 103 tonnes  $y^{-1}$ . When adding the DIN generated from PIN desorption, which would be produced when salinity increases in the estuary of the Burdekin River, the DIN load generated by the Bowen River catchment would increase to 156 tonnes  $y^{-1}$  on average (Figure 18). This is approximately 1.5 times the currently modelled DIN load at the end-of-catchment. The larger than modelled value at end-of-catchment (1.3 times the currently modelled DIN load) may be explained by the fact that system losses have not been included in the model (e.g., denitrification). Additionally, some of the BPN model assumptions need to be further revised including if fine sediment that settles in-stream mineralises at the same rates than suspended sediment.

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. As a reference, the BPN predevelopment model estimated that 80 tonnes  $y^{-1}$  of DIN were produced by sediment in a predevelopment erosion scenario.

The main sources of sediment in a catchment are not necessarily the main sources of DIN producing sediment. This is both true for erosion process source (gully, hillslope or channel erosion) and spatial source (areas in the catchment). In the Bowen River catchment the P2R model indicates that for the 28 year modelled period, gully erosion is on average the main source of sediment (62% contribution) followed by hillslope erosion (33% contribution) (Figure 19). BPN modelling results for the 28 year modelled period based on this distribution of sediment sources indicate that the main source of PN is hillslope erosion (56% contribution) (Figure 19) and that the main source of DIN producing sediment is also hillslope erosion (87%) (Figure 18). These findings can be explained by the higher content of PN in surface sediment compared to subsurface sediment (on average 3.1 times higher for the Bowen, SD = 2), as well as its higher bioavailability (Garzon-Garcia et al., 2018) (on average a mass unit of surface <20  $\mu\text{m}$  sediment has the potential to produce 13 times more DIN than a subsurface <20  $\mu\text{m}$  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.

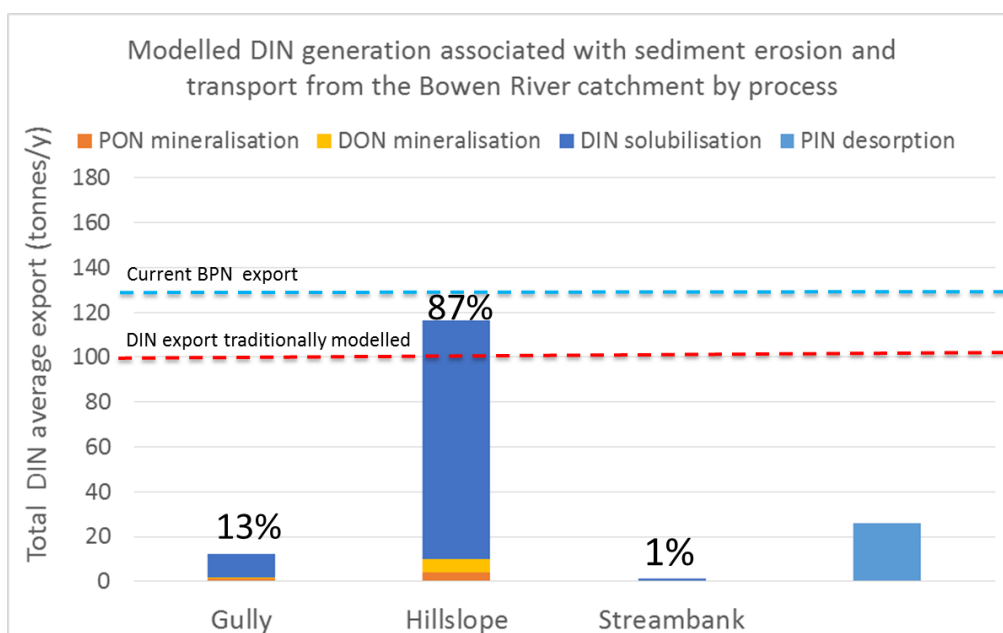


Figure 18 Annual modelled DIN generation associated with sediment erosion and transport from the Bowen River catchment by process

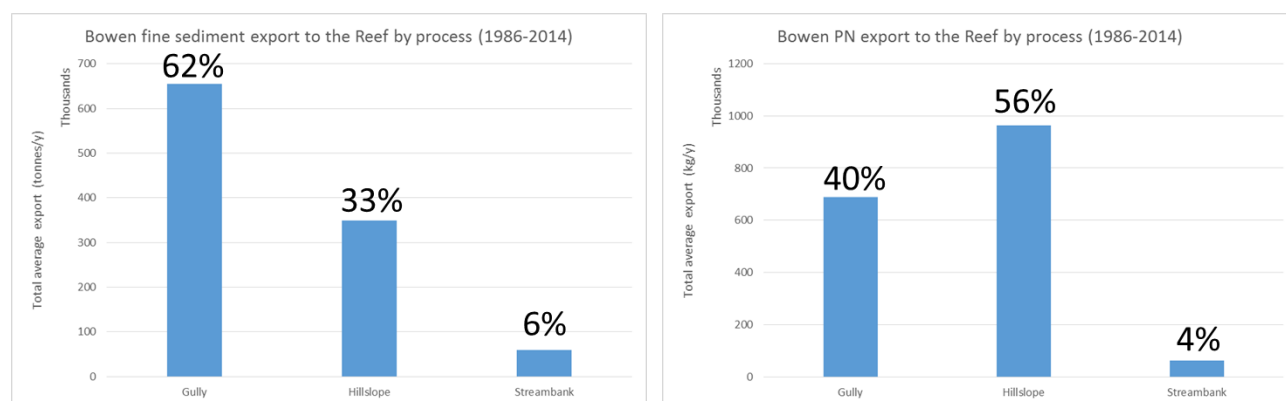


Figure 19 Main sources of fine sediment (<20  $\mu\text{m}$ ) (P2R modelled) (a) and PN (BPN modelled) (b) from the Bowen River catchment

DIN solubilisation is the main process contributing to the generation of the end-of-catchment DIN load from sediment with more than 70% of the load contributed from this process in association with hillslope erosion and a little over 50% in association with gully erosion (Figure 20). 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. Although PON mineralisation was not such a significant contributor to the end-of-catchment Bowen river DIN load, it is important to consider that sediment will continue to generate a significant DIN load from PON mineralisation as it is further transported in the Burdekin River and in the Burdekin River plume entering the marine environment (Garzon-Garcia et al., *In preparation*).

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 among others. For this project, DIN solubilisation was quantified for the different soil types on air-dried soil (40°C) for samples taken at one point in time in the catchment (after the wet season for the Bowen River catchment) (See the methods section in Appendix 1). 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 in the quantification of this process for different soil types.

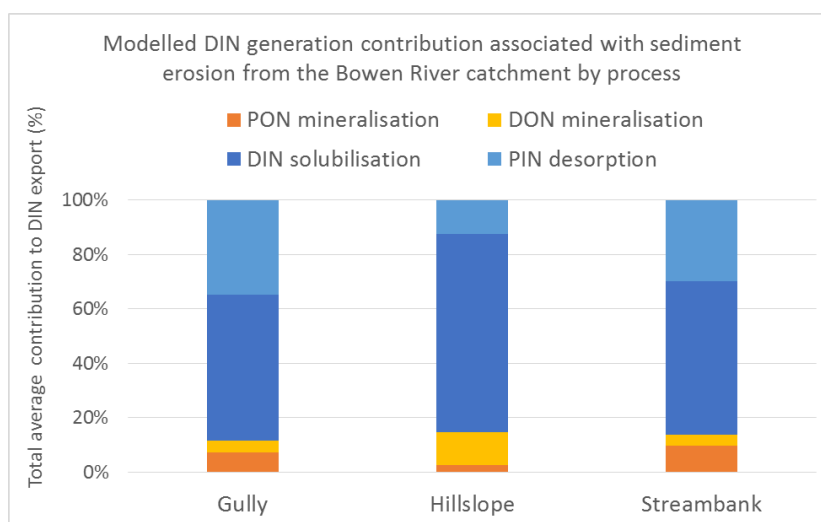


Figure 20 Contribution to DIN generation associated with sediment erosion from different DIN generation processes in the Bowen River catchment

Sediment source contribution is an important determinant of the total DIN load generated from sediment in the catchment. 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 is larger than the average P2R model estimates of 68% (Figure 19). It has also been found that this contribution varies depending on rainfall conditions in the previous years, with an estimate of 83% and 93% subsurface erosion contribution after a period of below and above average rainfall, respectively (Wilkinson et al., 2015). When we adjusted our results using the tracing data the total catchment exported DIN from sediment drastically reduced in both scenarios, to 96 tonnes  $y^{-1}$  in the former and 58 tonnes  $y^{-1}$  in the latter. 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 the two sources for the 93% subsurface contribution scenario (Figure 21).

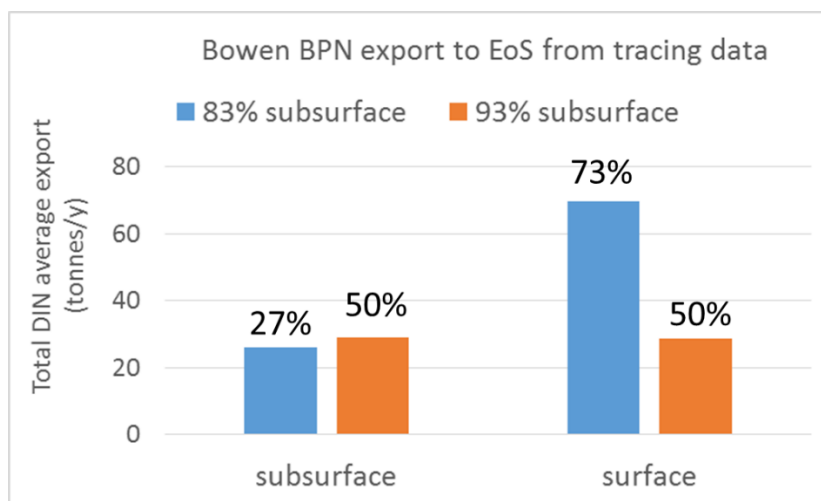


Figure 21 Annual estimated DIN generation associated with sediment erosion and transport under two sediment source contribution scenarios based on tracing studies in the Bowen River catchment

These findings highlight the importance of accurately modelling the distribution between surface and subsurface sediment sources in catchments towards accurately modelling DIN generation from sediment and also PN loads. Considering the important relative contribution of hillslopes to PN and DIN from sediment and the large sensitivity of PN and BPN 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.



## Johnstone River catchment

In the Johnstone River catchment the P2R 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) (Figure 22). P2R modelling results indicate that the main source of PN at the end-of-catchment is hillslope erosion (66% contribution), with minor contributions from other sources of erosion (Figure 22). 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, considering this erosion process is the main source of PN in the catchment. It is estimated that 77% of the Johnstone River catchment area is dominated by these land uses. The P2R modelling results estimated that on average 71% of the sediment and 48% of the PN in the catchment are sourced from these land uses. It is important to note that for the BPN models there was information for soil types corresponding to approximately 89% of the area in these land uses (61% for banana, 96% in conservation, 89% in dairy and 65% in sugarcane) from the existing BPN dataset (Burton et al., 2015; Garzon-Garcia et al., 2017a) and new data generated as part of this project.

The P2R model indicates that for the 28 year modelled period, conservation is the main source of hillslope erosion sediment at end-of-catchment (46% contribution) followed by sugarcane (35%) (Figure 23). BPN modelling results based on this distribution of sediment sources indicate that the main source of PN at the end-of-catchment is sugarcane (66%) (Figure 23).

It is important to note that the PN content in the <20  $\mu\text{m}$  sediment estimated from PN content in the bulk soil (SALI database) using pedo-transfer functions developed as part of this study (see Appendix 1) were often different to those calculated using the PN content in the <20  $\mu\text{m}$  sediment derived from the bioavailable nutrient dataset (Burton et al., 2015; Garzon-Garcia et al., 2017a) (Table 7). This is due to differences in the PN content in the bulk soil between the SALI database and the BPN dataset. The difference may be due to natural variability in PN soil content and/or the timing of sample collection post fertiliser application and land use management practices. Further consideration needs to be given to this before any recommendations about additional data collection in the Johnstone or similar multiple land use catchments is commissioned. It is important to note that there are very few SALI data points in conservation areas of the Johnstone River catchment.

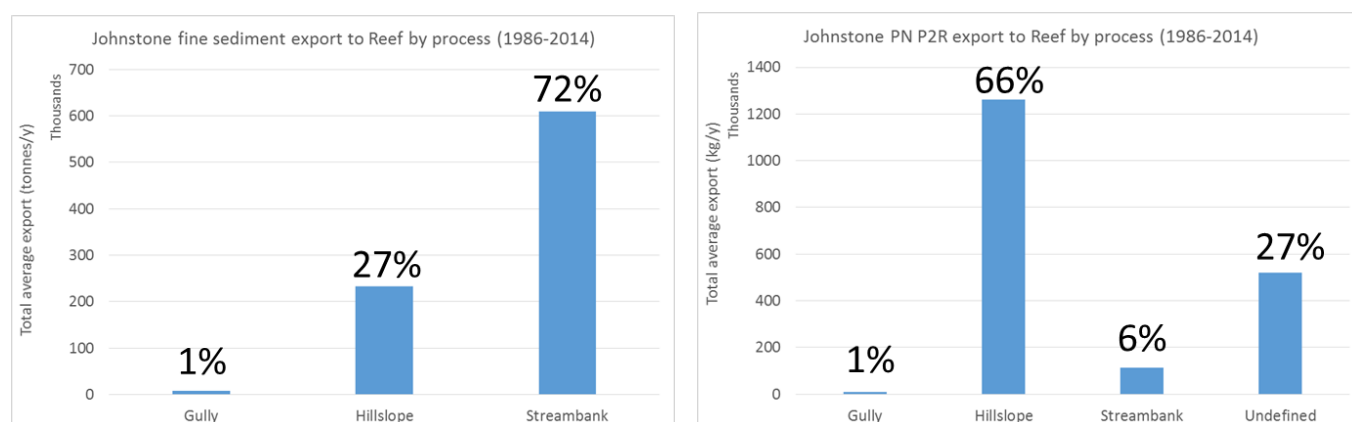


Figure 22 Main sources of fine sediment (<20  $\mu\text{m}$ ) (P2R modelled) (a) and PN (P2R modelled) (b) by erosion process from the Johnstone River catchment

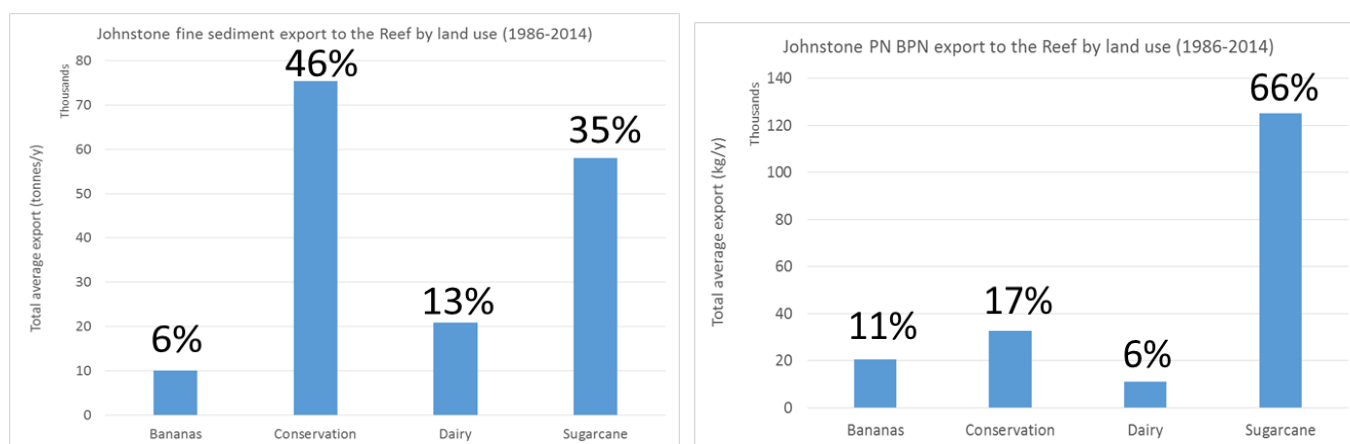


Figure 23 Main sources of fine sediment (<20  $\mu\text{m}$ ) (P2R modelled) (a) and PN (P2R modelled) (b) by land use from the Johnstone River catchment

Table 7 PN content in the <20  $\mu\text{m}$  sediment by land use in the Johnstone River catchment estimated from PN content in the bulk soil (SALI database,  $n = 1674$ ) using pedo-transfer functions and from the BPN dataset

Land use	Pedo-transfer functions applied to SALI PN in soil				BPN dataset				
	Mean	SD	min	max	Mean	SD	min	max	n
Banana	0.38	0.11	0.12	0.58	0.29	0.06	0.23	0.37	5
Conservation	0.32	0.16	0.07	0.67	0.51	0.16	0.31	0.74	6
Dairy	0.44	0.07	0.23	0.50	0.69	0.10	0.59	0.79	3
Sugarcane	0.30	0.10	0.09	0.67	0.22	0.04	0.17	0.30	5

In contrast to the Bowen River catchment results, the BPN 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 tonnes  $\text{y}^{-1}$  on average for the 28 year modelled period (1986-2014). This is approximately 3% of the currently modelled DIN load at the end-of-catchment of 1060 tonnes  $\text{y}^{-1}$ . When adding the DIN generated from PIN desorption, which would be produced when salinity increases in the estuary of the Johnstone River, the DIN load generated by the Johnstone River catchment would increase to 37 tonnes  $\text{y}^{-1}$  on average. This is approximately 3.5% of the currently modelled DIN load at the end-of-catchment.

Similarly to the Bowen River catchment, the main sources of sediment at the end-of-catchment were not necessarily the main sources of DIN producing sediment. Although conservation and sugarcane dominated sediment export, and sugarcane alone dominated PN export, BPN 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) (Figure 24).

The low relative contribution of sediment to DIN export at the Johnstone River end-of-catchment compared to the large contribution at the Bowen River end-of-catchment is caused by the very high modelled DIN yields from fertilizer use in the Johnstone (Figure 25) and not by a lower generation of 'DIN from sediment' in this catchment. In fact, 'DIN from sediment' yields (kg DIN generated from eroded sediment per hectare per year) in the Johnstone are much higher than in the Bowen river catchment, which indicates much higher bioavailability of these sediments (Figure 26). This confirms our previous research findings of higher bioavailability in sediments from the Johnstone River catchment using phytoplankton activity as an indicator (Garzon-Garcia et al., 2018).

It is important to consider that sediment will likely continue to generate DIN from PON mineralisation as it is further transported in the estuary and the marine environment. Our current research (NESP 2.1.5) indicates that this occurs in the Burdekin River sediment plumes and that this generation is significant relative to DIN end-of-catchment export (Garzon-Garcia et al., *In preparation*). In this project (see methods section Appendix 1), 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. It is likely that this is happening when sediment is transported in the Johnstone River and that there is potential for this sediment to be mineralised later in the marine environment. Given this, a significant contribution from Johnstone river sediment to DIN in the marine environment cannot be discounted at this stage.

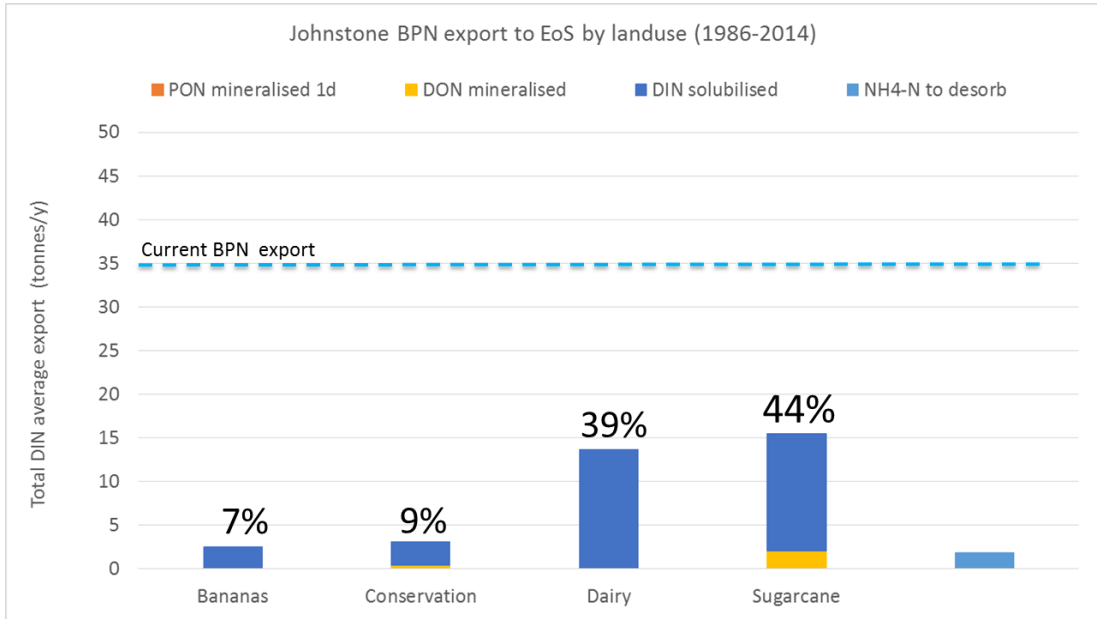


Figure 24 Annual modelled DIN generation associated with sediment erosion and transport from the Johnstone River catchment by land use

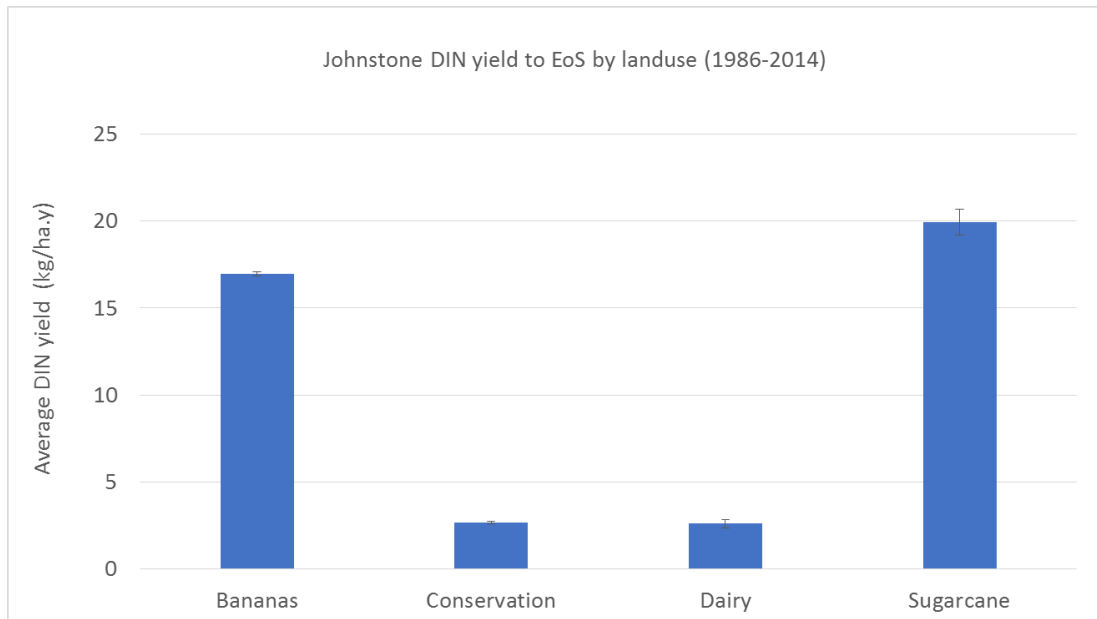


Figure 25 P2R modelled DIN yields at the Johnstone River end-of-catchment by land use

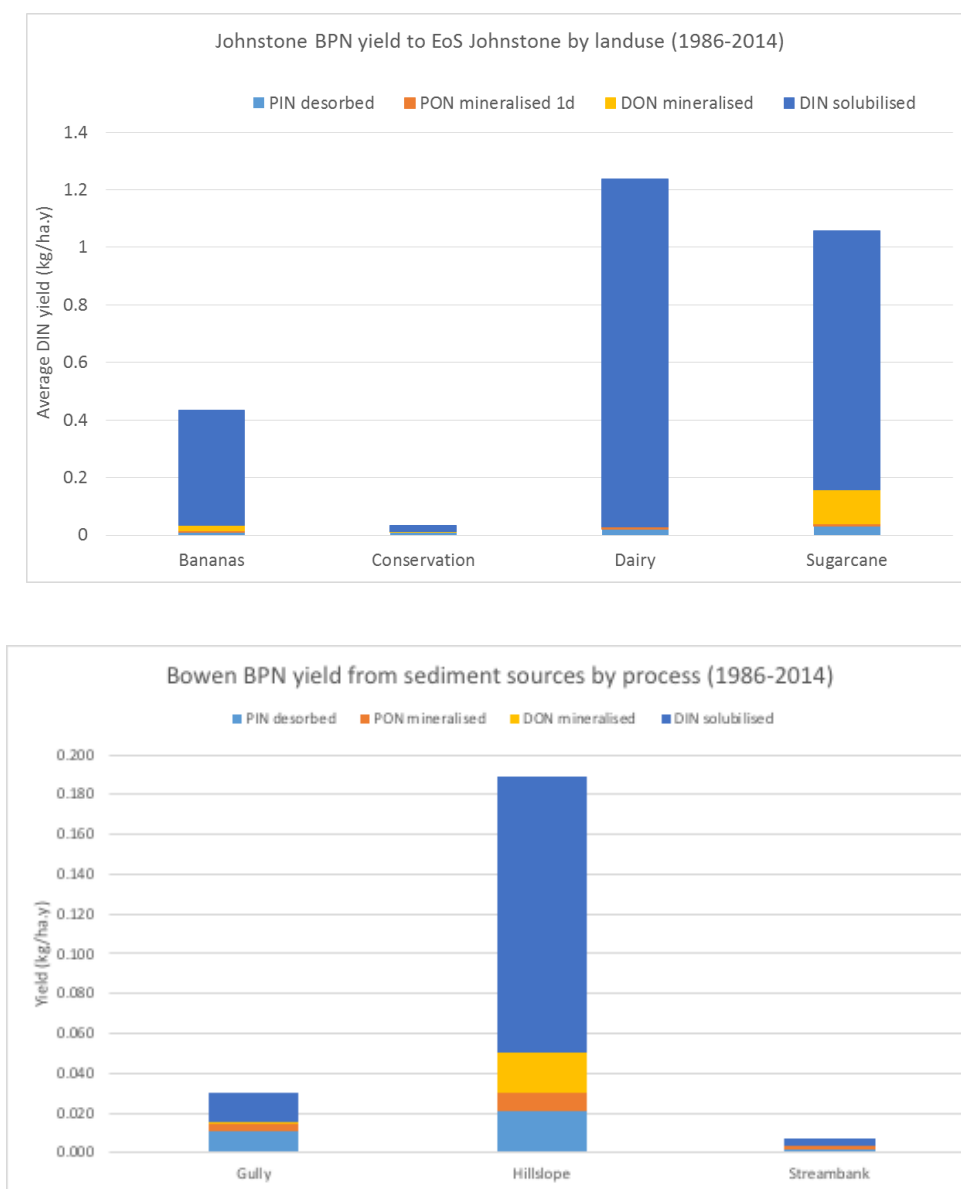


Figure 26 'DIN generation from sediment' yields by land use at the Johnstone River end-of-catchment (a) and by erosion process at the Bowen River end-of-catchment (b)

Similarly to findings for the Bowen River catchment (Figure 20), DIN solubilisation is the main process contributing to DIN generation from eroded soils. In the Johnstone 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 (Figure 27). 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.

It is interesting to note that DIN from solubilisation contributes a lesser proportion to 'DIN from sediment' in conservation areas compared to other land uses (65% in the Johnstone River catchment and 40% in the Bowen River catchment) (Figure 27). The fact that the 'DIN from solubilisation' pool, which is immediately available, is smaller in size in the conservation areas than it is in all other land uses indicates that anthropogenic land uses may have reduced the timeframes for particulate nutrient bioavailability.

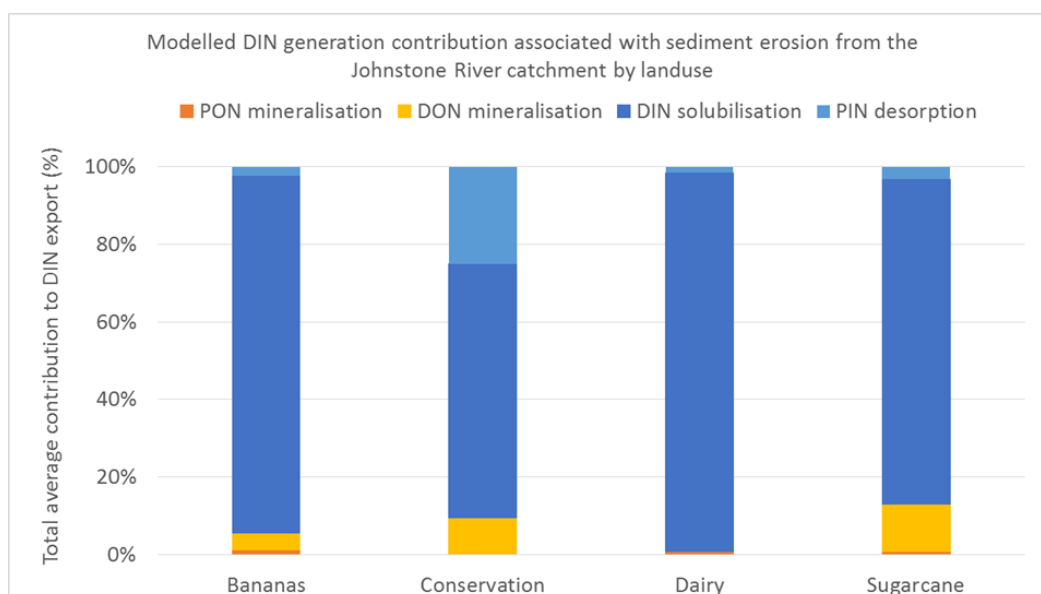


Figure 27 Contribution to DIN generation associated with sediment erosion from different DIN generation processes in the Johnstone River catchment

## Framework to account for PN and DIN reductions associated with erosion management

After the successful test run of a revised PN model and the new 'DIN generation' from eroded sediment model, we propose development of a formalised Dynamic SedNet (within Source) demonstration phase for sediment quality modelling (Figure 28). The method outlined in Figure 28 is that which was used in this report with a number of improvements. In brief, the method is to use parent soil data from SALI to estimate sediment PN and BPN pools, and ultimately 'DIN generation' from eroded sediment using a suite of pedo-transfer functions (multiple linear equations) (see previous methods section). The model is then run using the estimated sediment quality to generate end-of-catchment loads of PN and BPN pools. When added together, the BPN pools account for total DIN generation from eroded soils. A number of improvements to the existing SALI database and the PN and 'DIN generation' models outlined in this report are recommended.

SALI improvements:

- Spatial coverage – some land uses and geomorphic units (e.g. alluvial deposits) have not been sampled representatively. This was also identified in Prosser 2018.
- Update legacy datasets – in some cases datasets are quite old and nutrient data may not reflect current management practices.
- Additional parameters – archive samples can be analysed for the additional parameters recommended in the Appendix 1 section (see Table 9), where land use management has not significantly changed, enabling investigation of useful relationships that will make existing observations relevant to the new concept. Any new samples taken (based on dot points 1 and 2) should include analysis of the additional parameters.
- Subsurface data – currently there is little existing subsurface data for nutrients. Archive and new subsurface samples should also be analysed for the additional parameters.

Improvement to model for sediment PN and DIN generation:

- Delivery ratio – intrinsic soil properties are important in driving erosion transport and delivery of sediment particles to the stream network. Further process understanding is required to improve the delivery ratios currently used.
- Sediment modelling improvement – given the direct relationship between sediment and particulate nutrients, any improvements to the modelling of PN and 'DIN generation' need to be accompanied by improvement in sediment modelling [see (Prosser, 2018)].
- Management practice impact on soil quality, particulate nutrient export and 'DIN generation' from eroded soils: in order to track reductions in PN and 'DIN generation' from eroded soils associated with improved land management, it is necessary to understand how soil quality changes with management practice (e.g., reductions in bioavailable nutrient export from gully rehabilitation work).
- Particle size fractions required to accurately model PN and 'DIN generation' from eroded soils: by only modelling the <20 $\mu$ m fraction of sediment we may be underestimating end-of-catchment PN and 'DIN generation' loads (see section with Particle size analysis conclusions). Whilst the >20 $\mu$ m fraction of sediment that reaches the end-of-catchment mostly settles in the estuaries, it would still contribute to PN at

end-of-catchment and 'DIN generation' to the Reef. This is not accounted for in the existing model. We need to understand how significant the contribution from the >20µm fraction is.

Validation of pedo-transfer functions: To continue to use this approach for estimating PN and BPN pools from fine sediment erosion as part of P2R Dynamic SedNet (within Source) modelling, it is recommended that these pedo-transfer functions are validated at paddock scale within the same catchments for which they were developed (Johnstone and Bowen) and in other catchments with similar land-use characteristics, as well as for other sediment particle sizes (<63 µm). This validation requires the measurement of the additional parameters referred to in the Implications section – tracking investments (monitoring) on runoff samples.

Validation of PN and DIN generation model: in order to validate the proposed model, a number of additional parameters need to be monitored at end-of-catchment monitoring sites (see Implications section – tracking investments (monitoring)). Additionally the method needs to be applied in other grazing catchments.

## Demonstration Phase

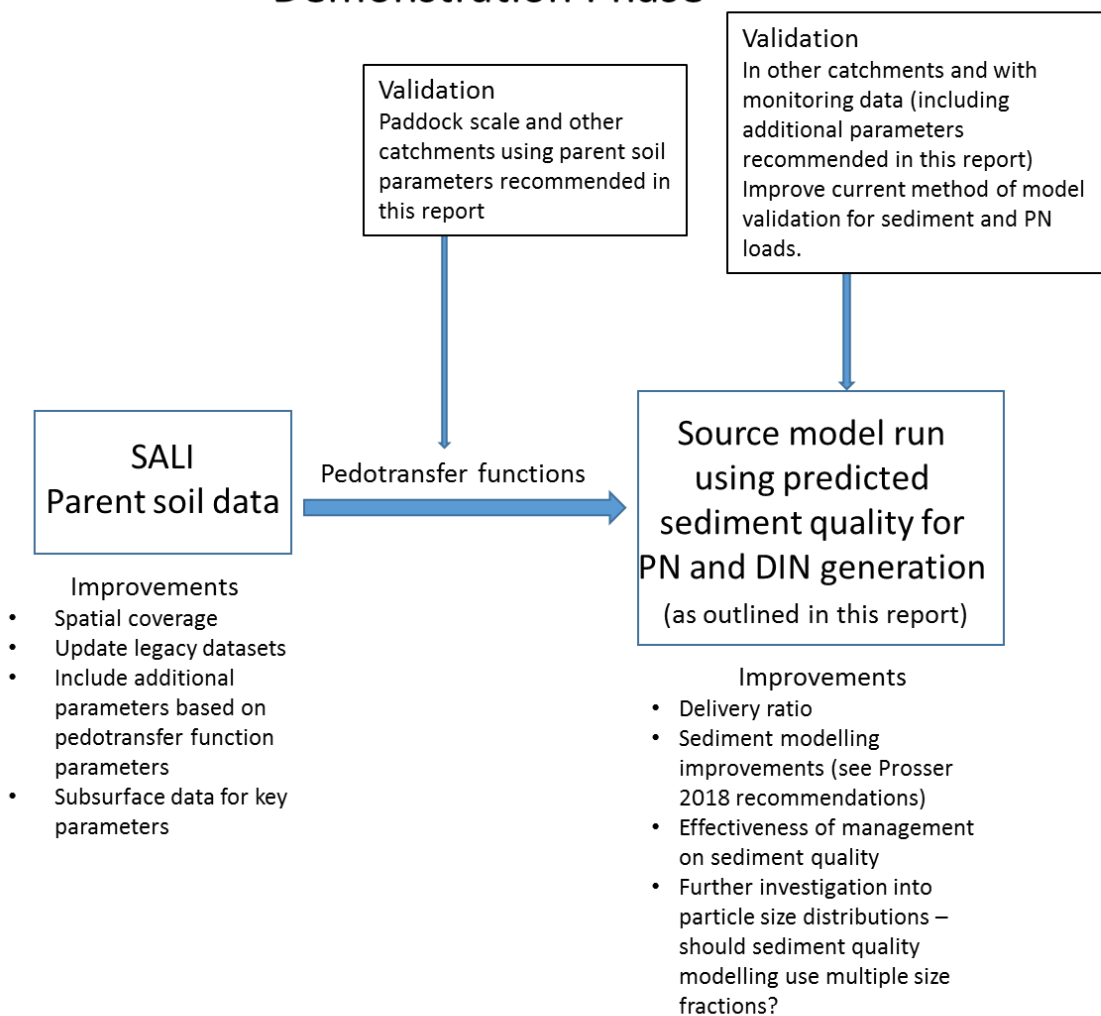


Figure 28 Framework to improve modelling of PN and DIN generation from eroded soils

## Conclusions - Contribution of eroded soils to DIN generation

The key outcomes and conclusions for the contribution of eroded soils to PN modelling and DIN generation from sediment:

- **A proposed new method for modelling PN and DIN generated from sediment was successfully tested under the P2R modelling platform.** PN modelling can be improved to account for the variability in fine sediment characteristics in the catchments including the variability in enrichment ratios of particulate nutrients in sediment from that of their parent soils.
- **A significant fraction of DIN is generated from the erosion of soils and their associated fine sediment in the Bowen river catchment** (1.2 to 1.5 times the currently modelled DIN load at the Bowen River end-of-catchment). **We hypothesize this would be the case in other grazing catchments of the GBR where yields from fertilizer use are not relatively high.**
- **DIN generation associated with sediment erosion and transport is not significant in the Johnstone river catchment** (around 3% the currently modelled DIN load at the Johnstone River end-of-catchment).
- Although **'DIN from sediment' yields** (kg DIN generated from kg of eroded sediment per hectare per year) **are much higher in the Johnstone than in the Bowen river catchment, the very large yields of 'DIN from fertilizer' dominate the DIN source in the former.**
- **A large part of the DIN generation associated with sediment erosion and transport is of anthropogenic origin and it is not targeted as such.** Considering its significance, **identifying, modelling and targeting this fraction in grazing catchments is important.**
- **The main sources of sediment in a catchment are not necessarily the main sources of DIN producing sediment.** For example, modelling in the Bowen River catchment indicated that although gully erosion is the main source of sediment, hillslope erosion is the main source of PN and 'DIN generation from sediment'. Our findings highlight the **disproportionate contribution of hillslope erosion to particulate and bioavailable nutrient catchment export per unit mass of eroded sediment**, when compared to subsurface erosion (gully and streambank). In the Johnstone River catchment, although conservation and sugarcane dominated sediment export, and sugarcane alone dominated PN export, BPN modelling results indicated that dairy may be an important source of 'DIN from sediment' at the end-of catchment (39% contribution) together with sugarcane (44% contribution).
- **Sediment source contribution (surface versus subsurface erosion) is an important determinant of the total DIN load generated from sediment in the catchment and of the source contributions to these loads.** Calculations using tracing data as a second line of evidence for the Bowen River catchment indicated large variability in surface versus subsurface source contributions to 'DIN generation from sediment' with changes in the proportion of sediment sourced from subsurface sources. Under a scenario with subsurface sediment contribution >93%, subsurface sediment would be an equally important source to 'DIN generation from sediment' as surface erosion. These findings highlight the **importance of accurately modelling the distribution between surface and subsurface sediment sources in catchments towards accurately modelling 'DIN generation from sediment' and also PN loads.**
- **It is fundamental to increase understanding of how land-use change and management (including vegetation type) have modified the quality of sediment (e.g. 'DIN generation from sediment') exported to the Reef.**
- **Sediment will likely continue to generate DIN from PON mineralisation as it is further transported in the estuary and the marine environment. A significant contribution from Johnstone river sediment to DIN in the marine environment cannot be discarded.**

## Implications

### Risk to water quality and ecosystem health in the GBR

- The results imply that 'DIN generated from sediments' eroded from grazing catchments accounts for a significant proportion of the EoS DIN measured and modelled in these catchments. This source of DIN is therefore likely to pose a significant risk to water quality and ecosystem health in the GBR.

### Target setting

- There is a need to specifically address bioavailable particulate nutrients for grazing catchments when the targets are revised for the WQIP update in 2022.
- Improvements in EoS DIN associated with erosion management are not currently being accounted for, and therefore not included in, progress towards the DIN reduction target.

### Prioritisation

- PN and bioavailable nutrients from eroded soil need to be prioritised separately from sediment.
- Including the potential for DIN generation in the prioritisation of areas for erosion management will multiply the benefit to water quality of these investments.
- DIN generation from erosion should be included when undertaking cost-benefit analysis of various management options for reducing DIN.
- Further targeting of effort to manage DIN from sediment requires additional information for refinement (see 'Further work').
- It is important to communicate that the understanding of nitrogen budgets in catchments has changed and that this new knowledge will influence (within) catchment prioritisation.

### Management

- Eroded sediments can now be viewed as an important source of bioavailable particulate nutrients (DIN) in grazing catchments with low relative fertilizer use.
- Erosion management practices that target different erosion sources should be considered in the context of generation of both sediment and 'DIN from sediment' yields per unit area. In order to reduce DIN from eroded sediment there is a need to develop and promote land management practices that reduce nutrient-rich fine sediments (i.e., surface soil erosion).
- Trading for nitrogen forms as part of nutrient markets/offsets should take into account the bioavailability of the different pools of bioavailable nitrogen, which directly relate to the identified DIN generation processes in this project.

### Tracking investments

- A framework towards reporting on DIN reductions from sediment management is available for implementation. This implementation process requires additional information (see 'Further work').

#### *Modelling*

- The proposed method for modelling PN in catchments could be further developed and implemented so that PN modelling is more accurate and supported by the most recent process-based knowledge. This method should be extended to the modelling of PP and we recommend the eventual inclusion of POC which is an important parameter in determining the bioavailability of particulate nutrients to marine phytoplankton (Garzon-Garcia et al., 2018).
- This case study has developed a method to include DIN generation from sediment in P2R modelling and is available to be implemented towards this objective. The implementation of this process is recommended for grazing catchments where this process generates significant DIN loads. It requires additional information and the coupled improvement of sediment modelling (see 'Further work').

#### *Monitoring*

- Monitoring of particle size should be included as a standard parameter in the GBRCLMP. This would enable the GBRCLMP to capture comparable datasets and would facilitate the validation of sediment and PN modelling data against monitored data.
- Include the main bioavailable particulate nutrient parameters (at least POC, DOC, adsorbed ammonium, and particle size distribution in addition to DON, soluble ammonium and nitrate) in routine loads monitoring or in strategic catchments (e.g., grazing catchments) and paddock monitoring to validate the modelling of bioavailable particulate nutrients (DIN from sediment) and estimate bioavailability to phytoplankton.
- Monitor and calibrate DIN reduction from erosion management. This needs to cover different erosion management techniques, different soil types and be carried out until stable state has been achieved (could



be >10years for gully rehabilitation works).

## Future work

Future work is required in the following areas:

### Soil mapping

- Expand the pedo-transfer function approach for estimating bioavailable nutrients from fine sediment erosion as part of P2R Dynamic SedNet (within Source) modelling. These pedo-transfer functions must be validated at paddock scale within the same catchment (Bowen and Johnstone River catchments) and in other catchments with similar land-use (grazing and agriculture), as well as for other sediment particle sizes (<63  $\mu\text{m}$ ). To do this intrinsic soil parameter data are required for other catchments, in particular grazing catchments (water dispersible silt and clay, POC, PN, adsorbed ammonium, SOC, SON, water soluble ammonium, nitrate, PP and DRP).
- High resolution soil mapping is required to improve the soil database in subsurface soil characteristics as well as for alluvial and floodplain soils and hillslopes surrounding gullies. Identify areas for priority soil mapping.
- Improvement and integration of gully mapping using LIDAR data.

### Prioritisation

- Include the bioavailability of particulate nutrients (e.g., potential DIN generation from sediment) to enhance the prioritisation of erosion management in catchments. Select areas where there is likely to be fine sediment and potentially bioavailable nutrient benefits (overlay maps) from erosion management.

### Research/monitoring/modelling

- A source to sink assessment of particle size methods and the role of aggregation and organics to inform an integrated approach to monitoring and modelling of particle size towards model validation.
- Improved modelling of process source contribution (surface versus subsurface erosion) and soil type x land use contributions to sediment in catchments to provide greater resolution of the model outputs. This should be accompanied by fine scale validation of the model outputs. Complete budgets for all sources to include other nutrient sources like rainfall (Packett, 2017), cattle contributions etc.

### Research

- Improved understanding and characterisation of bioavailable particulate nutrients and sediment linked to soil types and vegetation cover type
- Improved understanding and characterisation of the dynamics and time lags in the reduction of bioavailable particulate nutrients as part of different types of erosion management work (e.g. gully rehabilitation techniques, land management improvement practices etc.)
- Improved understanding and characterisation of the effect of vegetation type (i.e., carbon) on the bioavailability of particulate nutrients in-situ and as they are transported through catchments. This may influence on-ground management practices such as trash blanketing and choosing species and tree density to be used in rehabilitation.
- Improved understanding and characterisation of the links between sediment particle size, flow and bioavailable particulate nutrients
- Improved understanding and characterisation of how bioavailable particulate nutrients interact in wetlands and floodplains. Quantification of the wetland treatment efficacy needs to take this into account. Both N and P are important to investigate in wetlands as in freshwater algae respond to both.

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## Appendices

### Appendix 1 Pedo-transfer functions

Pedo-transfer functions are defined as mathematical equations that allow to estimate the value of a bioavailable particulate nutrient parameter in fine sediment from one or various bioavailable nutrient parameters measured on its parent soil. We have developed pedo-transfer functions for particulate nitrogen (PN) and for the identified N pools associated with DIN generation from <10 µm sediment identified in this report using the existing bioavailable particulate nutrient (BPN) dataset (Garzon-Garcia et al., 2017a) and new data generated as part of this project to quantify DON bioavailability (See Appendix 2).

#### Pedo-transfer functions for particulate nitrogen

The pedo-transfer functions (PTFs) for PN presented here were used to run the BPN models in this project. The PTFs allow for the estimation of PN in <10 µm sediment from Total Kjeldahl Nitrogen (TKN) in the parent/bulk soil (units used are % mass content for both PN and TKN). In the equations, the sub-index <sub>b</sub> indicates it is a bulk soil parameter. Some assumptions were made in the absence of information for specific soil types in the bioavailable nutrient dataset (Garzon-Garcia et al., 2017a). These PTFs may be improved by the inclusion of other parent soil parameters like water dispersible silt and clay, though the equations had a good enough fit to run the BPN models when using parent soil TKN only.

#### Bowen River catchment

In the Bowen River catchment, it was necessary to develop different functions for different **surface sediment** types.

Surface Vertosols (VE) (same function assumed for Calcarosols in this catchment)

$$(1) \text{ PN} = \text{TKN}_b^{0.976} \quad \text{Adjusted R}^2 = 0.69 \quad \text{p} < 0.001 \quad (\text{Figure 29})$$

Surface Ferrosols (FE) and Kandosols (KA) with light granulometry (i.e., texture) (clay loam- CL). The PTFs developed for Ferrosols in cane, banana and dairy in the Johnstone was used for these soil types because there was no information in the bioavailable nutrient database for these soil types.

$$(2) \text{ PN} = \text{TKN}_b^{0.825} \quad \text{Adjusted R}^2 = 0.89 \quad \text{p} < 0.001 \quad (\text{Figure 29})$$

For surface Dermosols (DE), Sodosols (SO) and Chromosols (CH) no significant PTF was found with the existing data. The PN in the sediment was relatively constant in DE and SO irrespective of changes in parent soil TN content. The following average values were assumed:

Surface DE:

$$(3) \text{ PN} = 0.23\% \quad (\text{SD} = 0.07) \quad (\text{Figure 30})$$

Surface SO:

$$(4) \text{ PN} = 0.27\% \quad (\text{SD} = 0.03) \quad (\text{Figure 30})$$

The PN in the sediment was variable for the same parent soil TN content for CH. Considering this, an average enrichment factor was assumed for this soil type.

Surface CH:

$$(5) \text{ PN} = 2.8 \times \text{TKN}_b \quad (\text{Figure 30})$$

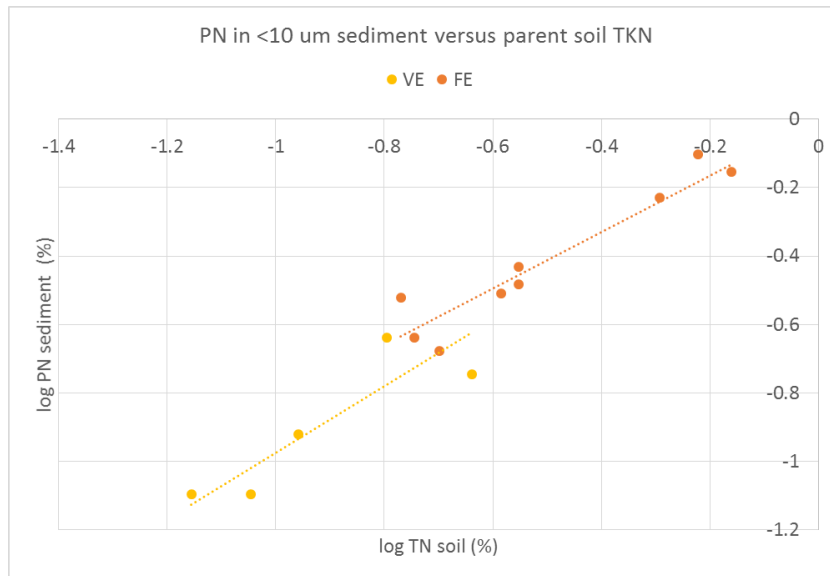


Figure 29 Linear regressions between PN in the <10 um sediment and TKN in the parent soil for surface Vertosols and Ferrosols in the Bowen and Johnstone River catchment, respectively

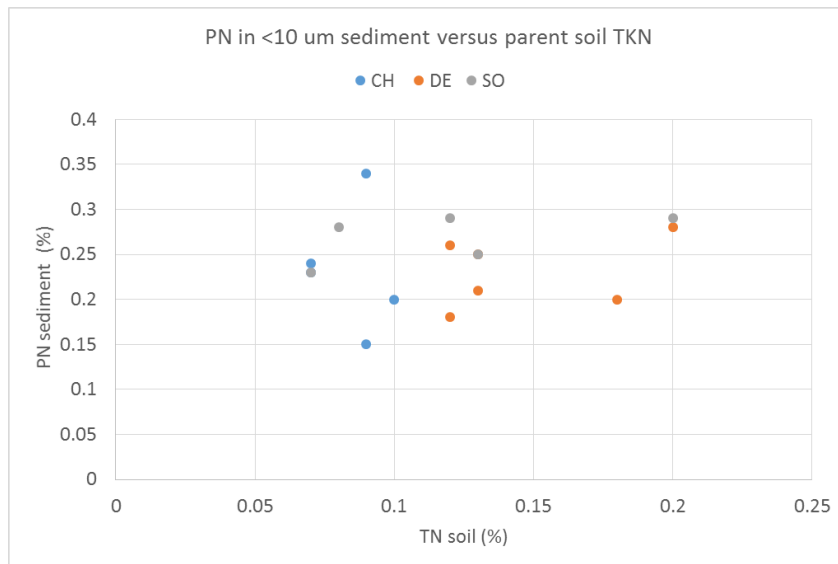


Figure 30 PN in the <10 um sediment versus TKN in the parent soil for surface Chromosols, Dermosols and Sodosols in the Bowen River catchment

One PTF fitted well for **subsurface sediments** of all types in the Bowen River catchment. It is assumed this PTF could be applied to obtain PN in sediments from other subsurface parent soil types in the Bowen River catchment.

Subsurface sediment all types included (VE, DE, SO, CH):

$$(6) \quad PN = TKN_b^{0.841} \quad \text{Adjusted } R^2 = 0.83 \quad p < 0.001 \quad (\text{Figure 31})$$

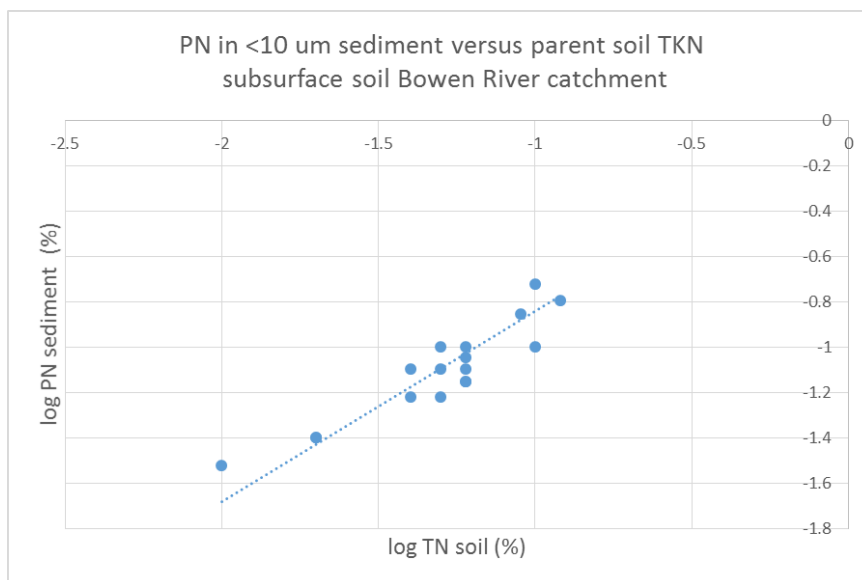


Figure 31 Linear regressions between PN in the <10 um sediment and TKN in the parent soil for subsurface sediments in the Bowen River catchment

### Johnstone River catchment

Pedo-transfer functions were developed only for surface soils in the Johnstone catchment because the available dataset does not include subsurface soils for this catchment (Garzon-Garcia et al., 2017a) because subsurface erosion is not significant in this catchment. The three forest sediments in the Johnstone dataset seem to have a different PTF than the other surface soils in the catchment. Initially, a different PTF had been calculated for this land use sediment type, but when it was applied to the TN soil values in the SALI database, the lower TN content in this dataset relative to the three sampled points in the Johnstone produced negative PN values in the sediment. Considering this, a unique PTF for all surface soils in the Johnstone River catchment was calculated and used in the BPN models. Further work needs to be done to determine if the difference in forest soil PN between the SALI database and the BPN database is due to natural or temporal variability, or if there is a source of error in one or the other databases. It is important to note that there are very few SALI data points in conservation areas of the Johnstone River catchment. Once this issue is resolved it would appear that a different PTF should be developed for forest soils.

(7)  $PN = TKN_b^{0.81}$  Adjusted  $R^2 = 0.92$   $p < 0.001$  (Figure 32)

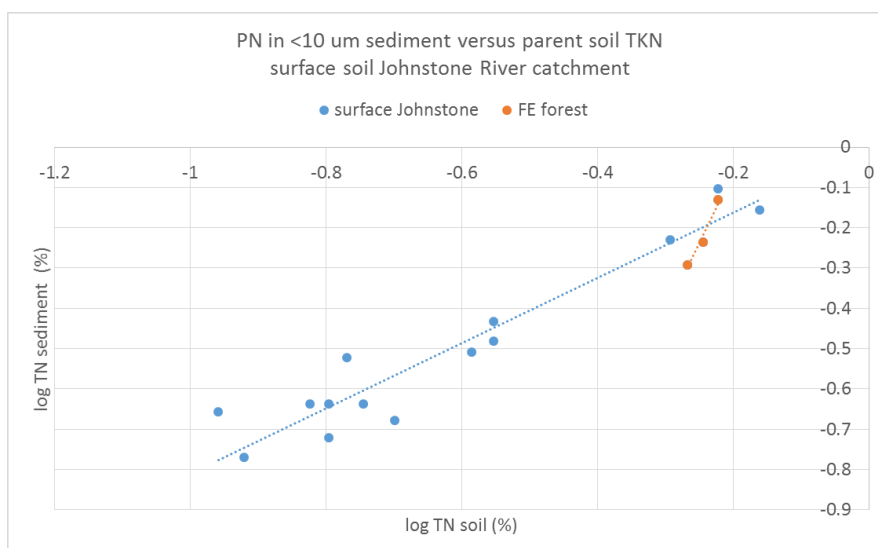


Figure 32 Linear regressions between PN in the <10 um sediment and TKN in the parent soil for surface sediments in the Bowen Johnstone River catchment

### Pedo-transfer functions for pools associated with DIN generation from sediment

The identified N pools associated with DIN generation from <10 μm sediment can be observed in Table 5 and

Figure 11 of the report and are presented here again. DIN from solubilisation pools which include nitrate and soluble ammonium ( $\text{NO}_3\text{-N} + \text{NH}_4^+\text{-Nsol}$ ) are pools to be directly measured on the parent soil (see methods at the end of this Appendix) hence there is no need to develop PTFs for them. Here, we present PTFs for potential mineralisable N (PON mineralisation), adsorbed ammonium (PIN desorption) and the bioavailable fraction of the DON (DON mineralisation) for the Bowen and Johnstone River catchments.

Table 8 DIN generation processes and corresponding N pools contributed by soil erosion to downstream aquatic environments

Process	N pool*
DIN Solubilisation	Nitrate + Soluble ammonium ( $\text{NO}_3\text{-N} + \text{NH}_4^+\text{-Nsol}$ )
PON mineralisation	Potential mineralisable N in 1 day (PMN1)
DON mineralisation	Bioavailable DON (DONb)
PIN desorption	Adsorbed ammonium ( $\text{NH}_4^+\text{-Nad}$ )

\*All of these pools are measured as generated DIN (mass content per unit mass of sediment)

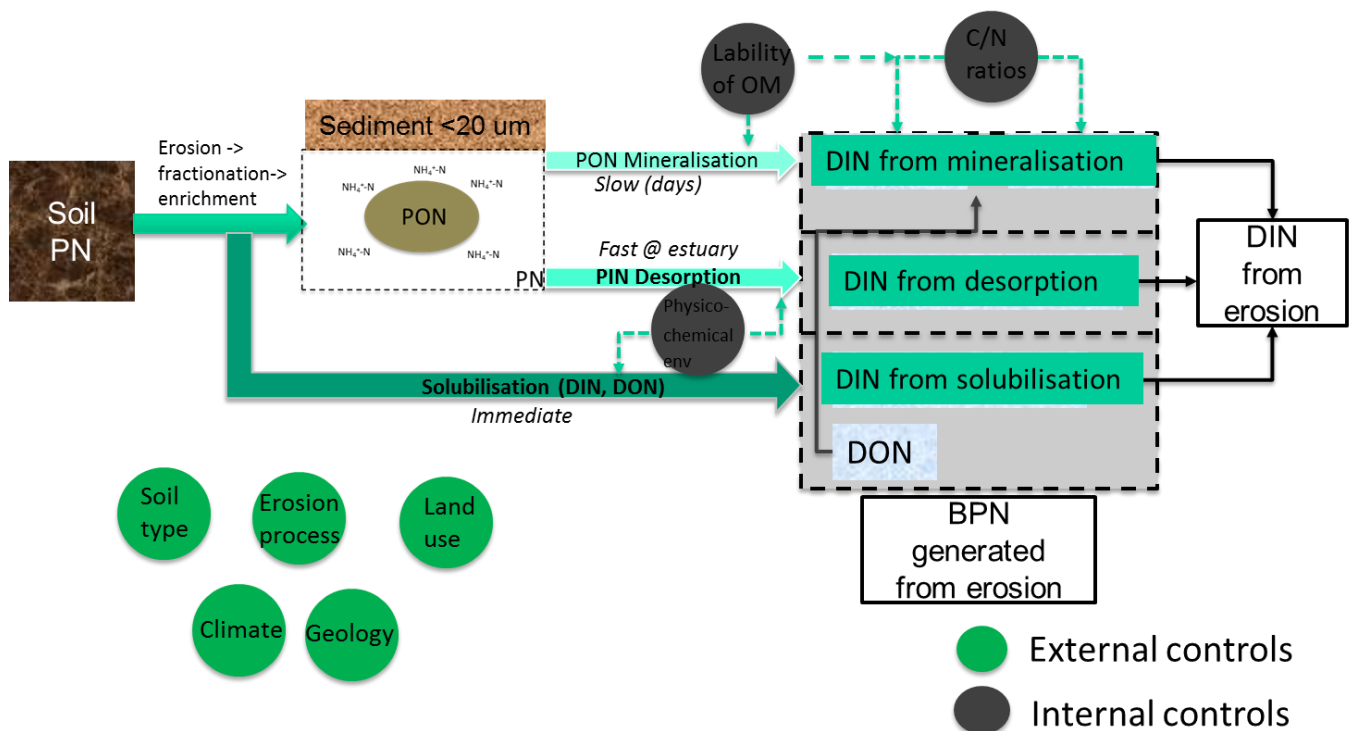


Figure 11 Conceptual diagram depicting the processes and controls underlying the generation of dissolved inorganic nitrogen (DIN) from eroded soil in water. \*BPN – Bioavailable particulate N

Pedo-transfer functions were developed from all-subsets step-up regressions using the leaps package in R (Lumley, 2017) to determine which combination of nutrient parameters measured on parent soil best explained the N pools associated with DIN generation from <10 μm sediment. This type of regression tests all the possible combinations of parameters and reports on the best subsets for each size (number of explanatory variables used in the regression). The multiple linear model with the best adjusted R<sup>2</sup> was selected considering this measure is an unbiased estimator of the model fit and allows comparison of R<sup>2</sup> between regressions with different numbers of variables. The predictive R<sup>2</sup>, a measure that helps determine how well the model predicts responses for new observations, was calculated for the selected models. This measure is calculated by systematically removing each observation from the data set, estimating the regression equation, and determining how well the model predicts the removed observation.

To obtain relatively good PTFs, it was necessary to separate the data between catchments and surface and subsurface soils. This indicates that PTFs would change with catchment characteristics like dominant land use, and would be different between surface and subsurface soils. The need to do this makes sense as we are using the

PTFs to predict the enrichment of fine sediments and the data indicate that enrichment ratios and their ranges vary between surface and sub-surface soils and between land uses (see Figure 15 and Figure 16 in main report). To continue to use this approach for estimating bioavailable nutrients from fine sediment erosion as part of P2R Dynamic SedNet (within Source) modelling, it is recommended that these PTFs are validated at paddock scale within the same catchment and in other catchments with similar land-use characteristics, as well as for other sediment particle sizes (<63 µm).

The potential mineralisable N PTFs had relatively good fit (adjusted  $R^2 > 0.56$ ) for specific mineralisation timeframes, which depended on the erosion process (Table 9). Pedo-transfer functions had a good fit (adjusted  $R^2 = 0.7$ ) for short timeframes (3 days) (PMN3) for subsurface sediment in the Bowen River catchment, but not for surface soils in either of the two catchments. The short timeframe mineralisation in surface sediments seemed to have a lot of unexplained variability, which may be associated with a stronger 'Birch effect' (the effect of antecedent wet-dry conditions on organic matter mineralisation) on these sediment types. This is supported by the finding of good fit in the PTFs for the potential mineralisable N between day 3 and 7 (removing the potential contribution of the Birch effect to mineralisation) (PMN7-PMN3) for surface soils in both catchments (Table 9). Selected PTF parent soil parameters, equation coefficients, variable significance and model fit and significance can be observed in Table 9. As can be seen in Figure 33, the PTFs tend to under-predict the potential mineralisable N, with the largest under-prediction occurring for surface soil in the Johnstone River catchment (~30% less). As can be observed in Table 9, the ratio of TOC to TN (an indicator of carbon lability) was an important predictive parent soil variable in all three PMN models. The role of this parameter varied in each model, sometimes having a direct influence and in other cases an inverse influence. This may indicate that carbon type differs between sediment types and is important in mediating the N mineralisation process. TOC:TN is also an important variable in estimating the bioavailability of sediment particulate nutrients to phytoplankton (Garzon-Garcia et al., 2018). It is likely that the use of other variables not included in this study (e.g., carbon functional group ratios) that better relate to carbon type/origin would improve the predictive power of these models. A better understanding of the mineralisation process including the role of carbon type in mediating the process is required to improve the predictive power of PTFs.

Table 9 Pedo-transfer functions for bioavailable nitrogen pools in <10 µm sediment from parent soil parameters. Pedo-transfer functions are multiple parameter linear models of the form: sediment parameter in <10 µm sediment = coefficient 1 \* soil parameter 1 + coefficient 2 \* soil parameter 2 + ... + coefficient x \* soil parameter x + b. Coefficients for equations, their significance, equation significance, adjusted  $R^2$  and predictive  $R^2$  are presented in the Table.

Catchment	Erosion process	Sediment parameter	Parent soil parameters										b	p	Adj $R^2$	Pred $R^2$	
			TOC (%)	TN (%)	TKN (%)	TOC/TN	SPOTS	NH <sub>4</sub> <sup>+</sup> -N (mg/kg)	DON-N (mg/kg)	WDSC (%)	DOC/DON	NO <sub>3</sub> -N (mg/kg)					
Bowen	Subsurface	PMN3 (mg DIN/kg)	-45.86**	669.4***		4.204**		-5.423**	-3.549					-22.854*	0.002	0.7	0.5
Bowen	Surface	PMN7 - PMN3 (mg DIN/kg)				-4.3**		-1.894	2.932***	0.587**			26.112	<0.000	0.62	0.5	
Johnstone	Surface	PMN7 - PMN3 (mg DIN/				10.453		6.264**	-0.757				-151.27	0.005	0.56	0.44	
Bowen	Subsurface	NH <sub>4</sub> <sup>+</sup> -Nad (mg/kg)	-25.855*		426.95**			6.561*					-3.39	0.008	0.49	-0.53	
Bowen	Surface	NH <sub>4</sub> <sup>+</sup> -Nad (mg/kg)						6.358***					-6.554	<0.000	0.46	0.13	
Johnstone	Surface	NH <sub>4</sub> <sup>+</sup> -Nad (mg/kg)						5.202***					-18.505*	<0.000	0.91	0.88	
Bowen	Surface	DONb (%)						-0.013					-0.01*	0.057**	0.124*	0.9	-1.14

The PTFs obtained for adsorbed ammonium in the <10 µm sediment were much simpler, with only parent soil extracted ammonium (see methods at the end of this Appendix) required to obtain the best fit possible for surface sediments (Table 9, Figure 34). The PTF for <10 µm subsurface sediment in the Bowen River catchment required two additional parameters to get a reasonable fit, though the predictive power of this function is not very promising (Table 9, Figure 34). Further validation is also recommended.

The PTF for the bioavailable DON fraction of DON solubilised from parent soils (see experimental details and results in Appendix 2) had a good fit for the surface Bowen catchment soils, though the predictive power of this function is not high (Table 9, Figure 35). There were very few data points to carry out a step-up regression for the other soil types. Variables explaining the bioavailability of DON included adsorbed ammonium and nitrate in the parent soil (available inorganic N) and the ratio of DOC/DON (an indicator of soluble organic matter lability) which indicates that soluble carbon type is of importance in mediating this process (Table 9). To further develop PTFs for this parameter it is necessary to quantify the bioavailability of DON for more soil types with the inclusion of true replicates. Similarly to PON mineralisation, a better understanding of the role of carbon type in mediating DON mineralisation would aid in the improvement of PTFs.



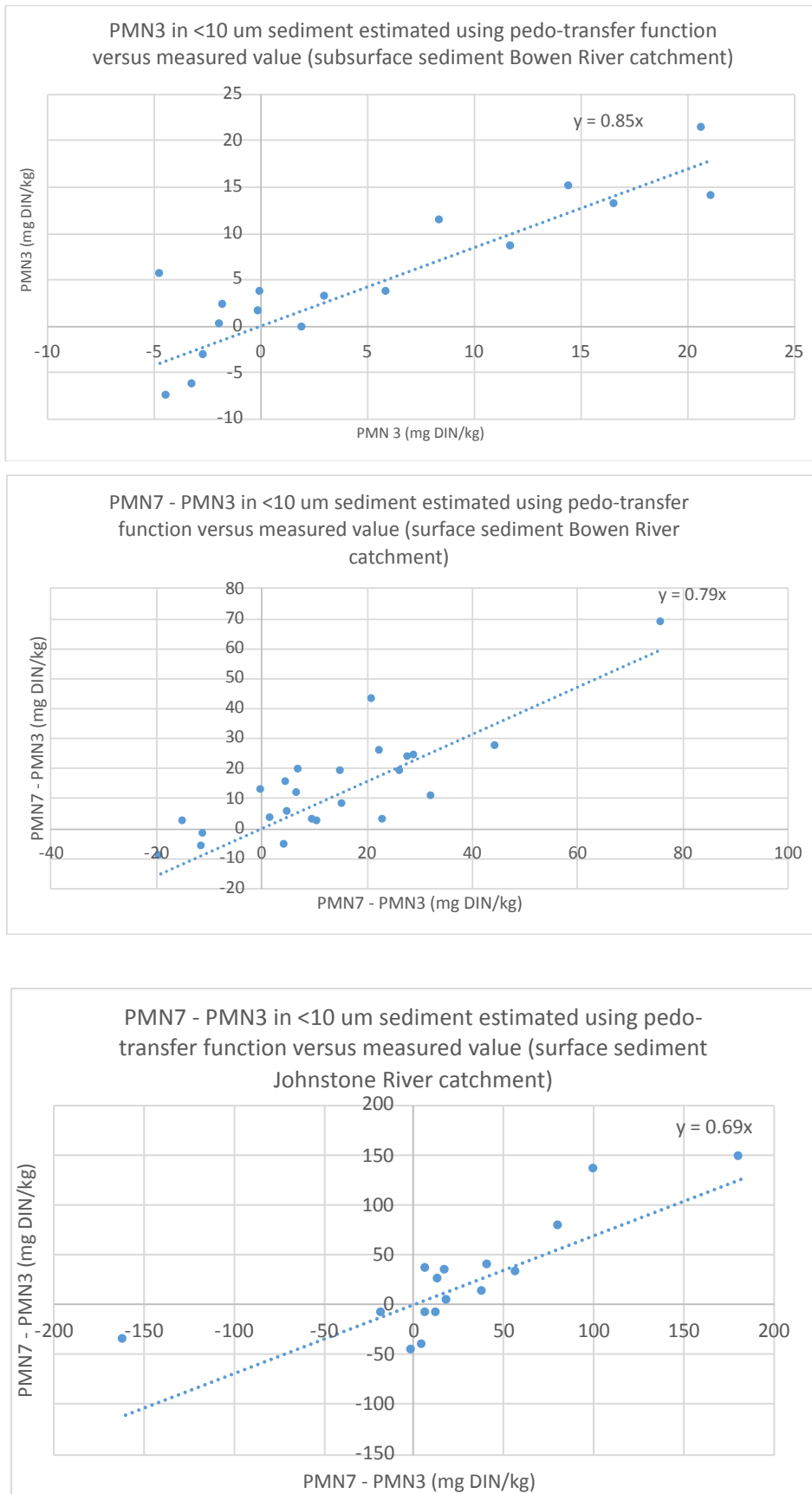


Figure 33 Pedo-transfer function estimates against measured data for potential mineralisable N in 3 days (PMN3) in subsurface Bowen River sediments (a), and N mineralised between 3 and 7 days (PMN7 – PMN3) in surface Bowen River catchment sediments (b) and surface Johnstone River catchment sediments (c).

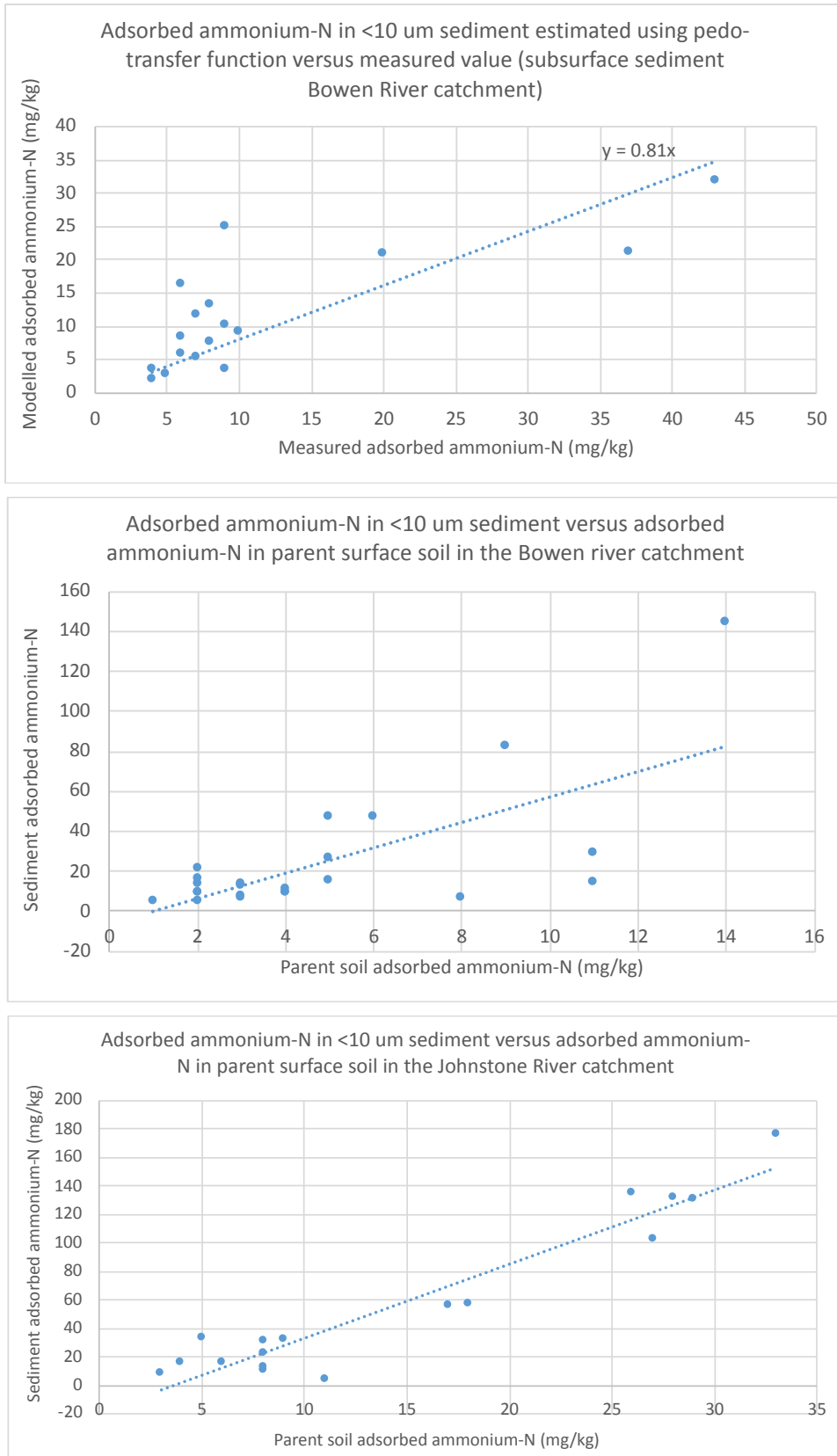


Figure 34 Pedo-transfer function estimates against measured data for adsorbed ammonium-N in subsurface Bowen River sediments (a) and adsorbed ammonium in the <10 um sediment versus adsorbed ammonium in the surface Bowen River catchment parent soils (b) and surface Johnstone River catchment parent soils (c).

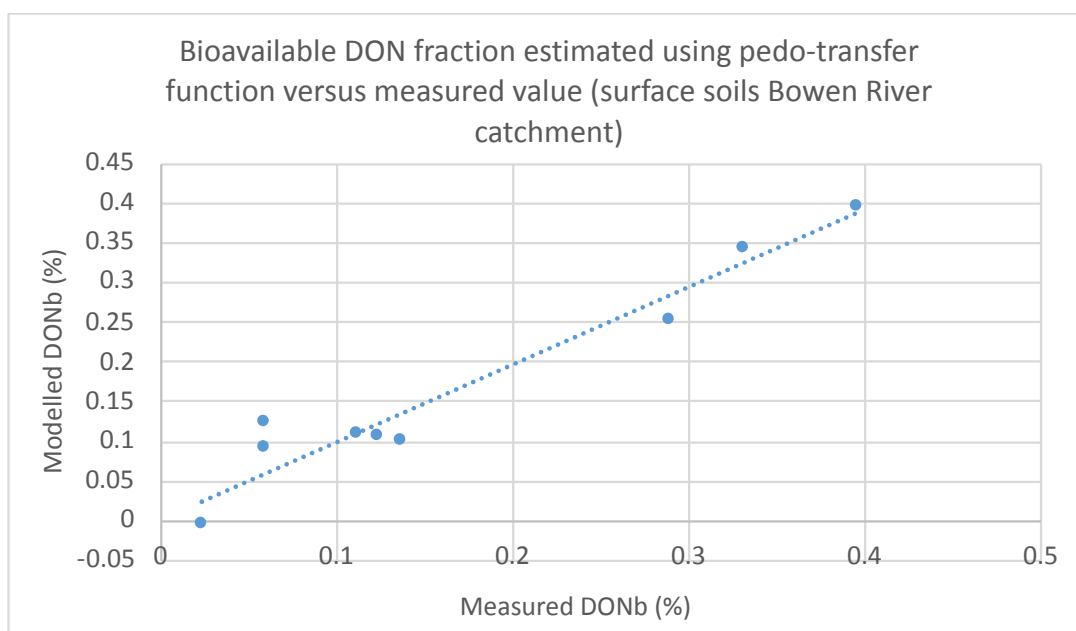


Figure 35 Pedo-transfer function estimates against measured data for the bioavailable DON fraction (DONb) from surface soils in the Bowen River catchment

## Analytical methods for sediment and selected soil parameters

Here we present a summary of the different parameter analytical methods used to develop PTFs in the previous sections. They apply to both sediment and bulk soil samples unless explicitly mentioned. A number of the following methods are performed based on those described in Soil Chemical Methods – Australasia (Rayment and Lyons, 2011) and the method code is referenced within the text where appropriate.

### Total Nitrogen (TN for parent soil and PN for sediment) and Total Organic Carbon (TOC for bulk soil and POC for sediment) – Dumas method

These parameters can be determined by catalysed, high temperature combustion methods in which the sample under analysis is combusted by heating to 900 - 1300°C depending on the instrument (see manufacturers manual) by a resistance furnace in a stream of high purity oxygen. The organic carbon content of the sample is determined by the total amount of CO<sub>2</sub> produced by combustion (Rayment & Lyons Method 6B2). Samples containing carbonate minerals should be pre-treated with dilute acid (Rayment & Lyons Method 6B3). The nitrogen content of the sample is determined by the total amount of N<sub>2</sub> produced by furnace combustion and subsequent reduction in a copper (Cu)-catalyst tube. Nitrogen is measured by a thermal conductivity detector while carbon is measured by an infrared radiation detector (Rayment & Lyons Method 7A5). Units used are % mass content.

### Total Kjeldahl Nitrogen (TKN)

The dried and ground sample is digested in concentrated sulfuric acid by Kjeldahl procedure. The digestate is diluted prior to automated colorimetric analysis. Soil samples are subjected to Kjeldahl digestion with sodium sulfate and selenium as catalyst (Bremner 1965). Following dilution with water, ammonium-nitrogen is determined by an automated segmented-flow colorimetric procedure based principally on the indophenol reaction with salicylate and sodium hypochlorite.

### TOC:TN ratio

This ratio is calculated by dividing the TOC in the bulk soil by the TN in the bulk soil. This parameter does not have units.

### Nitrate + water soluble ammonium (NO<sub>3</sub>-N + NH<sub>4</sub><sup>+</sup>-Nsol) in parent soils

These water-soluble pools which together make up the soluble DIN from soil erosion do not need PTFs as they can be quantified directly on the parent soil. Ideally, the parent soil would be in a stable state for the extraction (e.g., stable state phase of the mineralisation process after 3-5 days of incubating at field capacity), to remove the role of previous conditions like dry-wetting history on the soluble DIN present. More work is needed to define the ideal bench mark conditions to quantify these pools on parent soils.

The extraction method is as follows:

Parent soils sieved to <2mm and dried at 40°C in the oven are incubated at field capacity to obtain benchmark conditions (to be defined) and then are 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 is centrifuged at 4300 rpm for 20 minutes, then filtered (0.45µm). This method was adapted from the potential production of soluble organic carbon method, which in turn is an adaptation of the Potential Mineralisable Nitrogen in soils method (Bremner 1965).

The water soluble  $\text{NH}_4^+\text{-N}_{\text{sol}}$  is determined using the APHA/AWWA/WEF (2012) method 4500-NH<sub>3</sub>G and  $\text{NO}_3^-\text{-N}$  is determined using the APHA/AWWA/WEF (2012) method 4500-NO<sub>3</sub>-F. Units are mg N/kg sediment.

### **Adsorbed ammonium ( $\text{NH}_4^+\text{-N}_{\text{ad}}$ ), nitrate ( $\text{NO}_3\text{-N}$ ), dissolved organic nitrogen (DON), dissolved organic carbon (DOC)**

There are several possible methods to calculate these parameters in the bulk soil including water extracts, KCl extracts and  $\text{K}_2\text{SO}_4$  extracts. To facilitate the process and to be able to use the same method for all parameters a  $\text{K}_2\text{SO}_4$  extract was selected. The method is as follows:

Soils are extracted with a 0.5M  $\text{K}_2\text{SO}_4$  solution using a 1:10 soil to extractant water ratio (for 1 h at 25°C and 15 rpm in an end over end shaker). The suspension is centrifuged at 4300 rpm for 20 minutes, then filtered (0.45µm). The filtrate may need to be diluted to have enough volume to perform the following analytical procedures. The dilution factor needs to be recorded and the resulting concentrations from the analyses corrected for this dilution factor. This method was adapted from the Potential Mineralisable Nitrogen in soils method (Bremner 1965).

The extracted  $\text{NH}_4^+\text{-N}$  (SPOTS  $\text{NH}_4^+\text{-N}$ ) which is the parameter used in the PTFs, is directly measured on the filtrate using the APHA/AWWA/WEF (2012) method 4500-NH<sub>3</sub>G. Units are mg N/kg sediment.

The adsorbed  $\text{NH}_4^+\text{-N}$  ( $\text{NH}_4^+\text{-N}_{\text{ad}}$ ) is calculated from subtracting the water soluble  $\text{NH}_4^+\text{-N}$  ( $\text{NH}_4^+\text{-N}_{\text{sol}}$ ) from the extracted  $\text{NH}_4^+\text{-N}$  (SPOTS  $\text{NH}_4^+\text{-N}$ ). Units are mg N/kg sediment. This same method is used to measure adsorbed  $\text{NH}_4^+\text{-N}$  ( $\text{NH}_4^+\text{-N}_{\text{ad}}$ ) on sediment samples. The method for sediment recovery or extraction (i.e. extraction carried out directly on suspended sediment versus dried sediment) should take into account if the water soluble  $\text{NH}_4^+\text{-N}$  ( $\text{NH}_4^+\text{-N}_{\text{sol}}$ ) is present or not. If it is, it should be subtracted from the extracted ammonium.

Nitrate ( $\text{NO}_3^-\text{-N}$ ) is directly measured on the filtrate using the APHA/AWWA/WEF (2012) method 4500-NO<sub>3</sub>-F. This method should not give significant different results from the water-soluble method described previously. Units are mg N/kg sediment.

Soluble Organic Carbon is determined on the filtrate by high temperature combustion or wet oxidation with persulfate (APHA/AWWA/WEF (2012) method 5310). Units are mg N/kg sediment.

Soluble Organic Nitrogen is determined by subtracting the SPOTS  $\text{NH}_4^+\text{-N}$  from the Dissolved Kjeldahl Nitrogen (DKN) ((APHA/AWWA/WEF (2012) method 4500-N org D) or the  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  from the dissolved nitrogen measured using a wet oxidation with persulfate (APHA/AWWA/WEF (2012) method 5310). Units are mg N/kg sediment.

### **DOC:DON ratio**

This ratio is calculated by dividing the DOC by the DON solubilised from the bulk. This parameter does not have units.

### **Potential mineralisable N in fine sediment (PMN1, PMN3, PMN7)**

The method used to determine the potential mineralisable N (PMN) in fine sediment (<10 µm) at different timeframes, for which the PTFs were developed was described in Garzon-Garcia et al 2017a. PMN results were negative in fine sediments containing high concentrations of  $\text{NO}_3^-\text{-N}$  at day 0 of the incubation in this dataset (Figure 36). This indicates that when there are readily bioavailable sources of N, bacteria will not mineralise organic N. Considering this, to obtain the true mineralisation potential of sediment it was necessary to wash the  $\text{NO}_3^-\text{-N}$  out of these sediments (20 sediments) and carry out the PMN incubations once again. A summary of the procedure to remove the  $\text{NO}_3^-\text{-N}$  is presented here:

- Three grams of the sediments with high initial  $\text{NO}_3^-\text{-N}$  content were shaken in a tube with 30 mL of DI water for 20 seconds by hand.
- The suspension was centrifuged at 4300 rpm for 20 minutes and the supernatant was poured off.
- The wet recovered sediment weight is recorded to quantify the weight of water present. This has to be taken into account for the PMN incubation procedure.

A summary of the PMN incubation procedure is presented here:

This is a biological method, based on a method described by Bremner (1965), to provide an index of plant-available soil N. Samples were incubated using a 3:10 sediment:DI water ratio under aerobic conditions at 25°C for 0, 1, 3

and 7 days, respectively. The amounts of mineral-N formed at different times are measured after a 3M KCl solution extraction (this gives a 1:10 sediment:solution ratio in a 2M KCl solution) followed by automated colorimetric determination. Potentially mineralisable-N is calculated as the difference between the mineral-N before and after incubation.

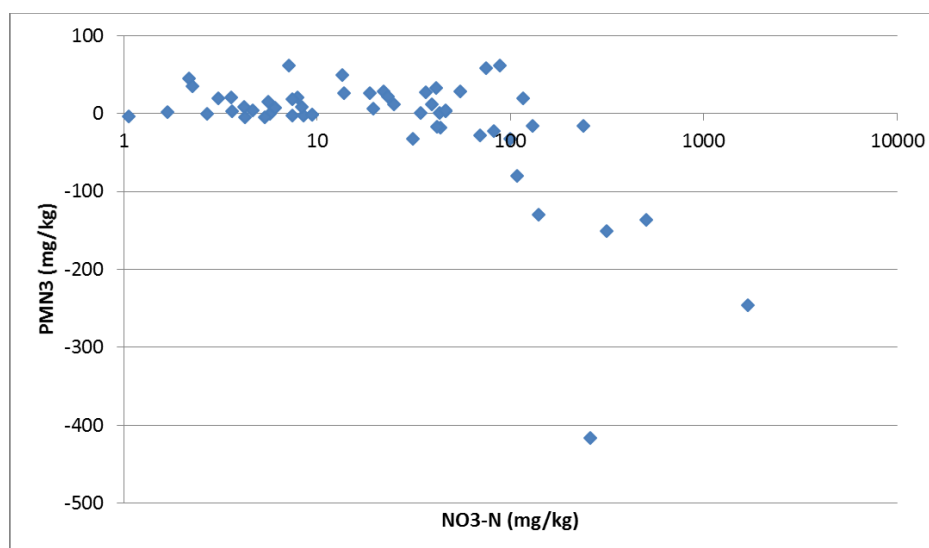


Figure 36 Potential mineralisable N in 3 days as a function of nitrate extracted at day 0 for 57 sediments in the bioavailable particulate nutrient dataset (Garzon-Garcia et al 2017a).

### Water dispersible silt and clay (WDSC)

The water dispersible silt and clay is calculated as follows:

$$WDSC (\%) = \text{silt and clay} (\%) \times R1$$

The silt and clay percent content is obtained with the hydrometer method (<20  $\mu\text{m}$ ) and the R1 is the ratio of aqueous dispersible silt and clay to total dispersible silt and clay i.e. that which is dispersed by chemical and mechanical means. The units are % by mass.

## Appendix 2 Bioavailability of dissolved organic nitrogen (DON<sub>b</sub>) experiment and data

A representative group of soils was selected from the bioavailable nutrient data set (Garzon-Garcia et al., 2017a) to carry out laboratory incubation experiments to quantify the bioavailability of the soluble organic nitrogen (DON) fraction.

### Experimental methods

Twenty (20) soils were selected, one from each combination of soil type and land use in each of the Bowen and Johnstone River catchments (see Table 10). To generate the DON sample from each soil, 100g of <2mm air-dried soil was suspended in 1.8 L of deionised water in settling columns by agitating for 1 min after a 2 min sonication bath. The suspension was allowed to settle for 48 minutes after which the supernatant was recovered, centrifuged for 20 minutes at 4300 rpm and filtered to <0.45  $\mu\text{m}$ . 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 percent of the DON present at day 0 that was lost to net mineralisation. This fraction was considered the labile fraction (DON<sub>b</sub>).

### Results

The estimated labile fraction of the DON is presented in Table 10.

Table 10 Soils selected for incubation experiments to estimate the bioavailability of the soluble organic N fraction and percent of the DON that was mineralised in experiments

Catchment	land use	Soil type	Erodibility	Erosion process	DONb (%)
Bowen	grazing	Chromosol	high	subsurface	13%
	grazing	Chromosol	high	surface	7%
	grazing	Chromosol	low	surface	29%
	grazing	Dermosol	high	subsurface	50%
	grazing	Dermosol	high	surface	12%
	grazing	Dermosol	low	surface	11%
	forest	Dermosol	low	surface	2%
	grazing	Sodosol	high	subsurface	21%
	grazing	Sodosol	high	surface	33%
	grazing	Sodosol	low	surface	14%
	grazing	Vertosol	high	subsurface	0%
	grazing	Vertosol	high	surface	40%
	grazing	Vertosol	low	subsurface	16%
	grazing	Vertosol	low	surface	6%
Johnstone	banana	Dermosol		surface	19%
	cane	Dermosol		surface	17%
	banana	Ferrosol		surface	25%
	cane	Ferrosol		surface	56%
	forest	Ferrosol		surface	0%
	dairy	Ferrosol		surface	0%
				Avg Bowen	18%
				Avg Johnst	23%