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Sources of Bioavailable Particulate Nutrients: Phase 1

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Executive summary

In this pilot project a limited number of surface and subsurface soil samples were collected from the Johnstone and Burdekin-Bowen Catchments. Samples covered a range of major soil types and land uses. Fine (<10um) sediments were recovered from the soil samples by repeated suspension and settling under laboratory conditions. Fine sediments and their parent soils were analysed to characterise the various pools and processes of the carbon, nitrogen and phosphorus cycles. Methods followed those used to assess nutrient bioavailability to agricultural crops, thereby allowing particulate nutrient bioavailability in sediments and their parent soils to be inferred under simulated freshwater and marine conditions. Phase 2 of this project will validate these inferences using algal bioassays.

Results indicated that:

- Fine (<10um) sediment from surface soil erosion processes is enriched in bioavailable nitrogen and phosphorus relative to fine sediment of sub-surface origin. The enrichment varied depending on the bioavailable nutrient pool and soil type.
- The contribution of surface and sub-surface sediments to end-of-system bioavailable nutrient loads will depend on the proportion of surface and sub-surface sediments reaching the end-of system. In a catchment like the Burdekin catchment where the contribution of sub-surface sediments is high (approx. 90%) compared to the contribution of surface sediments (approx. 10%), sub-surface sediments is likely to be a significant source of bioavailable nutrients.
- There was a general trend for land use to affect bioavailable nutrients in fine sediments, with quantities increasing in the order: grazing<cane=bananas<dairying.
- Bioavailable nutrient pools in fine (<10um) sediments could not be inferred with any certainty from analyses of the parent soil.
- For fine (<10um) sediments and their parent soils, total N is a reasonable predictor of soluble organic N and potentially mineralisable N at 7 days, but is a poor predictor of other pools of bioavailable N such as mineral N and potential particulate soluble organic N. Total P is a poor predictor of all bioavailable pools of P.
- Sediment P sorption properties and the quantity of N mineralised in 7 days were not affected when conditions changed from freshwater to marine.
- Cattle tracks may be a source of sediments with elevated levels of bioavailable N.

Implications of the results are:

- The relative contribution of sediments of surface origin to end-of-system loads of bioavailable nutrients will be higher than their contribution to end-of-system sediment loads. The quantity and nutrient enrichment of sediment generated by hillslope erosion (including that occurring in the surface catchment area of gullies and channel banks) relative to the quantity of sub-surface sediment generated by gully or channel bank erosion therefore becomes a metric for assigning priority of land surface management or sub-surface management for bioavailable particulate nutrients. Consequently, land surface management (maintaining surface cover, controlling stock movement and stock camping) will remain a high priority even in areas prone to active gullying or channel erosion.
- In catchments where sub-surface erosion is significant, management of these sources of sediment may result in significant reductions in loads of bioavailable nutrients delivered to the end-of-system. Such a reduction will be dependent on the management mechanisms applied and further exploration is required to understand the impact of different sub-surface erosion management interventions on bioavailable particulate nutrients.

- The observed release of mineralised N up to at least 7 days indicates that suspended fine sediments will be a continuing source of dissolved inorganic N (DIN) as the sediments move through the river system and disperse in the GBR lagoon. This source of DIN is currently unaccounted for in catchment nutrient modelling.
- Land use effects on sediment bioavailable nutrient content are apparent and will be further studied in the Phase 2 project by relating indicative nutrient budgets for generic land uses to the bioavailable nutrient content of parent soil.

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Introduction

Fine sediment, classified as the fine silt (4–16um) plus clay (<4um) fractions, is one of the key water quality parameters of concern to the health of the Great Barrier Reef (GBR) (Fabricius, 2005; De'ath and Fabricius, 2010; Brodie et al., 2013). Consequences of sediment delivery to the GBR include physical effects (e.g., increased turbidity, reduced light attenuation and smothering of seagrass meadows and corals) and chemical/biological effects related to the nutrients and organics associated with sediments (e.g., formation of marine snow, generation of DIN with impacts on crown of thorns starfish outbreaks, changes to coral calcification, coral death, reduced reef resilience).

To date much of the catchment-based research has focused on the physical characteristics (i.e., quantity) of sediment and its links to soil erosion processes. This research has shown that in recent decades fine silt and clay fractions of sediment delivered from a number Reef catchments (including Burdekin, Fitzroy and Normanby) to the Great Barrier Reef lagoon have been predominantly derived from the erosion of sub-surface sources (Bartley et al., 2004; Hughes et al., 2009; Tims et al. 2010; Olley et al. 2013; Wilkinson et al. in review). As a result the management of sub-surface erosion features such as gullies, channel banks and hillslope scalds and rills in grazing lands has been recommended to reduce the delivery of fine silts and clays to the GBR.

To characterise the nitrogen and phosphorus status of sediments for catchment modelling, total elemental concentrations (i.e., quantity) have been measured with little attention given to the bioavailability of nutrients and organics (i.e., quality) associated with fine sediments. Recent work by Bainbridge et al. (2012) indicates 80% of the total particulate nitrogen deposits near the mouth of the Burdekin River as the coarse sediment fraction (>16um). The remaining 20% in the flood plume disperses away from the mouth of the Burdekin River with organic-rich flocs forming around the fine-grained (<16um) suspended sediments. Importantly, these organic-rich suspended sediments in the flood plume impinge on coral reefs and seagrass meadows (Bainbridge et al., 2012), and similar material has been shown to be particularly detrimental to corals under laboratory conditions (Weber et al., 2006, 2012). A review by Brodie et al. (2015) suggests that a large proportion of particulate nitrogen is likely to be available for mineralisation. These results indicate that further understanding of the bioavailability and release rates of particulate nutrients and how they vary with sediment particle size, soil type, erosion process and land use is critical to inform management strategies and prioritisation of investment to improve the health and resilience of the GBR and to inform sustainable management of agricultural lands.

To this end, Reef Water Quality, Department of Environment and Heritage Protection, have funded a ‘proof of concept’ study which aims to:

1) test the concept that the bioavailability of nutrients and organics depends on soil type, erosion process, land use and particle size;
2) determine which bioavailable nutrient indicators (with particular focus on indicators used to assess nutrient availability in agricultural/pastoral production systems) are useful for measuring the bioavailability of terrestrially sourced nutrients in freshwater and marine systems.

It is worth noting here that bioavailable N has also been referred to in the literature as ‘potentially reactive N’ (Wooldridge et al., 2015). For the purpose of this document we define bioavailable nutrients as the components of the total N and P pools that are available or have the potential to become available to phytoplankton over a specified period of time.

Methods

Sample Collection

Samples have been collected from the sites listed in Table 1. At each cane site two samples have been collected – one to a depth of 0-15cm from the row or bed (nominally designated as 'surface soil' for the purposes of this experiment) and one to a depth of 0-15 cm from the furrow or inter-row (nominally designated as 'subsoil' for the purposes of this experiment). At each grazing site samples were collected from the surface (defined as 0-10cm) and sub-surface (below 10cm).

For surface and sub-surface samples at cane sites and surface samples at grazing sites, any vegetation was removed from the surface of the soil and then a shovel was used to collect the surface soil. At grazing sites, sub-surface soils were collected from gully walls below 10cm from the surface. First the gully wall was cleaned and then a sample was collected using a shovel or trowel. At all sites approximately 50kg of sample was collected and consisted of composited subsamples taken over an area of approximately 10m^2.

At two grazing sites (one dairy, one beef), the loose surface material was collected from cattle tracks.

Table 1 List of sampling sites

Land use	Catchment	Soil type/erodibility class	Aligned project/contact
Cane	Mackay	Vertosol	John Hughes DAFF
Cane	Mackay	Sodosol	John Hughes DAFF
Cane	Wet Tropics (Silkwood)	Hydrosol	P2R site Bronwyn Masters DNRM
Cane	Wet Tropics (East Palmerston)	Ferrosol	Bronwyn Masters DNRM
Banana	Wet Tropics (South Johnstone)	Dermosol	P2R site Bronwyn Masters DNRM
Grazing (dairy)	Burdekin	Ferrosol (low erodibility)	Soil erodibility mapping
Grazing (beef)	Burdekin	Dermosol (low erodibility)	Soil erodibility mapping
Grazing (beef)	Burdekin	Vertosol (high erodibility)	Soil erodibility mapping
Grazing (Beef)	Burdekin	Sodosol (high erodibility)	Soil erodibility mapping
Cattle track (dairy)	Burdekin	Ferrosol (low erodibility)	Soil erodibility mapping
Cattle track (beef)	Burdekin	Dermosol (low erodibility)	Soil erodibility mapping

Sampling preparation

The following steps were taken to prepare the samples:

- Organic matter (including litter, roots and charcoal) was removed from whole soil samples and placed in a separate labelled bag. Soil lumps were broken down by hand to as small as possible and samples were then air dried at 40°C. Once air-dried, samples were checked a second time to remove any remaining organic matter and then mixed well. A labelled sample jar was filled with soil aggregates and set aside for Emerson's dispersion test**.**
- The sample was then processed through a jaw crusher on setting 2. Any organic matter found was removed. The sample was then transferred to a large barrel and thoroughly mixed using a cement mixer.
- Once mixed, this sample was split into two sub-samples: (1) approximately 10kg of soil and (2) approximately 30-40kg of soil.
- Sub-sample 1 was processed through a 2mm sieve then split in two 5kg samples: (a) a whole soil sample for lab analysis, and (b) an archive sample. Sub-sample 1a was submitted to the Chemistry Centre DSITI and the analyses described in Table 2 were conducted in triplicate.
- Sub-sample 2 was further processed to separate the <10um fraction using the standard laboratory method for water-dispersible clay and the appropriate settling time based on Stoke's Law. Following separation the <10um fraction was dried at 40°C and then gently mixed and homogenised using a mortar and pestle. Following this, a 5g sub-sample was frozen and submitted to the Griffith University for microbial analysis listed in Section XX. The remaining sample was submitted to the Chemistry Centre DSITI and the analyses listed in Table 2 were conducted on the sediment samples in triplicate.

Sample analysis

Nitrogen (N) and phosphorus (P) analyses conducted in this project cover the key pools and processes in the nitrogen and phosphorus cycles (Figs 1 and 2). Carbon pools and processes and physical parameters were also measured (Fig. 3). These parameters will be used to explain N and P pools and processes. The parameters analysed are summarised in Table 2 with full methods and references provided in Appendix 1.

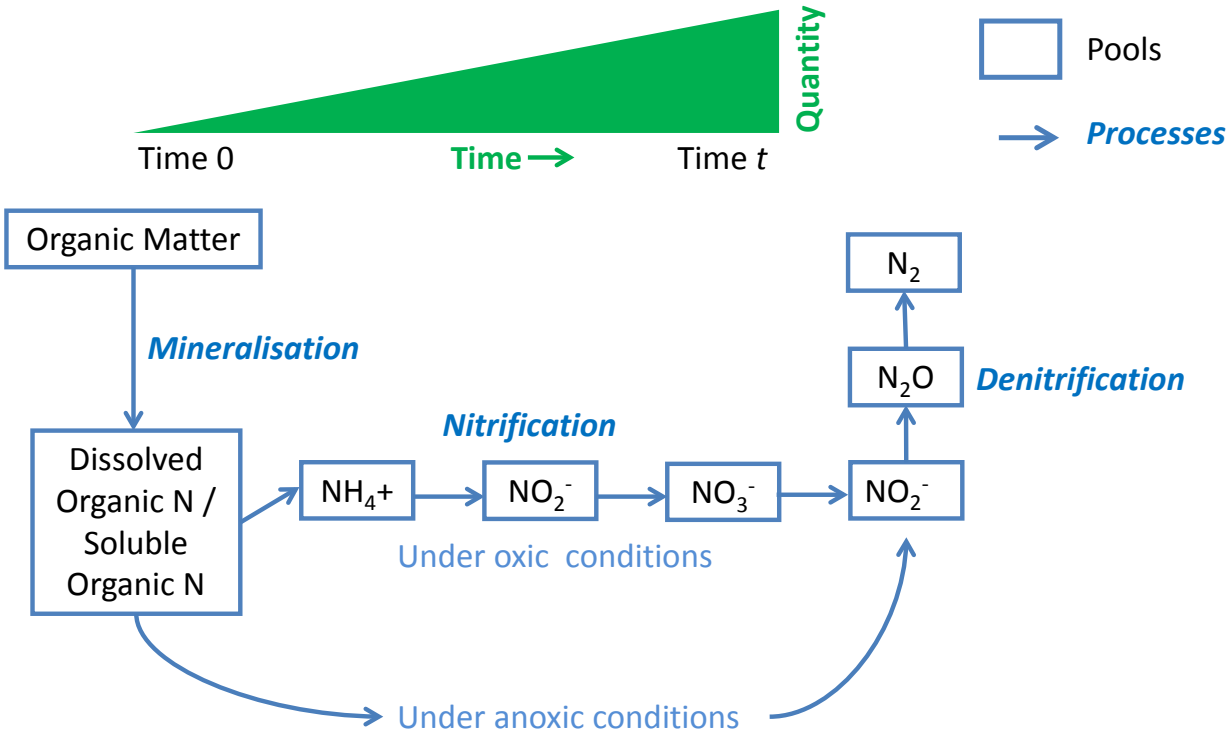


Figure 1 Key pools and processes of the nitrogen cycle. The trend of bioavailable nitrogen over time is indicated in the figure

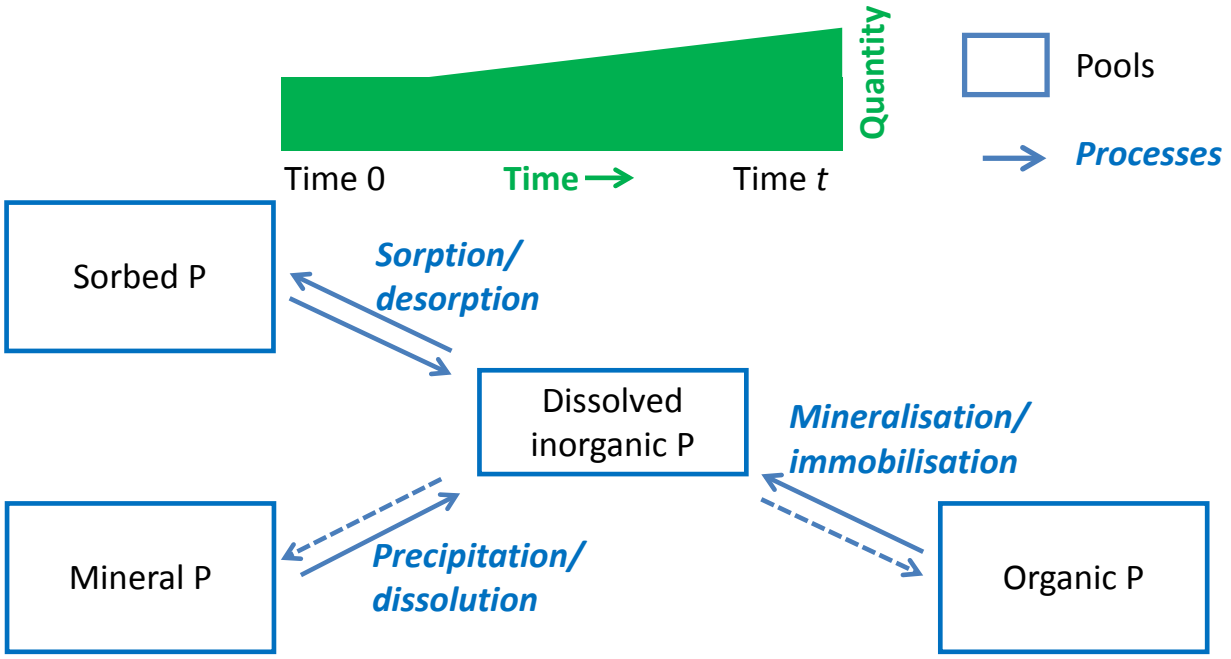


Figure 2 Key pools and processes of the phosphorus cycle. The trend of bioavailable phosphorus over time is indicated in the figure

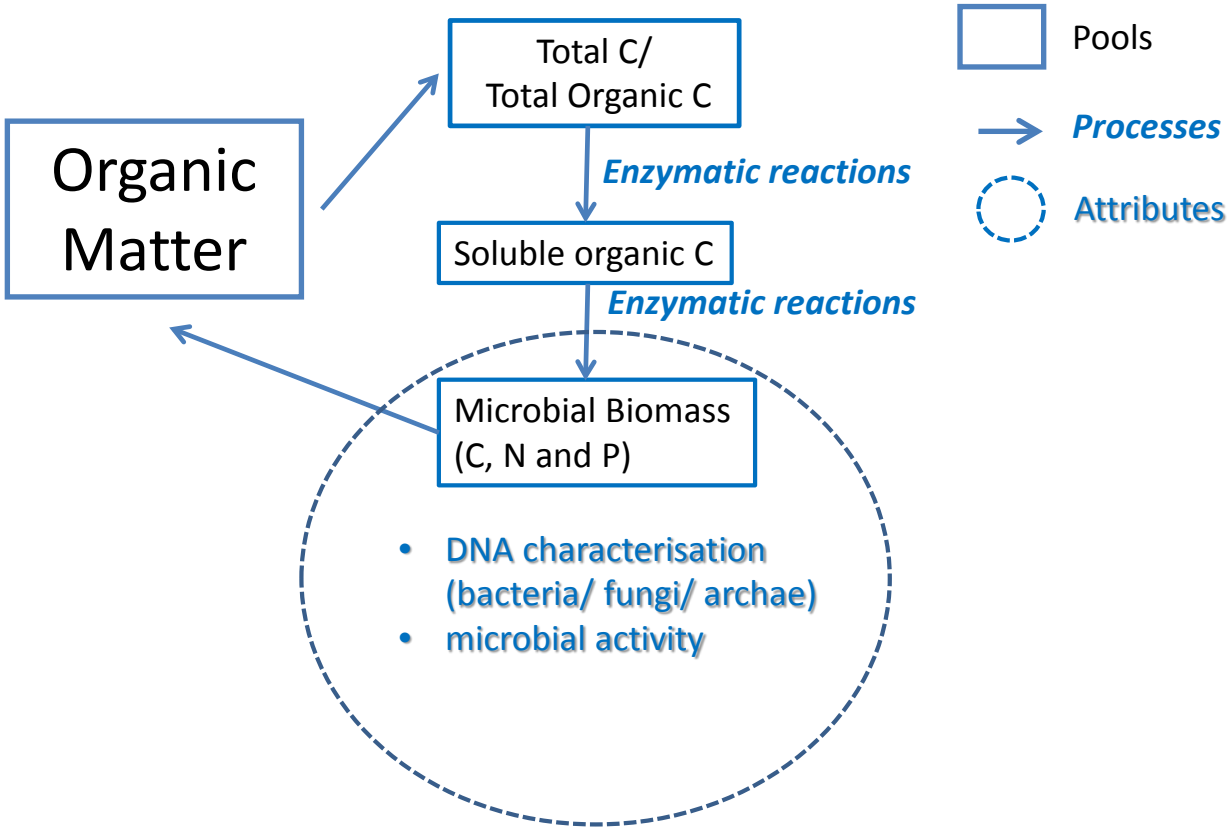


Figure 3 Key pools, processes and attributes of the carbon cycle

Table 2 Nitrogen, phosphorus, carbon and other physical and chemical parameters measured in soils and simulated <10um sediments

Nitrogen (N)	Phosphorus (P)	Carbon (C)/ organics	Other possible explanatory measures
• Total N* (refers to the total N pool) • Mineral N* (refers to NH_4^+-N plus NO_3^--N plus NO_2^-N) • Soluble organic N (SON)* • Potentially mineralisable N (PMN) under aerobic conditions (freshwater and marine)* • Potential production of soluble organic N (PPSON) • Microbial biomass N (MBN)	• Total P* (refers to the total P pool) • Sorbed P* (refers to the P sorbed to the soil/sediment surface that is extracted by the Colwell-P method) • Mineral P* (refers to P that is part of the soil/sediment mineral matrix. It is calculated as BSES-P minus Colwell-P) • Phosphorus Buffer Index (PBI)* (an indicator of how tightly sorbed P is bound to the soil/sediment surface) • Dissolved reactive P* (DRP) (calculated as Colwell-P/PBI) • Bioavailable P* (estimated using P sorbed by iron-oxide impregnated paper over 18h)**	• Total C* • Total organic carbon* (TOC) • Microbial biomass carbon (MBC) • Potential production of soluble organic C (PPSOC) • Microbial activity • Enzyme activity*** • Quantitative PCR analysis of 16S rRNA and 18S rRNA***	• Particle size (hydrometer and laser diffraction) • R1/R2 (dispersion ratio • Emerson's dispersion test • Clay activity ratio • Exchangeable cations • Exchangeable aluminium and acidity • Effective cation exchange capacity • pH • EC • Chloride • Acid digestible trace elements and heavy metals

***refers to analyses reported in this document**

****this analysis was only conducted on sediment samples**

*****these analyses were conducted on soil and sediment samples from Sodosol, Vertosol and Dermosol soil and sediment samples**

Results and Discussion

Note that this report presents the results and interpretation of key N, P and C parameters measured during Phase 1 of the project. Interpretation of other measured parameters is continuing and will inform and supplement findings from the Phase 2 project.

What do total N and total P tell us about bioavailability?

In the existing GBR Event Monitoring Program and Paddock to Reef Modelling Program, total nitrogen and total phosphorus are the only measures used to assess the concentration and loads of particulate nitrogen and phosphorus. We investigated how much these parameters can tell us about the bioavailability of the particulate N and P pools by assessing the relationships between the total pools and the bioavailable pools of N and P using a combined dataset of fine (<10um) sediments and their parent soils. The results indicate that total N may be a reasonable predictor of SON (R^2 = 0.59) and 7 day PMN (R^2 = 0.77) but it is a poor predictor of other pools of bioavailable N such as mineral N (R^2 = 0.36) and PPSON (R^2 = 0.03) (Fig.4). Total P is a poor predictor of all bioavailable pools of P and processes (Fig. 4).

These results indicate that in order to understand and predict pool sizes and processes of bioavailable nutrients, we need to measure and model more than just total N and total P. The methods applied in this work give information specific to bioavailable nutrient pool sizes and release rates.

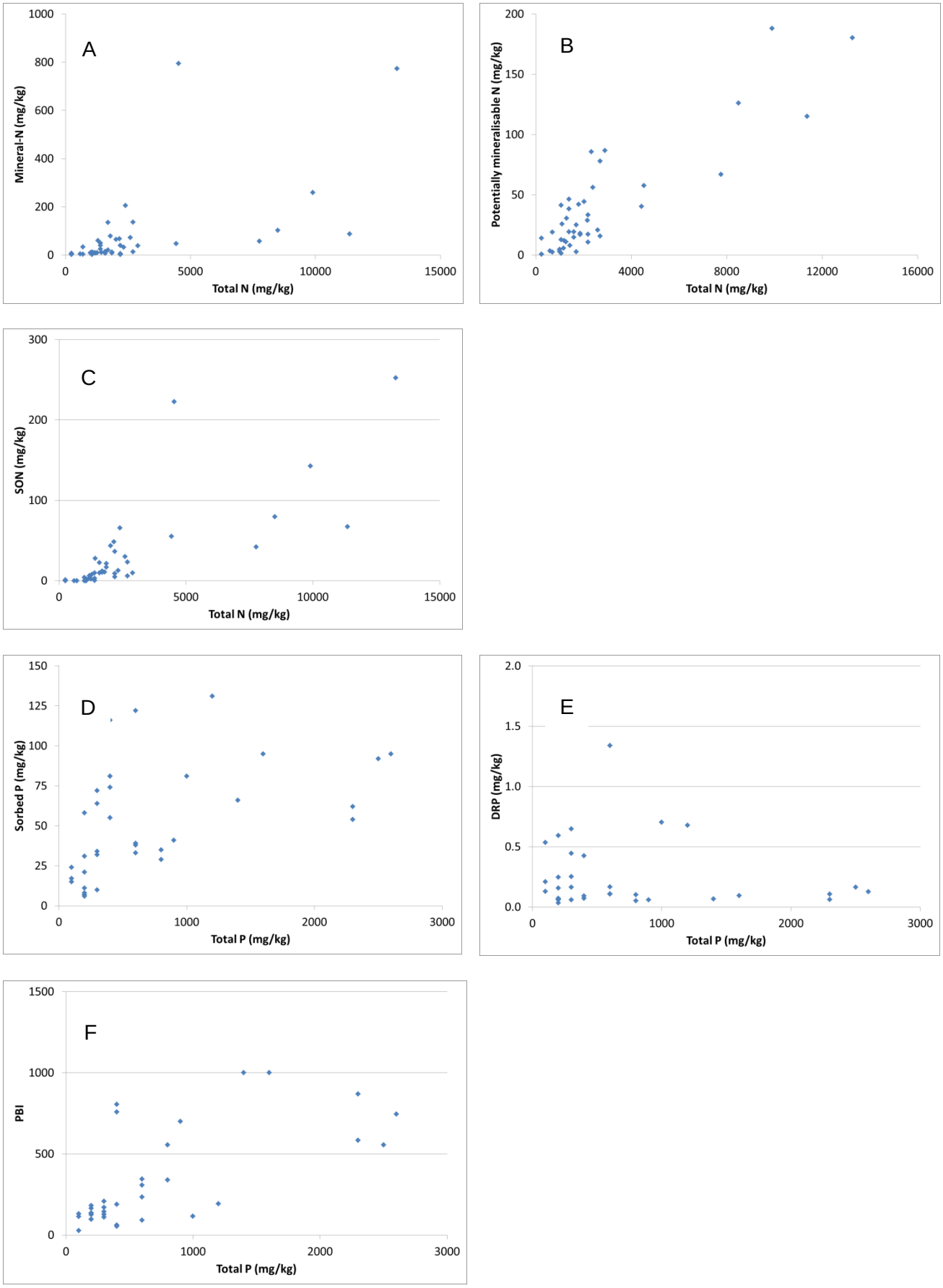
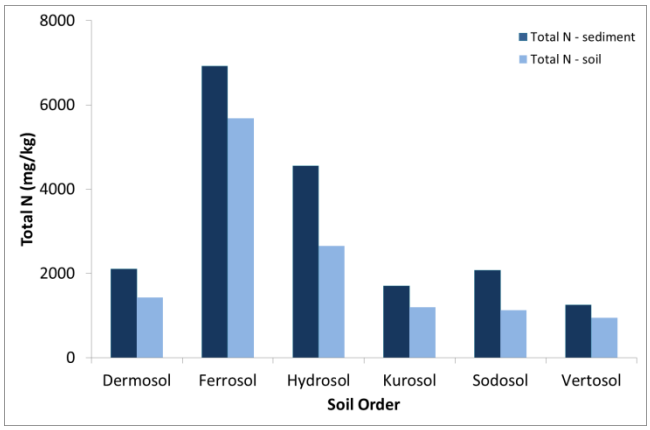


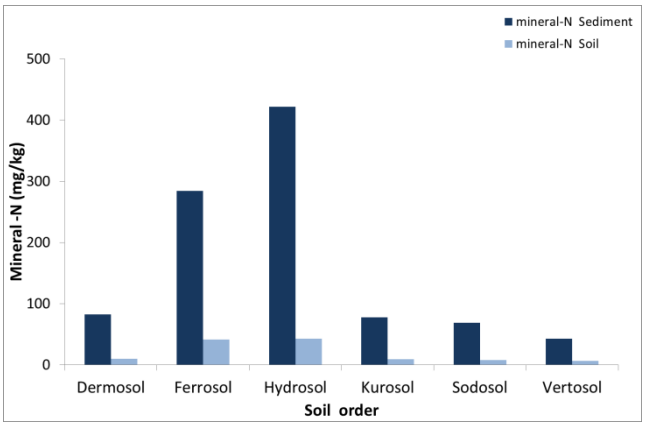
Figure 4 Relationship between bioavailable nutrient pools and total pools for nitrogen and phosphorus. (A) Mineral N and total N, R2 = 0.36; (B) 7 day Potentially Mineralisable Nitrogen (PMN) and total N, R2 = 0.77; (C) Soluble Organic Nitrogen (SON) and total N, R2 = 0.59; (D) Sorbed P and total P, R2 = 0.23; (E) Dissolved Reactive Phosphorus (DRP) and total P, R2 = 0.03; (F) Phosphorus Buffer Index (PBI) and total P, R2 = 0.46

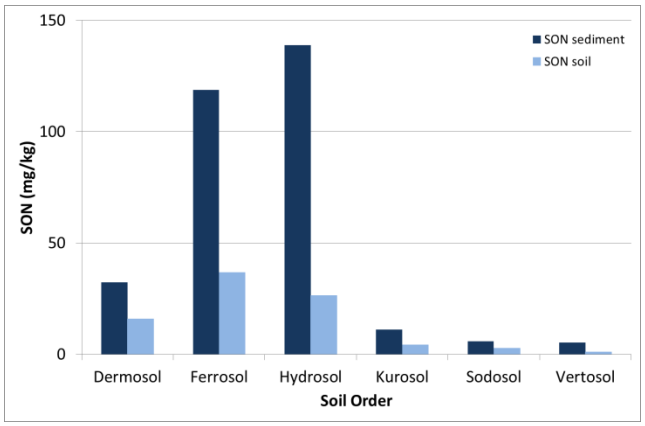
Bioavailable nutrient pools and processes in sediments compared to soils

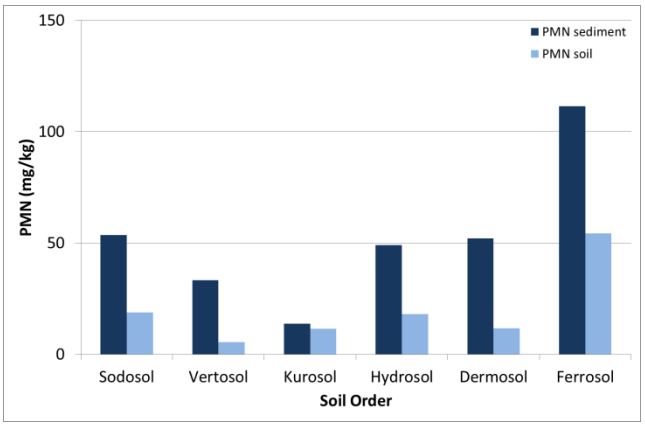
There is wide variation in the concentration of pools of bioavailable nutrients across different soil types (Fig. 5). Importantly, soil orders generally classified as highly erodible (e.g., Sodosols) don't always have the highest concentration of bioavailable nutrients.

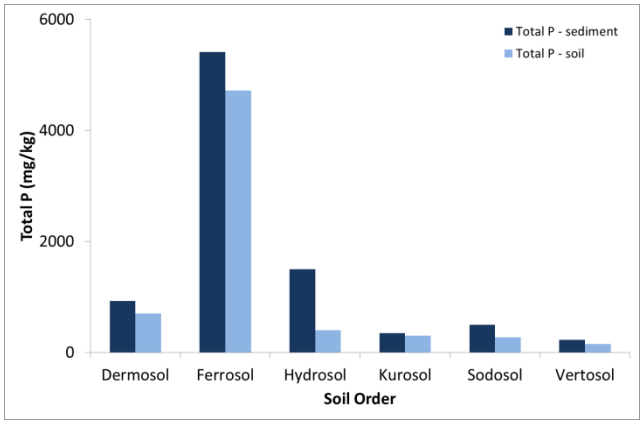
Fine sediments (<10um) were generally enriched in bioavailable nutrients compared to their parent soil and also differed in their ability to process N and adsorb P (Fig. 5). The relative nutrient enrichment in the fine sediments compared to their parent soils was variable between soil types and between bioavailability parameters. These results indicate that it is important to measure bioavailability parameters on the sediments themselves as it may be difficult to accurately infer these parameters from available soil data.

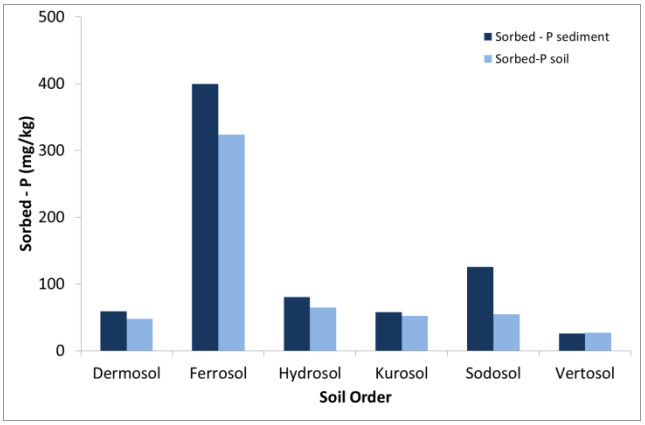


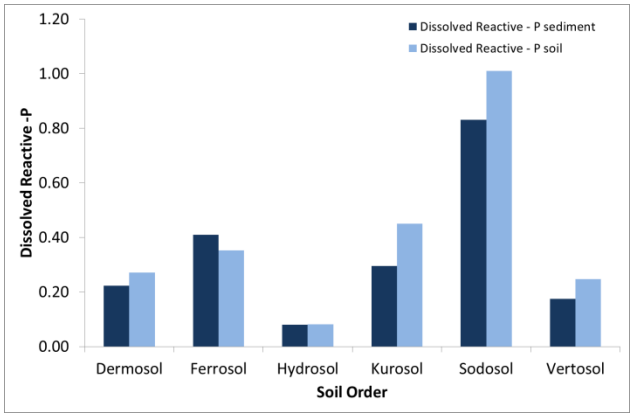


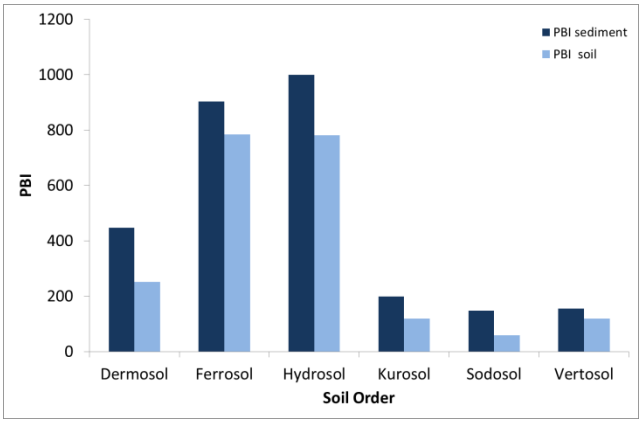












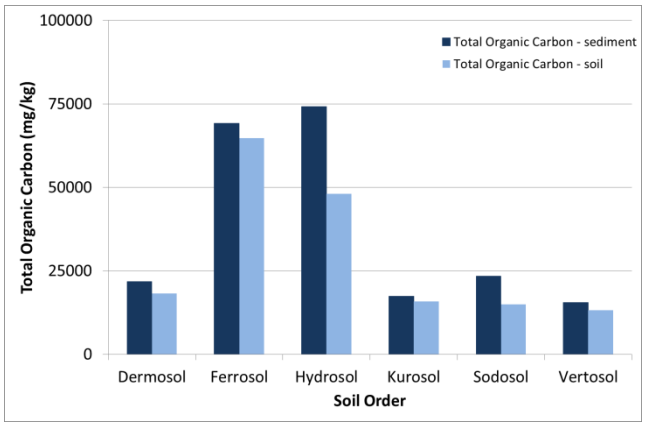


Figure 5 A comparison of bioavailable nutrient pools and processes among soil orders and between fine (<10um) sediments and their parent soil

In the absence of a long history of fertiliser P application and the accumulation of fertiliser reaction products in the surface soil, the soil/sediment mineral P pool primarily reflects the presence of apatites (calcium phosphates) sourced from the soil parent material. Across the soil types sampled in the Bowen-Burdekin, surface and subsurface samples of the Dermosol and Vertosol exhibited the presence of mineral P (average mineral P values of 86mg P/kg and 79mg P/kg, respectively). A similar result has been found for these soil types in the Queensland grain cropping area.

However, fine (<10um) sediments sourced from the Dermosol did not contain mineral P (average surface/subsurface sediment value: -15mg/kg, not significantly different from zero) whereas those from the Vertosol did (average surface/subsurface sediment value: 80mg/kg). These results suggest that apatites occurring in the Dermosol are in the coarser end of the silt (2-20um) fraction of the soil and not likely to be transported in the fine sediment fraction. However, the apatites in the Vertosol are of smaller particle size and likely to comprise a discrete bioavailable P source in the fine sediments derived from Vertosol parent soils. The larger number of soil samples being collected in the Phase 2 project will enable the implications of this P source as a bioavailable P source to be better assessed.

Bioavailable nutrient pools in different land uses

A comparison was made of bioavailable nutrient pools across banana, cane, dairy and grazing land uses (Table 3). Generally it was found that bioavailable nutrient concentrations in both sediments and their parent soils declined according to the sequence: dairy> bananas=cane> grazing.

For almost every measure of bioavailable nutrient across land uses, concentrations in fine (<10um) sediment were greater than in its parent soil, with the enrichment ratio of total N, total organic C and total P being lower than for other parameters that better reflected nutrient bioavailability (Tables 4-9).

Table 3 Mean, median and range of total N concentrations and enrichment ratios (<10um sediment/soil) in soils and sediments from the different land uses

	Total N - soil (mg/kg)			Total N - sediment (mg/kg)			Total N Enrichment Ratio		
	mean	median	range	mean	median	range	mean	median	range
Banana	1517	1517	1433 - 1600	2283	2283	2167 - 2400	1.5	1.5	1.4 - 1.7
Cane	1505	1233	250 - 2700	2380	1917	1300 - 4533	1.9	1.5	1.1 - 5.2
Dairy	9567	9567	7767 - 11367	11583	11583	9900 - 13267	1.2	1.2	1.2 - 1.3
Grazing	1261	1033	700 - 2200	1639	1400	700 - 2900	1.3	1.4	1.0 - 1.5

Table 4 Mean, median and range of mineral N concentrations and enrichment ratios in soils and <10um sediments from the different land uses

	Mineral N - soil (mg/kg)			Mineral N - sediment (mg/kg)			Mineral N Enrichment Ratio		
	mean	median	range	mean	median	range	mean	median	range
Banana	12.7	12.7	10.7 - 14.7	136	136	67 - 205	11.9	11.9	4.6 - 19.3
Cane	16.2	9.8	7.3 - 72.0	143	62	21 - 795	7.4	6.9	2.6 - 13.0
Dairy	72.5	72.5	57.0 - 88.0	516	516	259 - 773	6.7	6.7	4.6 - 8.9
Grazing	5.7	5.3	2.7 - 10.0	29.8	33	9.3 - 38.0	6.4	4.4	3.2 - 14.6

Table 5 Mean, median and range of soluble organic nitrogen (SON) concentrations and enrichment ratios in soils and <10um sediments from the different land uses

	SON - soil (mg/kg)			SON - sediment (mg/kg)			SON Enrichment Ratio		
	mean	median	range	mean	median	range	mean	median	range
Banana	25.0	25.0	22.4 - 27.6	57	57	48.3 - 65.7	2.3	2.3	2.2 - 2.4
Cane	10.6	4.4	0 - 30.0	21.3	10.8	5.8 - 55.1	2.8	2.4	0 - 4.6
Dairy	54.6	54.6	42.0 - 67.2	198	198	143 - 253	3.6	3.6	3.4 - 3.8
Grazing	3.8	2.1	0 - 9.6	4.34	1.7	0 - 12.7	0.5	0.3	0 - 1.3

Table 6 Mean, median and range of potentially mineralisable nitrogen (PMN) concentrations and enrichment ratios in soils and <10um sediments from the different land uses

	7 day PMN - soil (mg/kg)			7 day PMN - sediment (mg/kg)			PMN Enrichment Ratio		
	mean	median	range	mean	median	range	mean	median	range
Banana	13.7	13.7	8.0 - 19.3	42.3	42.3	28.7 - 56.0	4.2	4.2	1.5 - 7.0
Cane	16.8	14.8	5.7 - 41.3	40.0	41.2	2.7 - 78.0	2.7	2.3	0.2 - 7.4
Dairy	91.0	91.0	67 - 115	184	184.2	180 - 188	2.2	2.2	1.6 - 2.8
Grazing	7.2	3.8	1.3 -17.3	45.8	32.0	19.0 - 86.7	8.8	7.3	5.0 - 19.3

Table 7 Mean, median and range of total organic carbon (TOC) concentrations and enrichment ratios in soils and <10um sediments from the different land

	7 day PMN - soil (mg/kg)			7 day PMN - sediment (mg/kg)			PMN Enrichment Ratio		
	mean	median	range	mean	median	range	mean	median	range
Banana	13.7	13.7	8.0 - 19.3	42.3	42.3	28.7 - 56.0	4.2	4.2	1.5 - 7.0
Cane	16.8	14.8	5.7 - 41.3	40.0	41.2	2.7 - 78.0	2.7	2.3	0.2 - 7.4
Dairy	91.0	91.0	67 - 115	184	184.2	180 - 188	2.2	2.2	1.6 - 2.8
Grazing	7.2	3.8	1.3 -17.3	45.8	32.0	19.0 - 86.7	8.8	7.3	5.0 - 19.3

Table 8 Mean, median and range of total phosphorus concentrations and enrichment ratios in soils and <10um sediments from the different land uses

	Total P (mg/kg) soil			Total P (mg/kg) sediment			Total P Enrichment Ratio		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
Banana	600	600	600	850	850	800 - 900	1.4	1.4	1.3 - 1.5
Cane	700	350	100 - 2500	1020	650	200 - 2600	2.0	1.8	1.0 - 4.0
Dairy	7033	7033	6467 - 7600	8367	8367	7667 - 9067	1.2	1.2	1.2 - 1.2
Grazing	417	300	100 - 1000	550	450	200 - 1200	1.4	1.4	1.0 - 2.0

Table 9 Mean, median and range of sorbed phosphorus concentrations and enrichment ratios in soils and <10um sediments from the different land uses

	Sorbed P (mg/kg) soil			Sorbed P (mg/kg) sediment			Sorbed P Enrichment Ratio		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
Banana	36	36	33 - 38	35	35	29 - 41	1.0	1.0	0.9 - 1.1
Cane	60	60	24 - 116	88	65	31 - 339	1.4	1.1	0.9 - 2.9
Dairy	570	570	517 - 623	724	724	631 - 817	1.3	1.3	1.2 - 1.3
Grazing	39	28	7 - 81	53	23	6 - 131	1.1	1.2	0.8 - 1.6

Bioavailable nutrient pools – surface vs subsurface

When the concentrations of nutrients in sediments of surface and sub-surface origin were compared for grazing land samples only, the surface sediments were enriched compared to sub-surface sediments, except for the mineral N pool (Table 10). Nitrogen mineralisation (the rate of mineralisation of soluble organic N to mineral N as indicated by PMN) was considerably higher after 1 day in the surface sediments than the sub-surface sediments, and approximately 3 times higher after 3 days and 7 days. Although total P concentrations in surface and sub-surface sediments were similar, surface sediments were considerably enriched in DRP, sorbed P and FeO-P compared to sub-surface sediments. The PBI values for surface sediments are low (139), whereas PBI values for the sub-surface sediments are moderate (241). This means that sorbed P in the surface sediments is only weakly held and more easily displaced into the DRP pool than the sorbed P in the sub-surface sediments.

Table 10 Nitrogen and phosphorus pool sizes (concentrations) in the <10um sediment of surface and sub-surface soils in grazing lands (Burdekin/Bowen catchment)

	Surface sediment	Sub-surface sediment
Total N (mg/kg)	2111	1167
Mineral N (mg/kg)	26	33
Soluble Organic Nitrogen (mg/kg)	6	1
Potentially mineralisable N @1 day (mg/kg)	26	1
Potentially mineralisable N @ 3days (mg/kg)	47	14
Potentially mineralisable N @ 7 days (mg/kg)	66	26
Total C (mg/kg)	25000	12000
Total P (mg/kg)	667	433
Sorbed P (mg/kg)	88	17
DRP (mg/kg)	0.70	0.06
FeO-P (mg/kg)	31	6
PBI	139	241

These concentrations were used in a scenario to assess the potential nutrient contribution to end-of-system load from different erosion processes in the Burdekin catchment with grazing the dominant land use. The scenario used the work of Bainbridge et al. (2015) and assumed that 5.99M tonnes of the <10um sediment fraction is delivered to the end of the Burdekin River system each year. We then drew on the work of Wilkinson et al. (2015) which indicates that over the last decade or so approximately 10% of the <10um fraction of sediment is derived from surface (predominantly hillslope) erosion sources and 90% is from sub-surface (predominantly gully) erosion sources. The scenario also assumed that sediments derived from the three major soil orders in the catchment (viz., Dermosol, Sodosol and Vertosol) were equally mixed. (Note: we acknowledge equal mixing of sources is unlikely but we believe it is reasonable to use this for the purposes of the scenario).

With these assumptions, results show that <10um sub-surface sediments would deliver greater quantities of particulate nutrients than <10um surface sediments for all measured nutrient pools except N mineralised in 1 day. There was a wide range in the delivery ratios between surface and sub-surface sediments depending on the nutrient pool (Table 11). Apart from mineral N, surface sediments contributed a greater percentage of the quantities of nutrients reaching the end-of-system than expected from their proportion of the total end-of-system sediment load. Based on this limited data set, it appears that irrespective of the percentage mix of soil type sources in the Burdekin catchment (where there is a very high proportion of sediment derived from sub-surface erosion processes), the majority of particulate nutrient load would be derived from sub-surface sources.

Table 11 Load of nutrient in each pool delivered to end-of-system if 5.99 M tonnes of <10um sediment was delivered to the end of the Burdekin catchment (figures based on the average annual load of <10um sediment calculated by Bainbridge et al., 2015), with 10% of the total sourced from surface erosion processes and 90% of the total sourced from sub-surface erosion processes (Wilkinson et al., 2015)

	Surface sediment	Sub-surface sediment	Contribution of surface sediment to end of system load (%)
4 year average <10um sediment load (M tonnes)	0.6	5.4	10
Total N (tonnes/ year)	1265	6290	17
Mineral N (tonnes/ year)	16	179	8
Soluble Organic Nitrogen (tonnes/ year)	4	5	40
Potentially mineralisable N @ 1 day (tonnes/ year)	16	5	74
Potentially mineralisable N @ 3 days (tonnes/ year)	28	75	27
Potentially mineralisable N @ 7d (tonnes/ year)	40	140	22
Total C (tonnes/ year)	14975	64692	19
Total P (tonnes/ year)	399	2336	15
Sorbed P (tonnes/ year)	53	92	37
DRP (tonnes/ year)	0.42	0.35	54
FeO-P (tonnes/ year)	19	32	36

Nutrient bioavailability in marine conditions

Of the measured nutrient bioavailability indicators, it might be expected that a transition from freshwater to marine conditions would affect:

- the rate of production of potentially mineralisable N because of the possible biocide effects of seawater on the terrestrial bacteria mineralising soil organic N;
- the strength of adsorption of inorganic P on sediment surfaces due to changes in variable charge characteristics of the sorption surfaces as a result of increased salt concentration and pH.

Potentially mineralisable N

The potentially mineralisable N after 7 days is compared for the <10um sediments suspended in DI water (simulates freshwater conditions) or 0.5M NaCl (simulates marine conditions) in Fig. 6.

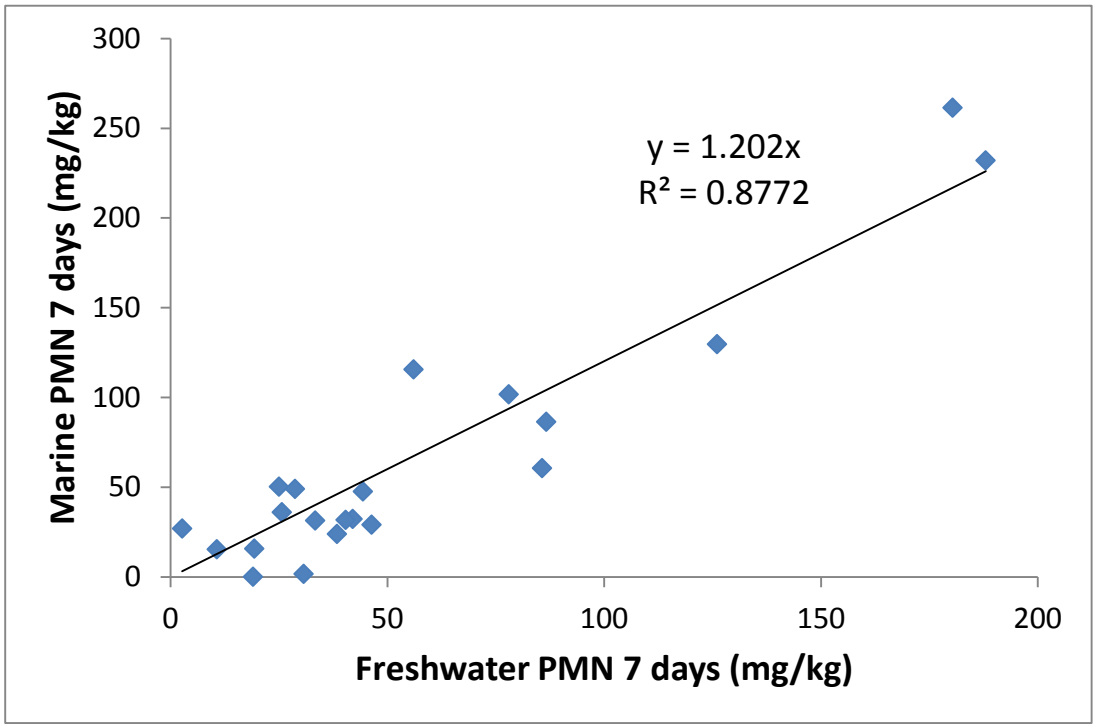


Figure 6 Potentially mineralisable N after 7 days in <10um sediments suspended in DI water (freshwater conditions) and 0.5M NaCl (marine conditions).

The regression equation indicates that, with the exception of two sediments, N mineralisation was essentially unaffected by the saline conditions. This finding is significant because it demonstrates that the sediments will continue to be a source of mineral N (i.e., DIN) even when moving into waters of the GBR lagoon.

P sorption

The relationship between PBI (a measure of sorption strength) of <10um sediments in DI water and PBI of the same sediments in 0.5M NaCl shows little effect of high salinity on the desorbability of the sorbed P (Fig. 7). It has been assumed in the past that under high salt conditions, sorbed P is displaced into solution by other anions- in the case of seawater, chloride and sulfate. However, this is not the case and the sediments will continue to retain sorbed P in the marine environment.

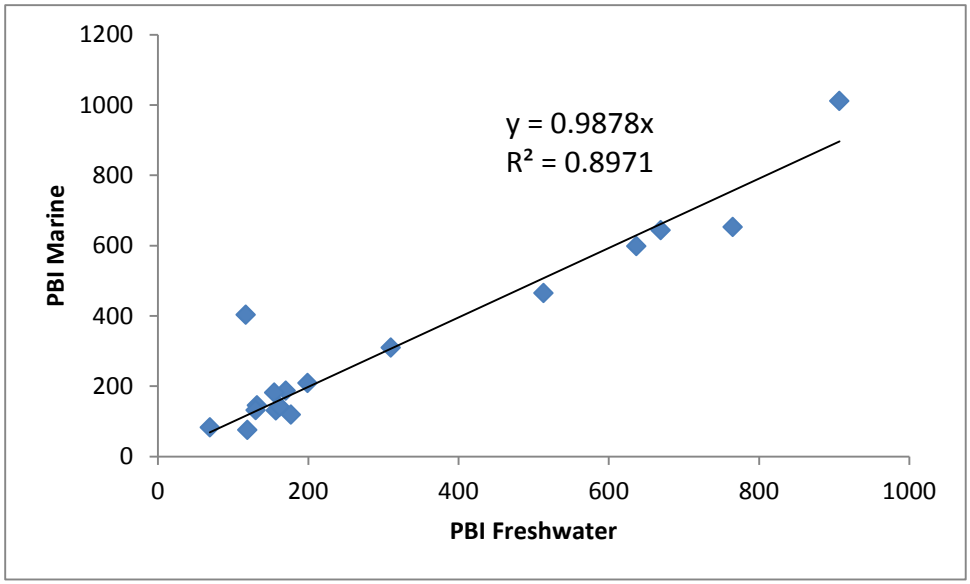


Figure 7 PBI of <10um sediments suspended in DI water (Freshwater) and 0.5M NaCl (Marine)

A note on cattle tracks

The bioavailable nitrogen produced from sediment sampled from cattle tracks is variable (Fig. 8). In some cases tracks may be sources of high concentrations of bioavailable nitrogen (similar to concentrations produced from surface soil) which is of concern as they are often connected directly to the river. Further exploration of cattle tracks is required.

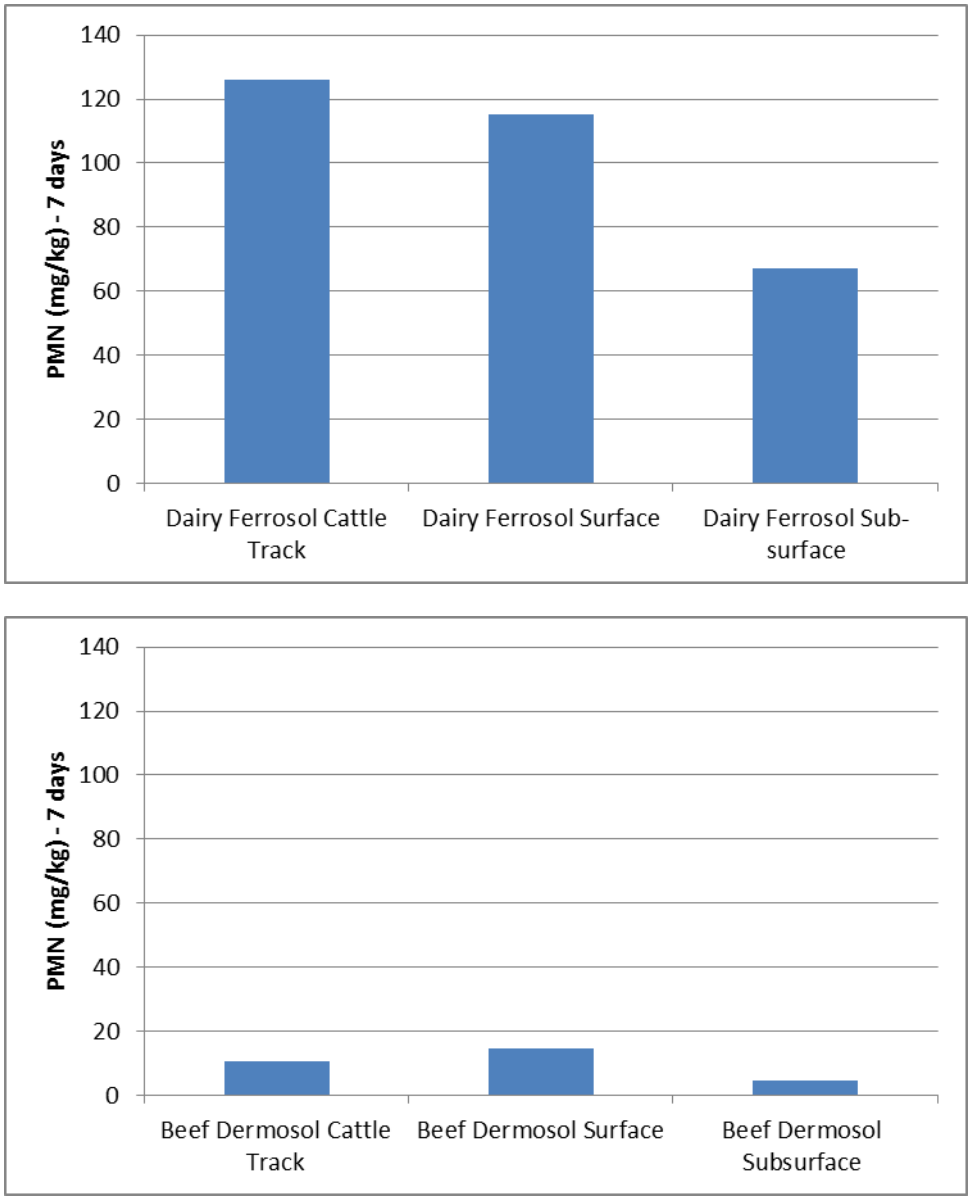


Figure 8 The amount of potentially mineralisable nitrogen produced from sediments collected from cattle tracks at a dairy farm on a Ferrosol (top) and a beef property on a Dermosol (bottom) in the Burdekin catchment

Conclusions

Because of the limited number of samples, the findings of this project must be regarded as preliminary and indicative only. However, soil test methods used to assess nutrient bioavailability to agricultural crops have been successfully modified and applied to sediments generated in the laboratory. This methodology has allowed particulate nutrient bioavailability to be inferred under both freshwater and marine conditions; in the Phase 2 project, these inferences will be validated using algal bioassays.

Based on indicative results, the following conclusions can be drawn:

- Fine (<10um) sediment from surface soil erosion processes is enriched in bioavailable nitrogen and phosphorus relative to fine sediment of sub-surface origin.
- The enrichment varies depending on the bioavailable nutrient pool, but ranged from 0.8 for mineral N to as high as 26 for 1 day mineralisable N.
- There was a general trend for land use to affect bioavailable nutrients with dairy>cane=bananas>grazing.
- Bioavailable nutrient levels varied widely across soil types, and there was no soil type that was consistently higher or lower across all bioavailable nutrient pools.
- The relative nutrient enrichment in the fine (sediments compared to their parent soils was variable between soil types and between bioavailability parameters.
- Bioavailable nutrient pools in fine (<10um) sediments could not be inferred with any certainty from analyses of the parent soil.
- In the Burdekin-Bowen catchment where 90% of the end-of-system fine (<10um) sediment load is of sub-surface origin, these sub-surface sediments also provided the bulk of end-of-system particulate nutrients. However, fine sediments of surface origin contributed a greater proportion to the end-of-system particulate nutrient load than expected from their contribution to total sediment load.
- For fine (<10um) sediments and soils, total N is a reasonable predictor of soluble organic N and potentially mineralisable N at 7 days, but is a poor predictor of other pools of bioavailable N such as mineral N and potential particulate soluble organic N.
- For fine (<10um) sediments and soils, total P is a poor predictor of all bioavailable pools of P.
- Sediment P sorption properties and the quantity of N mineralised in 7 days were not affected when conditions changed from freshwater to marine.
- Cattle tracks may be a source of sediments with elevated levels of bioavailable N.

Implications

- Sediments derived from surface soil have a higher content of bioavailable nutrients than sediments of sub-surface origin. The relative contribution of sediments of surface origin to end-of-system loads of bioavailable nutrients will therefore be higher than their contribution to end-of-system sediment loads. The quantity and nutrient enrichment of sediment generated by surface erosion (including that occurring in the surface of gullies and channel banks) relative to the quantity of sub-surface sediment generated by sub-surface erosion processes therefore becomes a metric for assigning priority of soil surface management to gully management. Consequently, land surface management (maintaining surface cover, controlling stock movement and stock camping) will remain a high priority even in areas prone to active gullying or channel erosion.
- The observed release of mineralised N up to at least 7 days indicates that suspended sediments will be a continuing source of dissolved inorganic N (DIN) as the sediments move through the river system and disperse in the GBR lagoon. This source of DIN is currently unaccounted for in catchment nutrient modelling. The Phase 2 project will undertake longer incubation times to quantify the total amount of sediment organic N that mineralises. This quantity will be related to other N measurements made on the sediments to assess whether any have use as predictors of this important property.
- Inferring sediment nutrient bioavailability from analysis of the parent soil will be problematic because of the numerous factors affecting sediment yield and sediment particle size such as dispersion/disaggregation of soil peds caused by the erosion process. A closer examination of these factors will be undertaken in the Phase 2 project with a larger soil/sediment dataset.
- Land use effects on sediment bioavailable nutrient content are apparent and will be further studied in the Phase 2 project by relating indicative nutrient budgets for generic land uses to parent soil bioavailable nutrient content.

References

AS 4863.1-2000 (ISO 13320-1:1999). Particle size analysis – Laser diffraction methods Part 1 – General Priciples. Standards Australia International Ltd, Straithfield, NSW, 2000.

AS 1289.3.6.3 - 2003. Methods of testing soils for engineering purposes - Soil classification tests - Determination of the particle size distribution of a soil - Standard method of fine analysis using a hydrometer "

Bainbridge, Z.T. Wolanski, E. Álvarez-Romero, J.G. Lewis, S.E. Brodie, J.E. 2012. Fine sediment and nutrient dynamics related to particle size and floc formation in a Burdekin River flood plume, Australia. Marine Pollution Bulletin 65, 236-248.

Bainbridge, Z.T. Lewis, S.E. Smithers, S.G. Wilkinson, S.N. Douglas, G. Hillier, S. Brodie, J.E. 2015. Clay mineral source tracing and characterisation of Burdekin River (NE Australia) and flood plume fine sediment. Journal of Soils and Sediments. DOI 10.1007/s11368-015-1282-4.

Bartley R, Olley J, Henderson A. 2004. A sediment budget for the Herbert river catchment, north Queensland, Australia. In: Sediment Transfer through the Fluvial System, Int Assoc Hydrological Sciences, pp: 147-154.

Bran and Luebbe (1990) - Individual/Simultaneous Determination of Nitrogen and/or Phosphorus in BD Acid Digests. Industrial Method No. 167-b590-XX / 329-74W/B, 1-9.

Bremner, J.M., 1965. Nitrogen availability indexes. In: Black, C.A. (Ed.), Methods of Soil Analysis, Part 2. American Society of Agronomy, Madison, WI, pp. 1324-1345.

Brodie J, Waterhouse J, Schaffelke B, Kroon F, Thorburn P, Rolfe J, Johnson J, Fabricius K, Lewis S, Devlin M, Warne M, McKenzie L. 2013. Land use impacts on Great Barrier Reef water quality and ecosystem condition. 2013 Scientific Consensus Statement. http://reefplan.qld.gov.au/about/assets/scientific-consensus-statement-2013.pdf.

Brodie, J., Burford, M., Davis, A., da Silva, E., Devlin, M., Furnas, M., Kroon, F., Lewis, S., Lønborg, C., O'Brien, D., Schaffelke, B., Bainbridge, Z. 2015. The relative risks to water quality from particulate nitrogen discharged from rivers to the Great Barrier Reef in comparison to other forms of nitrogen. TropWATER Report 14/31, Centre for Tropical Water & Aquatic Ecosystem Research, James Cook University, Townsville, 93 pp.

Burkitt LL, Moody PW, Gourley CJP and Hannah MC (2002). A simple phosphorus sorption index for Australian soils. Australian Journal of Soil Research, 40, 497–513.

Burton J, Chen C, Xu Z, Ghadiri H. (2007) Soluble organic nitrogen pools in adjacent native and plantation forests of subtropical Australia. Journal of Soils and Sediment. 39, 2723 – 2734.

Colwell JD, (1963), The estimation of the phosphorus fertiliser requirements of wheat in southern New South Wales by soil analysis. Australian Journal of Experimental Agriculture and Animal Husbandry, 3, 190-8.

De'ath G, Fabricius K. 2010. Water quality as a regional driver of coral biodiversity and macroalgae on the Great Barrier Reef. Ecol. Appl., 20: 840-850.

Eivazi F, Tatabai MA (1977) Phosphatases in soils. Soil Biology and Biochemistry 9, 167–172.

Eivazi F, Tatabai MA (1988) Glucosidases and galactosidases in soils. Soil Biology and Biochemistry 20, 601–606.

Fabricius KE. 2005. Effects of terrestrial runoff on the ecology of corals and coral reefs: review and synthesis. Marine Pollution Bulletin, 50: 125-146. http://dx.doi.org/10.1016/j.marpolbul.2004.11.028

Hughes AO, Olley JM, Croke JC, McKergow LA. 2009. Sediment source changes over the last 250 years in a dry-tropical catchment, central Queensland, Australia. Geomorphology, 104: 262-275. http://dx.doi.org/10.1016/j.geomorph.2008.09.003.

Jenkinson, D.S. and Powlson D.S. (1976) The effects of biocidal treatments on metabolism in soil –V. A method for measuring soil biomass. Soil Biology & Biochemistry 8, 209-13.

Kerr, H.W. and von Stieglitz, C.R. (1938) The laboratory determination of soil fertility. Bureau of Sugar Experiment Stations Technical communications No. 9.

Lennox LJ and Flanagan MJ, (1981) - An Automated Procedure for the Determination of Total Kjeldahl Nitrogen. Water Res. Vol 16, 1127-1133.

Loveday J, Beatty HJ and Norris JM (1972) Comparison of current methods for evaluating irrigation soils, CSIRO Australia, Division of Soils, Technical Paper No. 14.

Murphy J, Riley JP, (1962), A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27(C), 31–36.

Olley J, Brooks A, Spencer J, Pietsch T, Borombovits D. 2013. Subsoil erosion dominates the supply of fine sediment to rivers draining into Princess Charlotte Bay, Australia. Journal of Environmental Radioactivity, 124: 121-129. http://dx.doi.org/10.1016/j.jenvrad.2013.04.010.

Rayment GE and Lyons DJ (2011) Soil Chemical Methods —Australasia. CSIRO Publishing Collingwood Victoria.

Thorburn PJ and Shaw RJ, (1987). "Effects of Different Dispersion and Fine Fraction Determination Methods on Results of Routine Particle-Size Analysis." Australian Journal of Soil Research. 25 : pp347-360

Tims SG, Everett SE, Fifield LK, Hancock GJ, Bartley R. 2010. Plutonium as a tracer of soil and sediment movement in the Herbert River, Australia. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 268: 1150-1154.

Tucker BM (1971) Basic exchangeable cations in soils, CSIRO Australia, Division of Soils, Technical Paper No. 8.

Weber, M., Lott, C., Fabricius, K.E., 2006. Sedimentation stress in a scleractinian coral exposed to terrestrial and marine sediments with contrasting physical, organic and geochemical properties. Journal of Experimental Marine Biology and Ecology 336, 18-32.

Weber, M., de Beer, D., Lott, C., Polerecky, L., Kohls, K., Abed, R.M.M., Ferdelman, T.G., Fabricius, K.E., 2012. Mechanisms of damage to corals exposed to sedimentation. Proceedings of the National Academy of Sciences 109, E1558-E1567.

Wilkinson SN, Olley J, Furuichi T, Burton J. 2014. Identifying erosion processes and sources in the Burdekin dry tropics catchment – Technical Report: Knowledge Gap 1 – Erosion process tracing. Department of Science, Information Technology, Innovation and the Arts, Brisbane.

Wilkinson SN, Olley JM, Furuichi T, Burton J, Kinsey-Henderson AE. 2015. Sediment source tracing with stratified sampling and weightings based on spatial gradients in soil erosion. Journal of Soils and Sediments: In press. http://dx.doi.org/10.1007/s11368-015-1134-2.

Xian Liu, CR Chen, WJ Wang, JM Hughes, Lewis Tom (2013) Soil environmental factors rather than denitrification gene abundance control N2O fluxes in a wet sclerophyll forest with different burning frequency. Soil Biology and Biochemistry 57, 292-300.

Yeomans, J.C. and Bremmer, J.M. (1991). Carbon and nitrogen analysis of soils by automated combustion techniques. Comm. Soil Sci. Plant Anal., 22, 834–850.

Appendix 1 Sample analyses

Methods used by the DSITI Chemistry Centre generally follow the Australian Laboratory Handbook Method codes as per Rayment, G.E. and Lyons, D.J. (2011). “Soil Chemical Methods – Australasia”. This is the principal reference manual for soil analytical methods in Australia/New Zealand. Where methods follow the procedures specified in Rayment and Lyons (2011), they are referred to by manual’s method code in parentheses. Additional (original) references are provided for further information, or where the analytical method is not described in Rayment and Lyons (2011).

Air Dry moisture (2A1)

The Air Dried Moisture Content (ADMC) was determined gravimetrically. This determination (ADMC) expresses moisture content of air dried soils (dried at 40°C) as a percentage on an oven-dried basis, i.e. soils which have been further dried to 105°C for at least 16 h. It is necessary to determine ADMC where it is required to correct soil chemical results performed on air-dry samples to an oven-dry basis for consistency.

Total Kjeldahl Nitrogen (7A2) and Phosphorus (9A3a)

Total Kjeldahl Nitrogen (TKN) and Total Kjeldahl Phosphorus (TKP) were determined on soil samples subjected to Kjeldahl digestion with sodium sulfate and selenium as catalyst. Following dilution with water, ammonium-nitrogen was determined by an automated segmented-flow colorimetric procedure based principally on the indophenol reaction with salicylate and sodium hypochlorite. Similarly, after conversion of all, or almost all, P to orthophosphate, orthophosphate was determined colorimetrically, based on the reaction of ammonium molybdate and potassium antimony tartrate. This method covers procedures for the quantitative determination of total nitrogen, (excluding nitrates) and of phosphorus as orthophosphate in soils.

Mineral Nitrogen (7C2a) + Soluble Organic Nitrogen

Samples were extracted with 2 M KCl (1:10 soil to solution ratio for 1 h at 25°C) to determine their mineral-nitrogen concentrations automated colorimetric procedures to determine ammonium-nitrogen (NH_4-N) and nitrate-nitrogen (NO_3-N).

A 10mL aliquot was analysed for Organic Nitrogen and Organic Carbon by a high temperature catalytic oxidation method (Burton et al., 2007).

Potentially Mineralisable Nitrogen

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 at field capacity and at 30°C under aerobic conditions for 0, 1, 3 and 7 days, respectively. The amounts of mineral-N formed at different times are measured by 2M KCl extraction followed by automated colorimetric determination. Potentially mineralisable-N is calculated as the difference between the mineral-N before and after incubation.

To simulate a marine environment the procedure above was repeated but with the incubation of samples taking place in artificial seawater to emulate estuarine or marine conditions at Day 0 and Day 7 only.

Microbial biomass carbon and nitrogen

Soil microbial biomass measurement is one of the most common procedures used to assess soil health in sustainable cropping systems. The chloroform fumigation (CF) and chloroform fumigation-incubation (CFI) techniques were pioneered by Jenkinson and Powlson (1976).

To measure microbial biomass C and N, both non-fumigated (control) soil and chloroform fumigated soils are extracted in 0.25M K_2SO_4 immediately following fumigation, and the microbial biomass C is calculated by the difference in the amount of organic C extracted from fumigated and non-fumigated samples (Jenkinson and Powlson 1976). Organic C in the extracts is determined by wet digestion with potassium dichromate. Microbial biomass N is calculated by the difference in the amount of total N extracted from fumigated and non-fumigated samples. Microbial biomass P is calculated as the difference in the amount of total P extracted from fumigated and non-fumigated samples, corrected for soil P sorption determined by recovery of a known amount of inorganic P added to non-fumigated soil.

Enzyme assay, DNA Extraction and quantification of the gene abundance

Potential activities of β-glucosidase (BG), NAGase (N-acetyl-b-D-glucosaminidase) (NAG) and acid phosphatase (AP) in selected soils and sediments were measured as an indication of the microbial acquisition of C, N and P respectively (Sinsabaugh et al., 2009). Enzyme activities were measured colorimetrically using the methods of Eivazi & Tatabai (1988), Parham & Deng (2000), and Eivazi & Tatabai (1977) for β-glucosidase, NAGase and acid phosphatase respectively. DNA was extracted from 0.3 g of the soil and sediment samples using the MoBio PowersoilTM DNA Isolation Kit (MOBIO Laboratories, Carlsbad, CA, USA) according to the manufacturer's instructions, with 100 µL deionised water in the final elution step. The extracted DNA was diluted ten times and stored at −80 °C. We quantified bacterial 16S rRNA genes and functional genes (e.g. Alp, Chi genes) using respective primers and conditions as described by Liu et al. (2013).

Bicarbonate Extractable (Colwell) P (9B2) and Organic P

Colwell P (Colwell 1963) (referred to in this report as Sorbed P) was determined by extracting air dried sample with 0.5M $NaHCO_3$ buffered to pH 8.5 with NaOH at a 1:100 soil/solution ratio for 16 h at 25°C. The sample extract phosphorus concentration is determined by an automated modification of the Murphy and Riley (1962) colorimetric method.

To determine organic-P an aliquot of the extract was subjected to Kjeldahl digestion. A variation of the Kjeldahl procedure as described by Lennox and Flanagan (1982) and Bran & Luebbe (1990) is used to digest and solubilise organic P as orthophosphate. Samples are analysed colorimetrically (Bran & Luebbe, 1990). Organic P concentration is determined by subtracting the result of Colwell P from this result.

Acid Extractable (BSES)-P (9G2)

Air dried samples were extracted at the rate 1:200, with 0.005M H_2SO_4 on an end over end tumbler for 16 h. The orthophosphate level determined by an automated colorimetric by segmented flow analysis. This method is based on the extraction method developed by Kerr and von Stieglitz (1938) and Murphy and Riley (1962).

Adjusted Phosphorus Buffer Index (PBI) (9I2b)

Sample is equilibrated in an end-over-end shaker for 16 h in a 0.01M $CaCl_2.2H_2O$ solution containing 100 mgP/L with a soil/solution ratio of 1:10.

PBI is derived from the Freundlich equation for describing the relationship between total P sorbed and final solution P concentration (i.e. the P sorption curve). The total amount of P sorbed by the soil is calculated as the amount of previously sorbed P, plus the amount of freshly sorbed P. The previously sorbed P is estimated as the Colwell–P (Colwell 1963) status of the soil. Therefore, the 'total P sorbed' for use in calculating PBI is the addition of Colwell P to the amount of freshly sorbed P. The amount of freshly sorbed P in the soil (mg P/kg) is calculated as the difference between the initial amount of P added (=1000 mg P/kg at the specified soil/solution ratio of 1:10)

and the amount of P left in the equilibrating solution, expressed as mg P/kg air dry soil. Sample solution freshly sorbed P concentration is quantified by ICP-OES.

$$PBIadj = \frac{total\ P\ sorbed\ (mg/kg)}{residual\ P\ (mg/L)^{0.41}}$$

$$total\ sorbed\ P = Colwell\ P\ (mg/kg) + P\ added\ (mg/kg) - (residual\ P\ mg/L \times 10)$$

To simulate marine conditions, PBI was also carried out using the above procedure but with 0.5M NaCl replacing 0.01M $CaCl_2.2H_2O$ as the background solution.

Iron oxide extractable Phosphorus

Sediment (<10um) samples (1g) were weighed into 50mL graduated plastic tubes, 40mL 0.002M $CaCl_2$ solution added, and one strip of FeO-impregnated filter paper (2cm x 10cm) added to each tube. The tubes were capped and shaken end-over-end for 16-18 h overnight.

The following day, the suspension was allowed to settle, the strip removed and placed into another 50mL plastic tube. Following drying at 25^{o}C, 40mL 0.2M H_2SO_4 was added and the tube shaken for 2 h.

Inorganic P in the acid extract was determined by an automated colorimetric by segmented flow analysis based on the Murphy and Riley (1962) procedure.

Total Organic Carbon (6B3)

Following acid pre-treatment to remove carbonates, samples (<0.5mm) are analysed by Dumas high temperature combustion and infrared/thermal conductivity detection on a C-N Analyzer.

Particle size –

By hydrometer

Samples were disaggregated in an aqueous solution by means of chemical reagents (Calgon (sodium hexametaphosphate) and sodium hydroxide) and mechanical dispersion. Coarse and fine sand fractions are determined gravimetrically and the silt and clay fractions are determined using a hydrometer following Thorburn and Shaw (1987) and AS 1289.3.6.3 - 2003. Primary particle sizes are classified according to four ranges defined as follows:

Coarse sand	200-2000 (0.2-2.0 mm)
Fine sand	20-200 (0.02-0.2 mm)
Silt	2-20 (0.002-0.02 mm)
Clay	<0.002 mm

By laser diffraction

Samples were re-suspended in water and dispersant added prior to introduction into the Malvern Mastersizer 2000 and the particle size distribution determined after ultrasonic dissipation following AS 4863.1-2000 (ISO 13320-1:1999).

Exchangeable Cations

Samples with pH <7.5 (15A1)

Samples were extracted for one hour with mechanical shaking with aqueous 1M NH_4Cl at pH 7.0 (Loveday et al. 1972) at a soil:solution ratio of 1:20. There was no pre-treatment to remove soluble salts, no suppression of carbonate dissolution, nor correction for gypsum. A correction was applied for soluble sodium on the assumption that all chloride is present as sodium chloride where the EC of the soil >0.3 ds/m. Exchangeable cation concentrations were determined on the clarified extract using inductively coupled plasma optical emission spectrometry (ICP-OES) techniques.

Samples with pH >7.5 (15C1) and Cation Exchange Capacity (CEC) (15I3)

This method is preferred (Loveday et al. 1972) for precise estimates of exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and cation exchange capacity when the soil contains solid phase carbonate, and/or when soil pH >7.5.

Samples were leached with sixty per cent alcohol (ethanol) initially to remove soluble salts prior to extraction of cations by leaching with alcoholic 1M NH_4Cl at pH 8.5 at a soil to solution ratio of 1:20 (Tucker 1971). Exchangeable cations were determined in the leachate using inductively coupled plasma optical emission spectrometry (ICP-OES).

Cation exchange capacity was determined by colorimetric finish using a continuous flow analyser, after displacing ammonium (and chloride) with a solution of 15% KNO_3 plus 6% $Ca(NO_3)_2.4H_2O$. This K-Ca solution combination has a multiple capacity for effectively displacing ammonium from differing kinds of exchange sites (Loveday 1974).

Exchangeable Aluminium and Acidity (15G1)

Where the pH of the sample was <6.5 the exchangeable aluminium and acidity were determined by extracting air-dry sample with 1M KCl for 1 hr at 25°C at a soil/solution ratio of 1:10. Filtered solutions were analysed by titration with NaOH to pH 8.0 using an auto-titrator to determine Exchangeable Acidity (Al^{3+} + H^{+}). To determine the Exchangeable Aluminium an excess of KF was added to complex the aluminium and the resulting KOH is back titrated with HCl to pH 8.0.

Effective Cation Exchange Capacity (ECEC) (15J1)

The ECEC is calculated as the sum of the exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) from method 15A1 plus the exchange acidity (Al^{3+} + H^{+}) from 15G1.

pH (4A1), Electrical Conductivity (3A1) and Chloride (5A2a)

The pH and EC were determined on a 1:5 soil to water suspension after a 1 h shake then the chloride concentration determined colorimetrically on the clarified solution.

Acid digestible trace elements and heavy metals (17B2)

The sample was digested in a microwave under pressure in a mixture of nitric and hydrochloric acids (reverse aqua regia). The digestate is diluted, and particulate matter allowed to separate out or centrifuged. Trace elements and metals are determined by ICP-OES and ICP–MS.