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Contrasting sediment and nutrient export patterns across different hydrological regimes: A case study in the Great Barrier Reef catchments

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Abstract: Stream water quality is highly variable in both space and time. A sound understanding of spatial and temporal changes in stream water quality is of great importance for the effective prioritisation of funding for pollution mitigation measures adopted in different agricultural sectors. Concentration-discharge (C-Q) relationship is a useful tool to characterise and identify solute and particulate export patterns, which provides critical information on processes that control constituent source, mobilisation, transformation and delivery at the catchment scale. Previous studies revealed that this relationship is not only varying across different catchments due to heterogeneity in climate and landscapes, but also varying within each catchment across different temporal scales. For example, changes in hydrological regimes, e.g., baseflow-dominated seasonal flow vs. quick flow-dominated storm event flow, would result in contrasting export patterns for solutes and sediments. However, routinely available water quality monitoring records (e.g., monthly) might not be capable of capturing the detailed response of concentration to changes in discharge over storm events.

To overcome this, in this study, we used event-based water quality monitoring data set collected as part of the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program in the Great Barrier Reef (GBR) catchments. This study focuses on Total Suspended Solids (TSS) and dissolved Oxidized Nitrogen (NO_X) from 12 GBR catchments. We used a Bayesian modelling framework to investigate the difference in sediment and nitrate export patterns at various temporal scales, i.e., seasonal and event scales. Our main findings are:

- The export patterns at event scale are more consistent than those at seasonal scale. During storm events, TSS and NO_X in most of the catchments demonstrate a mobilisation pattern. In contrast, non-significant concentration-discharge relationship (*C*-*Q* slope) at seasonal scale, suggesting that the response of *C* is invariant to the temporal change in *Q* during baseflow periods.
- Catchment topography and land use are the two most influential groups of characteristics that control the export patterns for both TSS and NO_X, which are relevant to temporal changes in sources and transport pathways across different hydrological regimes.

The presented modelling results demonstrate that the export behaviours for solute and sediment are varying at different temporal scales, determined by heterogeneity in catchment landscape characteristics. These site-specific export patterns should be considered when prioritising future management strategies for the purpose of reducing loads of different constituents.

Keywords: *Concentration-discharge relationship, Great Barrier Reef catchments, Bayesian hierarchical modelling, hydrological regimes, sediment, nitrite*

1. INTRODUCTION

Over the past century, stream water quality has declined worldwide, in part due to significant expansion of agricultural land and urban areas, widespread use of fertilizers, and the increase in population (Basu et al., 2022). In Australia, the Great Barrier Reef has suffered a decline in water quality in recent decades, and one of the underlying causes of such decline is land-derived runoff. To manage and reduce the impact of runoff from the catchments on the Great Barrier Reef ecosystem, we need to obtain a better understanding of spatial and temporal variability of instream water quality and how it responses to hydrological and biogeochemical processes in a catchment. This requires a reliable model to integrate the monitoring data into both human and natural processes. To achieve this, the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program (P2R) has collected a range of water quality indicators across six Natural Resource Management (NRM) regions. The monitoring data from this program was used for calibrating and validating catchment water quality models, providing critical information to assess the health of the reef, as well as to identify areas where interventions are needed to improve its resilience. However, the conceptualization of processes within modelling framework relies on an adequate understanding of pollutant export patterns and spatiotemporal controls on water quality dynamics, which is still a challenge.

Investigations of the relationship between river chemistry concentration (*C*) and discharge (*Q*) (referred to as *C-Q* hereafter) have been widely used as a powerful means to characterize and identify solute and particulate export patterns, and what the driving factors that influence dynamics of this pattern at the catchment scale are (Guo et al., 2022; Lintern et al., 2021; Liu et al., 2022). Typically, a power-law function is employed to describe the general relationship between *C* and *Q* (i.e., $\boldsymbol{C = a\,Q^{b}}$), and slope term $\boldsymbol{b}$ can be obtained from the linear fit on *log(C)–log(Q)* scale. A positive *C-Q* slope (e.g., $\boldsymbol{b} > 0.2$) indicates a flushing/mobilisation export pattern, partially due to the transport-limited with sufficient substance storage. On the other hand, a negative *C-Q* slope (e.g., $\boldsymbol{b} < -0.2$) suggests a dilution pattern associated with source limitation. A close to zero slope could be interpreted as a constant export pattern that concentration is insensitive to discharge. *C-Q* relationship is particularly useful as it integrates information of catchment response to changes in disturbances, such as climate, land use and hydrology. Most of the *C-Q* studies investigated long-term routine water quality monitoring (e.g., at monthly frequency) data. For example, Minaudo et al. (2019) explored the difference in *C-Q* dynamics of nitrate and total phosphorus between short-term storm events and seasonal baseflow at 219 French catchments, using monthly water quality samples from 2008 to 2016. However, Fazekas et al. (2020) found that low-frequency water quality measurements may be inadequate to describe *C-Q* responses to different hydrological regimes (e.g., baseflow and stormflow conditions). Insufficient monitoring data on water at high frequencies, especially during storm events, could lead to an inadequate depiction of how export patterns change over time, as well as the variations in export patterns in different flow conditions/regimes. New advancements in the techniques used for monitoring water quality at high frequencies, such as the use of sensors, could offer a better understanding of the behaviour of substances in the water. However, the duration of the monitoring may be limited. The P2R program collected both intensive event-based water quality sampling during high-flow events as well as monthly sampling during low or baseflow (ambient) conditions. Therefore, investigation of event-based water quality monitoring data in GBR catchments would provide more insight into the solute and particulate export pattern and how this pattern varies across different temporal scales.

In this study, we investigated export patterns of fine sediment (TSS) and oxidized nitrogen (NO_X – a significant component of dissolved inorganic nitrogen) due to their potential impact on the marine environment, e.g., contributing to the crown-of-thorns starfish outbreak. Their export patterns across different hydrological regimes at 12 GBR catchments were investigated, using long-term (2006 to 2018) event-based (more dense observations over storm events) water quality monitoring data. The specific questions that we aim to address are:

1. Do the export patterns of TSS and NO_X vary across hydrological components?
2. What are key catchment characteristics that control the difference in export patterns of TSS and NO_X?

To address these questions, we examined the differences in export patterns during both quick (i.e., event scale) and slow (i.e., seasonal scale) flow periods using a Bayesian Hierarchical Modelling structure. In addition, different categories (e.g., topography, climate, land use, land cover, soil and hydrology) were investigated to associate with export patterns of TSS and NO_X using multivariate data analysis techniques. Our findings highlight the importance of understanding the dynamics of sediment and nutrient export across different hydrological regimes. Investigation of *C-Q* relationship allows assessing solute and particulate delivery mechanisms to streams, informing conceptualisation of water quality models, as well as effective management practices for protecting the water quality and health of the Great Barrier Reef.

2. METHOD

2.1. Study area and materials

We selected 12 water quality monitoring sites across 6 NRM regions within the P2R monitoring network (Figure 1), with contrasting climate, land use and hydrological conditions. The climate in these catchments varies from tropical to subtropical, with rainfall varying significantly across the regions. Coastal regions, including Cape York, Wet Tropics, and Mackay-Whitsunday experience more rainfall compared to inland regions (e.g., Burdekin, Fitzroy). Typically, coastal catchments have more concentrated urban settlements and intensive agricultural landscapes (e.g., sugarcane), while dry inland catchments are dominated by cattle grazing.

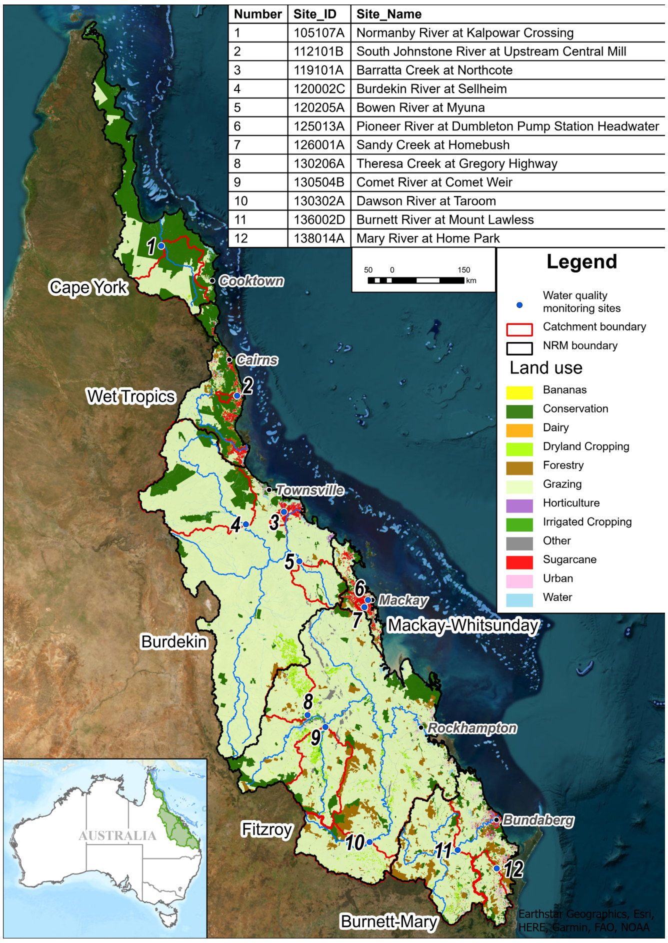

Figure 1. Locations and land use of 12 GBR water quality monitoring sites

Daily discharge records for the same period as the water quality data were extracted from the Water Monitoring Information Portal (https://water-monitoring.information.qld.gov.au/). Discharge data was further decomposed into slow and quick components, using *hydroEvents* package in *R* (Wasko and Guo, 2022). A baseflow recursive filter method was applied (with a filter coefficient of 0.975) to separate discharge into short-term quick flow (event-scale dynamics) and long-term slow flow (seasonal-scale dynamics). The resulting two hydrological components were used in following statistical analyses to investigate the temporal changes in *C-Q* relationships (more details in Sect 2.2), which addresses research question 1. Figure 2 shows an example of a hydrograph with TSS observations at gauge105107A, where the water quality dynamics for most events were well-captured.

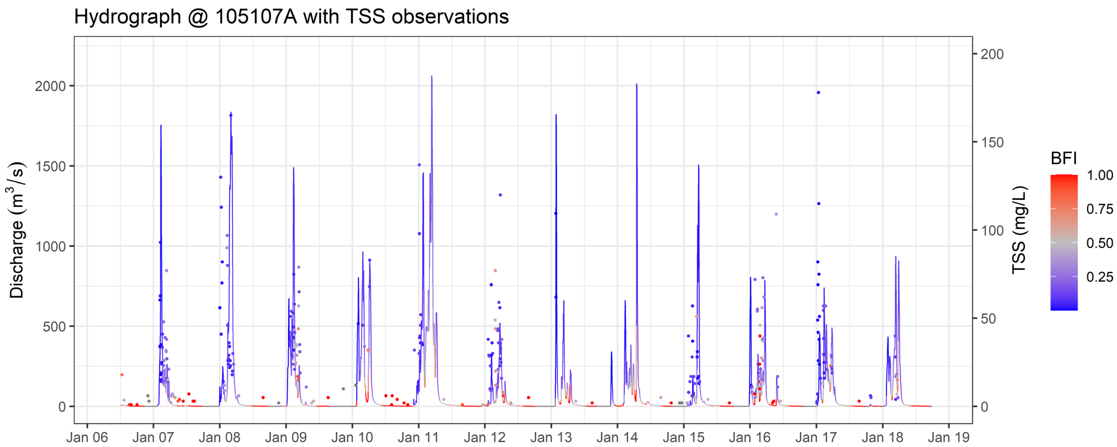

Figure 2. Hydrograph with TSS observations at gauge 105107A Normanby River at Kalpowar Crossing. The curve presents continuous daily discharge, with colour indicating contribution of baseflow, quantified by Baseflow index (BFI) (red – high BFI, and blue – low BFI). Points represent individual TSS observations, with colour indicating BFI for the day that the sample was taken.

We collated 36 catchment characteristics that are expected to influence the solute/sediment export patterns from publicly available datasets (Lintern et al., 2018). These characteristics can be categorized into six groups: topography, land cover, land use, soil, climate, and hydrology. Table 1 provides a detailed description of each group of catchment characteristics. The data sources include Geoscience Australia's National Environmental Attributes Database, Soil and Landscape Grid of Australia's National Soil Attribute Maps provided by the Terrestrial Ecosystem Research Network. More details on these catchment characteristics can be found in Liu et al. (2021a) and Liu et al. (2022). These catchment characteristics were used to associate the fitted *C-Q* relationship under different hydrological regimes, which addresses research question 2.

Table 1. Summary of 36 catchment characteristics and their abbreviations used in this paper

	Catchment characteristic &Abbreviation	Description		Catchment characteristic &Abbreviation	Description
Topography	Area	Catchment area (km^2)	**Land cover**	Grass	Catchment grasses cover (%)
	Elevation	Catchment average elevation (m)		Shrubs	Catchment shrub cover (%)
	UpstreamDist	Maximum flow path length (km)		Forest	Catchment forests cover (%)
	TWI	Topographic Wetness Index		Woodland	Catchment woodland cover (%)
	CatRelief	Catchment relief ratio		Bare	Catchment bare cover (%)
	StreamDensity	Stream density (km/km^2)	**Soil**	TN_soil	Mass fraction of total nitrogen in the 0–5 cm soil by weight (%)
	Slope	Mean channel slope (%)		TP_soil	Mass fraction of total phosphorus in the 0–5 cm soil by weight (%)
Climate	Temperature	Catchment average annual mean temperature (°C)		Sand	0–5 cm soil sand content (%)
	Rainfall	Catchment average annual rainfall (mm)		Clay	0–5 cm soil clay content (%)
	Radiation	Catchment average annual mean solar radiation (MJ/m^2/day)		PAWC	plant available water capacity (mm)
Land use	Conservation	Catchment that is conservation land (%)		Ksat	Catchment average Saturated Hydraulic Conductivity
	Sugar	Catchment that is sugar cane (%)		Carbonate	Areal proportion of catchment comprising carbonate sedimentary rocks (%)
	Grazing	Catchment that is grazing (%)		Unconsolidated	Catchment underlain by regolith (%)
	Horticulture	Catchment that is horticulture land (%)	**Hydrology**	Runoff	Catchment annual average runoff (mm)
	Forestry	Catchment that is forestry use (%)		R-B Flashiness	Richard-Baker Flashiness Index
	Irrigated	Catchment that is irrigated land (%)		BFI	Catchment annual average Baseflow Index
	Fertiliser	Land where fertiliser is likely to be used (%)		RunoffCV	Coefficient of variation of annual surface runoff
	Pesticide	Land where herbicides/pesticides is likely to be used (%)		Perenniality	Contribution to mean annual discharge by the six driest months of the year (%)

2.2. Statistical analyses

To investigate the export patterns under different flow regimes, we used a Bayesian Hierarchical Model (BHM) that allows the effect of predictor variables varying across different groups of observations to be quantified. This is achieved by assuming that the model parameters are drawn from a common distribution, which allows for 'borrowing strength' across groups (Guo et al., 2020; Liu et al., 2021b, 2020). The different slopes for quick/slow flow can be backed up by a similar model structure in a previous study by Minaudo et al. (2019). By assuming that the effects of the group-level predictors and observations within each group are exchangeable, we can obtain a more precise estimate of the overall effect of hydrological components (i.e., slow and quick flow) through information sharing. The amount of borrowing strength can vary across different sites, making BHM a suitable tool for dealing with unbalanced sample sizes and heterogeneity effects of hydrological regime on particulate and solute export patterns. The proposed general modelling framework is as follows:

$$\log(C_{i,j}) \sim N(\mu_{i,j}, \sigma) \qquad (1)$$

$$\mu_{i,j} = \beta_{0,i} + \beta_{slow,i} \log(Q_{slow,i,j}) + \beta_{quick,i} \log(Q_{quick,i,j}) \qquad (2)$$

where, *log* ($C_{i,j}$) – the logarithm (with a base of 10) of j^{th} observed concentration TSS or NO_X in the i^{th} catchment, following a normal distribution (~*N*), with mean of $\mu_{i,j}$ and standard deviation of σ; $\mu_{i,j}$ is further described as a linear additive function of slow (Q_{slow}) and quick flow (Q_{quick}); $\beta_{0,i}$, $\beta_{slow,i}$ and $\beta_{quick,i}$ are regression intercept, coefficients for slow flow and quick flow for i^{th} catchment, respectively. We assumed that the parameters were independent and non-informative prior distributions were assigned, then updated using

Markov chain Monte Carlo (MCMC) along with Gibbs sampling to obtain the posterior distribution of parameters and simulations. The BHM framework was implemented using *runjags R* package (Denwood, 2016).

We first assessed model performance using Nash-Sutcliffe efficiency (NSE). Then the posterior distributions of $\beta_{slow,i}$ and $\beta_{quick,i}$ were evaluated to investigate differences and/or similarity in the export patterns under different hydrological regimes. In addition, multiple factor analysis (MFA), accounting for different variabilities among the groups of variables, was used to integrate all the groups of catchment characteristics into a common space to investigate their associations with solute and particulate export patterns (i.e., fitted median $\beta_{slow,i}$ and $\beta_{quick,i}$).

3. RESULTS AND DISCUSSION

3.1. BHM modelling performance

The BHM modelling framework can explain moderate level of variability in observed TSS and NOx, with an overall NSE of 0.44 and 0.42 (Figure 3), respectively. At an individual site level, the NSE ranges from 0.10 to 0.62 for TSS, and 0.10 to 0.41 for NO_X. The potential causes for sites with low NSE could be attributed to: (1) a number of observations were at detection limits (i.e., evident with the vertical 'categorical' behaviour towards the lower end of the observations in the Figure 3); (2) more detailed biogeochemical processes were not captured in this simplified statistical modelling framework; and (3) *C-Q* relationship might exhibit temporal variability within storm events due to solute and sediment hysteresis behaviour (e.g., contrasting *C-Q* slope over rising and falling limbs of the hydrograph). However, the overall model performance was still satisfactory, given that there were 5605 and 5385 TSS and NO_X observations across all 12 sites.

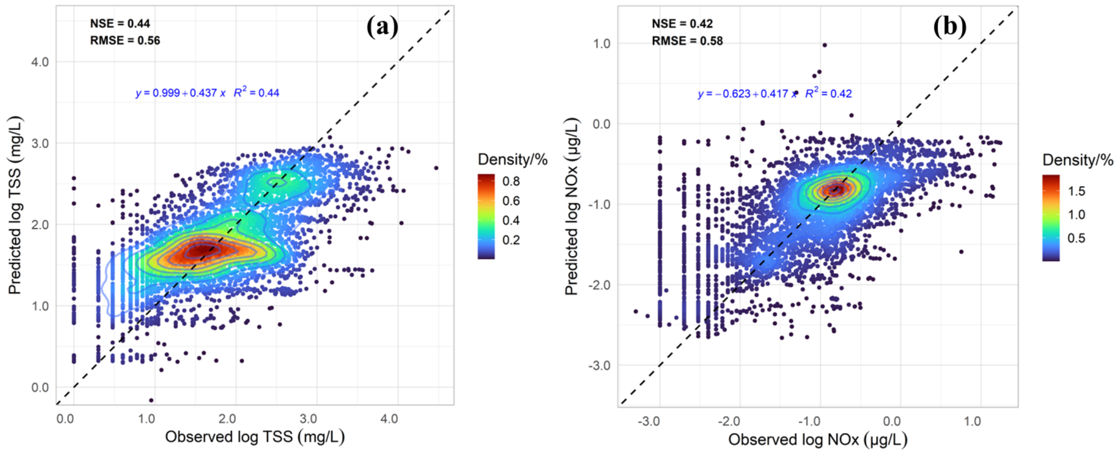

Figure 3. Scatter plots of observed and predicted concentrations for: (a) TSS; and (b) NO_X. Different colours indicate density of the data. *Note*: variables are transformed using logarithm with a base of 10 as per Equation 1.

3.2. Sediment and nitrate export patterns at seasonal and event scales

The assessment of the marginal posterior distributions of fitted β_{slow} and β_{quick} indicated that there were different export patterns for both TSS and NO_X (Figure 4) at both seasonal (effect of slow flow component - blue bar in Figure 4) and event (effect of quick flow component - red bar in Figure 4) scales, while the magnitude of difference varies across sites. Overall, the export patterns at event scale for both constituents were consistent - with most sites exhibited a positive *C-Q* slope at storm event scale, suggesting mobilisation pattern of both sediment and nitrate. It is likely to be attributed to sufficient supply of fine sediment through hillslope, gully, and streambank erosion processes. In addition, the interaction between surface and subsurface flow, as well as the large store of nitrate at the near surface soil profile, which potentially facilitates the transportation of nitrate from below root zone/soil to streams during storm events.

The seasonal scale *C-Q* relationship exhibits greater variability in comparison to the export pattern at event scale. This finding contradicts the results reported by Minaudo et al. (2019). With some sites showing non-significant (i.e., $\beta_{slow} \approx 0$) pattern, suggesting the response of *C* is insensitive to the temporal change in *Q*. This is also supported by the fact that majority of the pollutant loads discharging to the GBR lagoon is delivered during high flow wet periods. In addition, we found that NO_X at 119101A (Barratta Creek at Northcote) in Burdekin shows a strong anti-covariation seasonal export pattern. This site is operating under full irrigation on sugarcane, indicating that changes in nutrient transport pathways may lead to different response behaviours between baseflow and nitrate concentrations at this site.

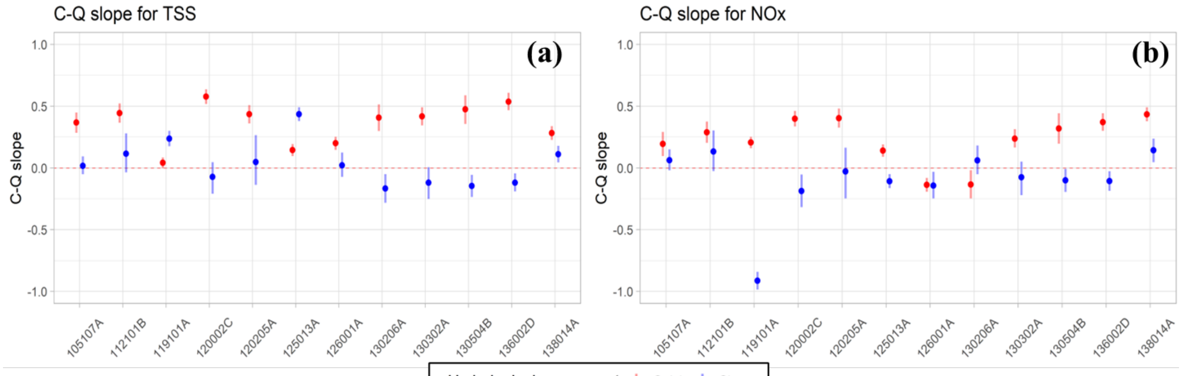

Figure 4. Posterior distribution of β_{slow} and β_{quick} for: (a) TSS; and (b) NO_X, for individual sites. Different colours indicate the coefficients of slow (red) and quick (blue) flow. The dots and bars represent median and 95% credible interval, respectively.

The multiple factor analysis (MFA) result (Figure 5 (a)) indicates that catchment topography has the largest association with fitted *C-Q* slopes for both TSS and NO_X, in line with findings in Liu et al. (2022). For TSS, the seasonal scale export pattern (slow flow *C-Q* slopes) is influenced by a few topographic characteristics, e.g., stream density (Pearson's ρ = 0.65). High stream density results in a more developed flow pathway, increasing the export of sediments through subsurface (e.g., sustained baseflow). In terms of NO_X, TWI (topographic wetness index, which quantifies the degrees of accumulating water in catchments, representing the topographic controls on hydrological processes) shows a strong negative relationship with its export pattern (ρ = -0.65) at seasonal scale (Figure 5 (c)), which can be attributed to negative cross-correlation between TWI and slope (ρ = -0.88), as flat areas typically associated with higher groundwater table and higher contribution of groundwater to streams.

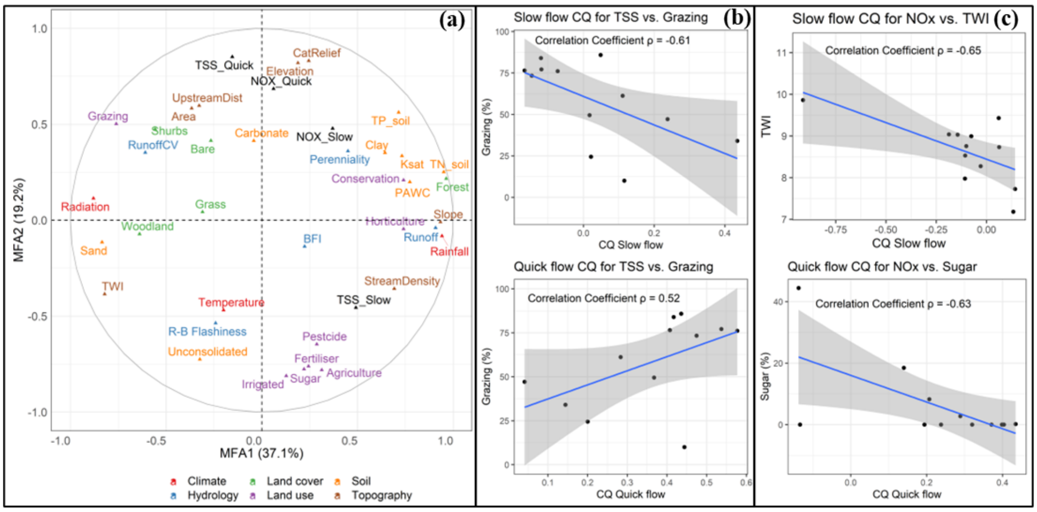

Figure 5. (a) MFA biplot of catchment characteristics associated with fitted *C-Q* slopes for different hydrological components, with different colour representing different groups of catchment characteristics; (b) relationship between TSS *C-Q* slope for slow flow vs. grazing (upper panel) and *C-Q* slope for quick flow vs grazing (lower panel), respectively; and (c) relationship between NO_X *C-Q* slope for slow flow vs. TWI (upper panel) and NO_X *C-Q* slope for quick flow sugar (lower panel), respectively.

Land use was also identified as the most important factor. Grazing shows contrasting effects on seasonal and event scale export patterns for TSS (Figure 5 (b)). Grazed catchments could experience anti-covariation export patterns, compared with catchments with less grazed area (covariation between *C* and *Q*), indicating grazing activity, interacting with other catchment characteristics (e.g., rainfall), might alter the long-term sediment mobilisation and transport pathways (Liu et al., 2018). The opposite effect of grazing on event scale export pattern, suggests that grazing activities increase the sources of sediment and degree of mobilisation of sediment over short-term storm events. In addition, the negative correlation between event scale NO_X export pattern and sugarcane land use indicates that for catchments with large proportions being used for sugarcane farms, less nitrate can be transported during storm events.

4. CONCLUSIONS AND RECOMMENDATIONS

In this study, we used a Bayesian modelling approach to investigate the difference in sediment and nitrate export patterns across temporal scales, i.e., seasonal and event scales. We found that the event scale export patterns are more consistent compared with seasonal scale export patterns. TSS and NOX at most of the sites show a mobilisation pattern during storm events. The multivariate data analysis indicated that catchment topography and land use were the two most significant factors that control the export patterns at both seasonal and event scales. Future applications of modelling structure developed in the study to a broader GBR catchments could be useful for: 1) classification of catchments based on differences in export patterns across temporal scales; and 2) gaining a better understanding of the underlying catchment controls that determine the temporal changes in export pattern.

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