Synthesizing the impacts of baseflow contribution on C-Q relationships across Australia using a Bayesian Hierarchical Model

Danlu Guo[1], Camille Minaudo[2], Anna Lintern[3], Ulrike Bende-~~Michl[4]~~Michl[1], Shuci Liu[1], Kefeng ~~Zhang[5]~~Zhang[4], Clément ~~Duvert[6,7]~~Duvert[5,6]

[1] Department of Infrastructure Engineering, University of Melbourne, Victoria, 3010, Australia
[2] EPFL, Physics of Aquatic Systems Laboratory, Margaretha Kamprad Chair, Lausanne, Switzerland
[3] Department of Civil Engineering, Monash University, Victoria, 3800, Australia

[4] ~~Bureau of Meteorology, 2601 Canberra, Australia~~

[5] Water Research Centre, School of Civil and Environmental Engineering, UNSW Sydney, ~~High St, Kensington,~~ NSW 2052, Australia
[6~~5~~] Research Institute for the Environment and Livelihoods, Charles Darwin University, Darwin, NT, Australia
[7~~6~~] National Centre for Groundwater Research and Training (NCGRT), Australia

~~*Corresponding author's email address: anna.lintern@monash.edu~~

Correspondence to: Danlu Guo (~~danlu.guo@unimelb.edu.au~~danlu.guo@unimelb.edu.au)

Formatted: Font: 9 pt, Font color: Black

Abstract. ~~The spatial and temporal variation of~~Understanding concentration-discharge (C-Q) relationships can inform catchment solute and particulate export processes. Previous studies have shown that the extent to which baseflow contributes to streamflow can affect C-Q relationships in some catchments. However, ~~these~~ the current understanding on the effects of baseflow contribution in shaping the C-Q patterns ~~have not yet been investigated~~is largely derived from temperate catchments. As such, we still lack quantitative understanding of these effects across ~~large spatial scales. To address this, the~~a wide range of climates (e.g., arid, tropical and subtropical). The study aims to assess how baseflow contributions, as defined by the median ~~catchment~~and the range of daily baseflow ~~index~~indices within individual catchments (*BFI_m* and *BFI_range*, respectively), influence C-Q slopes across 157 catchments in Australia spanning five climate zones. This study focuses on six water quality variables: electrical conductivity (EC), total phosphorus (TP), soluble reactive phosphorus (SRP), total suspended solids (TSS), the sum of nitrate~~-~~ and nitrite (NO_x) and total nitrogen (TN). The impact of baseflow ~~contribution~~contributions is explored with a novel Bayesian hierarchical model.

~~We found that *BFI_m* has a strong impact on C-Q slopes. C-Q slopes are largely positive for nutrient species (NOx, TN, SRP and TP) and are steeper in catchments with higher *BFI_m* across all climate zones (for TN, SRP and TP). On the other hand, we also found a generally higher variation in instantaneous BFI for catchments with high *BFI_m*. Thus, the steeper C-Q slopes found in catchments with high *BFI_m* may be a result of a larger variation in water sources and flow pathways between low (baseflow-dominated) and high (quickflow-dominated) flow conditions. In contrast, catchments with low *BFI_m* may have more homogeneous flow pathways at both low and high flows, resulting in less variable concentrations and thus a flatter C-Q slope. Our model can explain over half of the observed variability in concentration of TSS, EC and P species across all catchments (93% for EC, 63% for TP, 63% for SRP, and 60% for TSS), while being able to predict C-Q slopes across space by *BFI_m*. This indicates that our parsimonious model has potential for predicting the C-Q slopes for catchments in different climate zones, and thus improving the predictive capacity for water quality across Australia.~~

For sediments and nutrient species (TSS, NO_x, TN and TP), we generally see largely positive C-Q slopes, which suggest a dominance of mobilisation export patterns. Further, for TSS, NO_x and TP we see stronger mobilisation (steeper positive C-Q slopes) in catchments with higher values in both the *BFI_m* and *BFI_range*, as these two metrics are positively correlated for most catchments. The enhanced mobilisation in catchments with higher *BFI_m* or *BFI_range* is likely due to the more variable flow pathways that occur in catchments with higher baseflow contributions. These variable flow pathways can lead to higher concentration gradients between low flows and high flows, where the former is generally dominated by groundwater/slow subsurface flow while the latter by surface water sources, respectively. This result highlights the crucial role of flow pathways in determining catchment exports of solutes and particulates. Our study also demonstrates the need for further studies on how the temporal variations of flow regimes and baseflow contributions influence flow pathways and the potential impacts of these flow pathways on catchment C-Q relationships.

Formatted: Font: 9 pt, Font color: Black

1 Introduction

Understanding the causes of spatiotemporal variability in riverine chemistry is critical to support water quality management strategies for both human and environmental end-uses. The relationship between the river chemistry and streamflow (concentration-discharge, or C-Q relationship) often shows distinct patterns that are specific to water quality variables and catchments. These C-Q patterns are determined by (i) the spatial distribution of constituent sources within ~~the catchment~~individual catchments; and (ii) the interplay between the biogeochemical and hydrological processes, which controls constituent mobilisation and transport through ~~the~~each catchment (Ebeling et al., 2021; Godsey et al., 2019; Musolff et al., 2015). The C-Q relationship therefore tells us about the key catchment processes controlling river water quality. As such, the C-Q relationship can help ~~informing~~inform catchment management and mitigation strategies to improve catchment water quality (Dupas et al., 2019; Moatar et al., 2020).

However, it is challenging to identify the key catchment processes from analysing C-Q relationships, due to the high variability in water quality across both space and time. First, water chemistry and streamflow characteristics can vary significantly across multiple spatial scales, from small headwater catchments (where key processes are easier to identify) (Dupas et al., 2021; Jensen et al., 2019; McGuire et al., 2014) to basin and continental scales (e.g., Dupas et al., 2019; Ebeling et al., 2021~~; Heiner M. et al. under review).~~). Many previous studies have assessed the spatial variations in C-Q relationships for nutrients, carbon and geogenic water quality variables~~, which identified land use and management, lithology, and topography as~~. These studies highlighted a number of critical drivers for these spatial variations, such as land use, land management, lithology and topography (e.g., Ebeling et al., 2021; Minaudo et al., 2019). Second, high-frequency water quality monitoring studies have shown high temporal variability in water chemistry (e.g., Kirchner et al., 2004; Rode et al., 2016). Besides variation in concentrations, recent high-frequency monitoring also highlighted the high variability of C-Q relationships over time~~ and especially between runoff events; these~~. These temporal changes in C-Q relationships are driven by a series of mechanisms such as chemical build-up and flushing under varying flow magnitudes, and also by contrasting baseflow contributions during different stages of ~~runoff events~~the hydrograph (Bende-Michl et al., 2013; Knapp et al., 2020; Musolff ~~A:~~ et al~~.;~~., 2021; Rusjan et al., 2008; Tunqui Neira et al., 2020).

~~In the existing studies that explore the variation of C-Q relationships, hydrological~~Hydrological characteristics of catchments have been highlighted as ~~a~~ key influencing ~~factor~~factors of the C-Q relationships of a catchment, as ~~it~~the catchment hydrology defines the flow pathways and magnitudes that are critical to the transport processes (Tunqui Neira et al., 2020a, 2020b). ~~Several studies have highlighted~~Prior studies have explored the links between C-Q relationships and baseflow index (BFI) and similar hydrological metrics at an interannual scale (e.g., Ebeling et al., 2021; Moatar et al., 2017; Musolff et al., 2015) or at the scale of storm events (e.g., Knapp et al., 2020; Minaudo et al., 2019; Musolff et al., 2021). Across both long and short timescales, a consistent finding is that, within a particular catchment, the C-Q relationship (and thus export behaviour) is

Formatted: Font: 9 pt, Font color: Black

dependent on whether streamflow is dominated by baseflow or quickflow, i.e., the baseflow contribution to total flow (Gorski & Zimmer, 2021; Knapp et al., 2020; Minaudo et al., 2019). ~~However, there is little understanding~~These studies also identified baseflow contribution as a key driver of ~~how the overall~~the variation in C-Q relationships across catchments (Musolff et al., 2015; Moatar et al., 2017). For example, Knapp et al. (2020) found that for solutes that are partly derived from atmospheric inputs, such as nitrate and chloride, mobilisation behaviours (i.e., positive C-Q slopes) often occur during events with drier antecedent conditions. For nitrate, baseflow contributions can further affect the C-Q relationships via changing the connectivity between surface flow and groundwater (Minaudo et al., 2019). Baseflow variation also affects the capacity of nutrient removal via changing the relative importance of hydrological and biogeochemical processes (Moatar et al., 2017). Further, the variation in the baseflow contribution of a catchment ~~impacts the catchment's C-Q relationship, and thus the catchment's export regime. Further, most existing studies that explored~~ is also a key feature that can be linked to the shift between different dominant flow paths during low- and high-flow (e.g., von Freyberg et al., 2018), leading to contrasting sources and mobilisation behaviours for solutes and particulates. Although a substantial body of knowledge has been established on the impact of baseflow ~~contribution~~contributions on C-Q relationships, the existing studies have largely focused on catchments in temperate climates in Europe and North America (~~e.g.,~~ Knapp et al., 2020; Gorski & Zimmer, 2021; Minaudo et al., 2019; Musolff et al., 2015). ~~This leads to~~The narrow range of climate conditions explored so far implies a potential limitation in transferring and systematically comparing new findings to other climate zones and other parts of the world~~.~~, because climate is proven a key control of the hydrological regime, especially regarding the baseflow contribution and flow paths of individual catchments (Beck et al., 2013; von Freyberg et al., 2018).

The current knowledge gap in understanding catchment export regimes for regions other than Europe and North America was partially addressed in Lintern et al. (~~in review) and Liu et al. (in preparation~~2021), which ~~explored C-Q metrics over a range of climate zones in Australia. Both studies highlighted consistencies in C-Q patterns across contrasting climates for individual~~ focused on differences in water quality ~~variables~~status and ~~suggested that~~ the ~~inherent properties of each water quality variable determine its~~ C-Q relationships~~. However, the role of~~ across different ~~baseflow contributions on C-Q~~ climate zones in the Australian continent. One remaining question that Lintern et al. (2021) highlighted is our lack of understanding of the substantial variations in C-Q relationships ~~has not yet been examined.~~ within each climate zone.

This study aims to assess the impact of catchment baseflow ~~contribution~~contributions on the C-Q relationships of sediment, nutrients and ~~salts~~electrical conductivity across ~~a large number of~~ catchments within different climate zones in Australia. ~~We hypothesise that catchments located in different climate zones would show very different ranges and distributions of~~ Our research questions are:

1. How well can we explain the spatial variation in C-Q slopes across Australian catchments with baseflow contributions~~, leading to contrasted responses in terms of catchment export patterns, as represented by~~?

4

Formatted: Font: 9 pt, Font color: Black

2. How do baseflow contributions influence C-Q slopes~~. With this analysis~~ within and across climate zones?

For the first question, we ~~also~~ hypothesise that ~~the~~ a substantial proportion of spatial variation in C-Q slopes in Australian ~~catchments~~catchment can be ~~predicted across space by~~ explained by baseflow contribution. Based on the above-mentioned literature, we hypothesise that the median baseflow contribution~~. We test these~~ of a catchment is a key control of the C-Q slope of that catchment. We also hypothesise that the range of variation in the baseflow contributions of a catchment is a key control of the C-Q slope of that catchment, because a high (low) range of variation likely reflects the diversity (uniformity) of flow pathways contributing to streamflow, which may influence the activation and mobilisation of different chemical species.

Since climate strongly influences the hydrological regimes of catchments, our hypothesis for the second research question is that baseflow contributions will affect C-Q relationships differently in different climate zones. We answer our research questions and test our hypotheses with a Bayesian hierarchical ~~modelling~~model (BHM) (Gelman et al., 2013), which is an integrated framework that enables sharing information across catchments to strengthen the statistical power of explaining variation in individual catchments. The model is a powerful approach~~, which will i) add new understanding to the sources and export patterns of~~ to capture water quality ~~variables; ii) improve the predictive capacity of~~ variability across catchments of varying conditions and record lengths, which is the case for Australian water quality ~~variables by better prediction of C-Q relationships over space.~~data (Guo et al., 2019, 2020; Liu et al., 2021). We use a subset of the grand dataset that Lintern et al. (2021) used, which enables us to focus on representative catchments with water quality records captured under a wider range of flow conditions. As such, by analysing the impacts of baseflow contributions on C-Q relationships, this study will i) explain the variations in C-Q relationships within individual climate zones; ii) broaden the existing knowledge of how baseflow contribution impacts C-Q relationships to a wider range of climate conditions, and thus infer key constituent transport pathways in different climate zones.

2 Method

2.1 Data and study catchments

2.1.1 Water quality and flow data

This study relies on water quality and streamflow data collected across Australia by seven state agencies. These include: the Department of Land, Water and Planning (VIC DELWP, Victoria); WaterNSW (New South Wales); Department of Resources and Department of Environment and Science (QLD DNRME, Queensland); Department for Water and Environment (SA DEW, South Australia); Department of Water and Environmental Regulation (WA DER, Western Australia); Department of Primary Industries, Parks, Water and Environment (TAS DPIPWE, Tasmania) and Department of Environment, Parks and Water Security (NT DEPWS, Northern Territory).

Formatted: Font: 9 pt, Font color: Black

All available water quality data were obtained from all seven state agencies in late 2019 and collated into a single national-scale database (see more details in Lintern et al., ~~in review~~2021). Quality control of the data was performed using quality codes, flags and detection limits provided by individual state agencies~~.~~ (as detailed in Table S1, Supplementary Materials). The dataset consists of a mixture of grab samples and high-frequency (continuously measured) water quality data~~; a~~. A daily average is taken if more than one water quality sample was collected ~~for~~on any day at any site~~.~~ – see the percentage of records where more than one samples were taken in one day individual catchments in Table S2 (Supplementary Materials). This is because that streamflow in Australia is largely recorded at a daily timestep, which limits our ability to analyse all high-frequency water quality. This study focuses on six water quality variables: total suspended solids (TSS), total phosphorus (TP), soluble reactive phosphorus (SRP), total nitrogen (TN), the sum of nitrate~~-~~ and nitrite (NO_x) and electrical conductivity (EC). These six variables have been included because they are of key concern for Australian riverine water quality and are well monitored across Australia both spatially and temporally, as illustrated in Lintern et al. (~~in review~~2021).

For each monitoring site for the abovementioned six variables, we also obtained the corresponding available daily streamflow data~~. These daily streamflow data were obtained~~ from the same seven state agencies as listed above. At each site, any missing or erroneous data were identified by the quality code (~~as detailed in~~ Table S1, Supplementary Materials) and removed for subsequent analyses. The daily streamflow data generally had good quality, with a ~~< 5%~~ median ~~percentage~~ of < 5% missing or erroneous data for individual water quality variables across individual monitoring sites (Table S2, Supplementary Materials). These gaps and low-quality samples in the daily streamflow records were then filled in using streamflow modelled by the Australian Bureau of Meteorology (BoM)'s operational landscape water balance model (AWRA-L), which simulates daily streamflow across Australia (Frost et al., 2016).

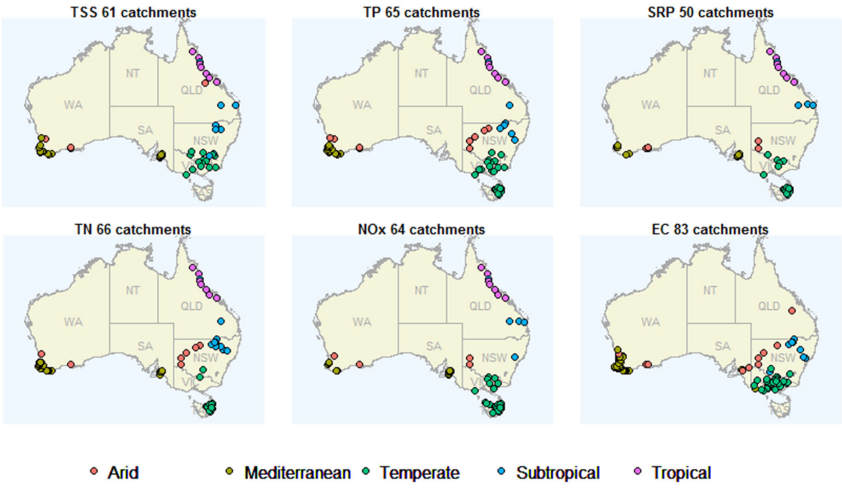
For this study, we focused only on monitoring sites (catchments) with water quality and flow data that satisfy the following criteria:

1) Having over 50 pairs of corresponding concentration and flow data points; this ~~is to ensure~~ensures that the C-Q relationships observed are ~~unaffected by~~more robust against outliers (Lintern et al., ~~in review~~2021).
2) Having water quality time-series that ~~spans~~span at least 3 years; this ensures that a wide range of water quality and flow conditions are captured (e.g., across different seasons, high and low flows).
3) At least 75% of the range of flow quantiles (with unconstrained bounds e.g., 5 to 80%, 10 to 85%) is covered by water quality samples; this ensures that C-Q relationships are not biased by samples obtained at only high or low flows for individual catchments.

~~We~~We performed the above catchment selection for each water quality variable, and found a total of 157 sites (catchments~~) that met the above criteria across all the six water quality variables.~~). As the monitored water quality variables vary between catchments, there ~~were~~are 50-83 catchments used to investigate each variable. These catchments are distributed across five

Formatted: Font: 9 pt, Font color: Black

main Australian climate zones as defined by Lintern et al. (~~in review~~2021): arid, Mediterranean, temperate, subtropical and tropical (Figure 1). A summary of the temporal coverage of water quality and flow data is provided in Figure S1 in the Supplementary Materials. Water quality data generally cover the full range of flow quantiles of individual catchments (Figure S2, Supplementary Materials). Some sites are biased towards high flows, which is likely due to i) monitoring priority for high flow events to better represent export loads; ii) practical constraints to sample low flows in intermittent rivers and ephemeral streams.



Formatted: Font: 9 pt, Font color: Black

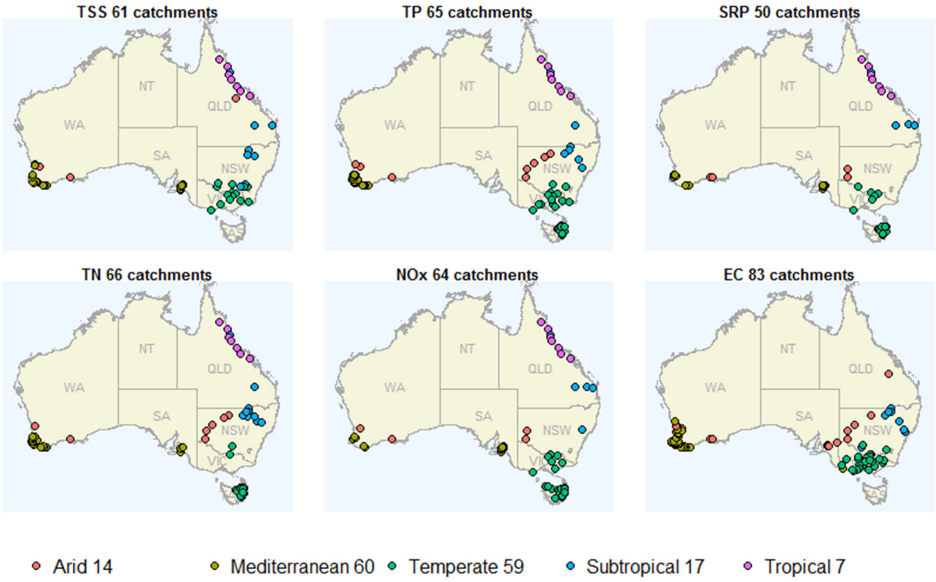


Figure 1. Catchments included in the study for each water quality variable (total number of catchments shown in panel titles). The colours denote five key climate zones in Australia. States and territories of Australia on the map are: New South Wales - NSW, Queensland - QLD, South Australia - SA, Tasmania - TAS, Victoria -VIC, Western Australia -WA, and Northern Territory - NT. The number of catchments across all six water quality variables for each climate zone is specified in the legend.

2.1.2 Representing catchment baseflow contribution with baseflow index

~~To represent the overall~~ We summarise catchment baseflow contribution ~~of baseflow to total streamflow in each catchment and explore how this impacts the C-Q relationships across space, we used catchment~~ with the baseflow index (BFI~~). BFI~~), which represents the proportion of discharge that occurs as baseflow (Eckhardt, 2008; Lyne & Hollick, 1979; Nathan & McMahon, 1990; Zhang et al., ~~2017). We computed the catchment median BFI, *BFI_m*, based on daily BFIs derived from all flow records for each of the 157 catchments.~~2017). The daily BFIs were estimated using a Lynne-Hollick baseflow filter with Alpha = 0.98 and a burn-in period of 30 days at both ends of the time series, as recommended for the Murray-Darling Basin in ~~the~~ south-eastern Australia (Ladson et al., ~~2013), within which a large number of the study catchments are located. We expect that the *BFI_m* can represent the typical flow regime at a catchment level and differentiate between catchments with higher and lower baseflow contributions. In this way, we expect catchments with contrasting *BFI_m* to be dominated~~

Formatted: Font: 9 pt, Font color: Black

~~differently by surface flow and groundwater sources of water chemistry. Besides, *BFI_m*, we also computed the 10th and 90th percentiles of daily BFIs (*BFI_l*, *BFI_h*, respectively) for individual catchments to explore how the distribution of BFI of each catchment can affect C-Q relationships.~~2013), within which a large number of the study catchments are located.

We aim to test our hypothesis that the median and the range of variation in catchment baseflow contributions are key controls of the C-Q slopes, based on previous literature. Therefore, for each of the 157 catchments we used two metrics of the daily BFI, namely *BFI_m* and *BFI_range*. *BFI_m* takes the median of all daily BFIs, which represents the overall baseflow contribution of the catchment. *BFI_range* is the difference between the 10th and 90th percentiles of daily BFIs (*BFI_10th* and *BFI_90th*). These quantile-based metrics were preferred over the mean and standard deviation as they are more robust against outliers.

2.2 Modelling the impacts of catchment baseflow contribution on ~~concentration~~C-Q slopes

We developed a Bayesian hierarchical model (BHM) to explore the effect of catchment ~~BFI~~baseflow contributions on C-Q ~~slope~~slopes. The key reason for choosing this model is the high heterogeneity in the national C-Q dataset in both the record period and the representation of individual climate zones, as illustrated in Section 2.1.1. BHM is ~~advantageous in its~~effective in handling data-limited situations via its 'information sharing' or 'borrowing power' across space (Gelman et al., 2013; Webb & King, 2009), which ~~is~~has been shown to be highly effective ~~to explain~~in explaining variability in spatial-temporal data under data-limited situations. ~~Bayesian~~This has been highlighted in several recent studies in modelling ~~is also effective for incorporating~~water quality over large regions in Australia (Guo et al., 2019, 2020; Liu et al., 2021). Another advantage of BHM is the ability to account for uncertainty, which is ~~necessary when~~especially important for analysing water quality data, as ~~they~~these data are often associated with high uncertainty due to ~~incomplete~~sparse sampling of ~~its~~the natural variability of chemical species in river flow (Guo et al., 2020; Liu et al., 2021).

The model considered a classic C-Q relationship for any site s at any time-step t (Eqn. 1), where β_s specifies the C-Q slope for a catchment (Godsey et al., 2009):

$$\cancel{\log(C_{s,t}) = \alpha_s} \log\left(C_{s,t}\right) = \alpha_s + \beta_s \cancel{\log} \log\left(Q_{s,t}\right) \quad (1)$$

Our model ~~used~~is based on such a ~~modified version of Eqn. 1~~single C-Q relationship at each catchment. However, our model enables the slope term (β_s) for individual catchments to change according to their baseflow contributions. This model conceptualisation is based on previous literature on the effects of baseflow contribution on C-Q slopes within individual catchments (Gorski & Zimmer, 2021; Minaudo et al., 2019~~).~~), while aiming to further explore the impact of baseflow contributions on C-Q slopes across multiple catchments. We assume that for each water quality variable, the C-Q slopes of all catchments ~~are following a normal distribution with~~ have a 'grand mean', β_0. Then the variation of C-Q slopes between catchments, away from β_0, ~~are~~is explained by changes in the catchment ~~BFI~~baseflow contribution. The use of a mean C-Q

Formatted: Font: 9 pt, Font color: Black

slope here is based on our preceding study across Australian catchments, which suggested that for each water quality variable, export patterns (– as represented by C-Q slopes) – did not differ between climate zones (Lintern et al., in review). The model conceptualization is illustrated in Figure 2 with observed flow time series from two catchments and calculated baseflow (panel a) and median BFI (*BFI_m*) (panel b); panel c) illustrates the2021). Our model conceptualisation also assumes that the catchment baseflow contribution is the only controlling variable of the spatial variation of C-Q slopes, enabling us to understand how well the C-Q slopes can be explained solely by differences in baseflow contributions across catchments. We chose to investigate the effects of baseflow contributions for individual climate zones separately to identify any statistically significant differences of these impacts between climate zones. If there is no significant difference between climate zones, the model is also capable of indicating this – as would be shown with similar, undistinguishable modelled catchment C-Q slope with *BFI_m* considered as the main predictor. Two alternative model versions were also developed to incorporate the impacts of *BFI_l* and *BFI_h* in the same way.

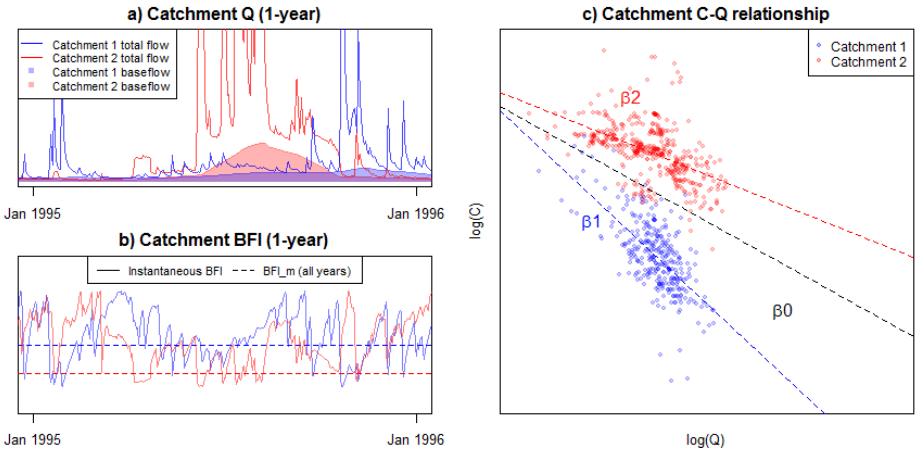


Figure 2. Illustration of conceptualization of the BFI-based C-Qeffects of baseflow contribution for individual climate zones. Thus, our BHM incorporates different models with two catchments, with the catchment median BFI (*BFI_m*) as the main predictor of C-Q slope. a) flow time-series with shaded regions showing the baseflow contribution; b) BFI time-series and the corresponding *BFI_m*; and c) catchment C-Q relationships, in which the shift of C-Q slope of each catchment (β_1, β_2) away from the grand mean β_0 is determined by *BFI_m*. Both time-series for the instantaneous flow and BFI (a) and b)) are only shown for for individual climate zones and compares them within one year for visualisationcomprehensive modelling framework.

Formatted: Font: 9 pt, Font color: Black

Thus, the resultant catchment C-Q slope β_s is:

$$\beta_s = \beta_0 + \cancel{BFI\_m_s} BFI_s \times \cancel{\delta BFI_{climate}} \delta_{BFI\_climate} \quad (2)$$

In Eqn. 2, BFI_s is a catchment-scale metric of the ~~model parameter, $\delta BFI_{climate}$, represents the~~ baseflow contribution, i.e., *BFI_m* or *BFI_range*. For each of these two metrics, its effect ~~of *BFI_m*~~ on the C-Q slope~~. This effect~~ is considered ~~as a~~with the climate-specific model parameter $\delta_{BFI\_climate}$ to assess whether the ~~catchment BFI~~ effects of baseflow contribution differ between climate~~. Such conceptualization of the~~ zones.

The model conceptualisation is illustrated in Figure 2 with daily flow time series from two catchments (panel a) and the time-series of daily BFIs along with its median (*BFI_m*) and the 10th and 90th percentiles used to calculate *BFI_range* (panel b). Figure 2c illustrates the modelled C-Q slope for EC for the two catchments, β_1 and β_2, for which *BFI_m* was considered as the main predictor following Eqn. 2. The alternative model structure with *BFI_range* as the main predictor of C-Q slope was developed following the same rationale.

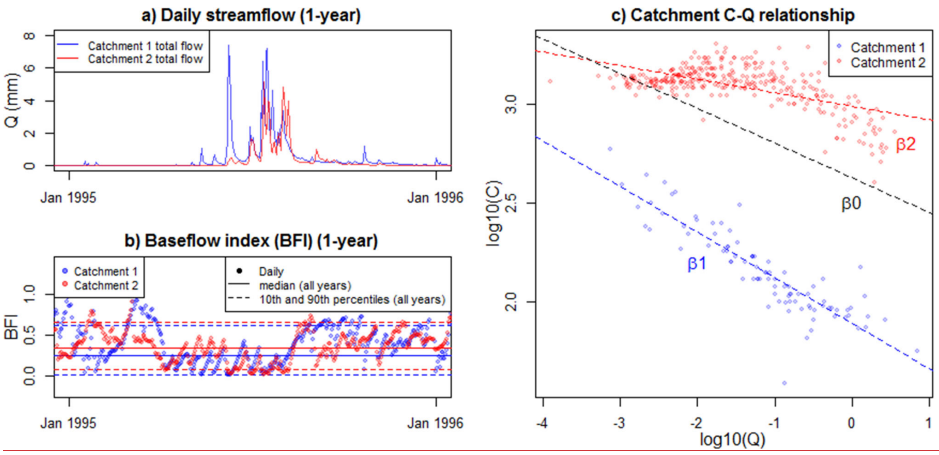


Figure 2. Illustration of conceptualisation of the BFI-based C-Q models (Eqn. 2) with the flow and EC data from two catchments. The catchment median BFI (*BFI_m*) is used as the main predictor of C-Q slope. a) daily flow time-series; b) daily BFI time-series and the corresponding median (*BFI_m*) and the 10th and 90th percentiles. c) C-Q relationships for the two catchments, where the shift in C-Q slope (β_1, β_2) away from the grand mean β_0 is determined by *BFI_m*. Both time-series for the daily flow (a) and BFI (b) are only shown for one year for visualisation.

Our conceptualisation of the effects ~~would then lead~~of baseflow contribution leads to a modified C-Q relationship for each catchment as:

Formatted: Font: 9 pt, Font color: Black

$$log\left(C_{s,t}\right) = \alpha_s + (\beta_0 + \cancel{BFI\_m_s} BFI_s \times \cancel{\delta BFI_{climate}} \delta_{BFI\_climate}) \times log\left(Q_{s,t}\right) \quad (3)$$

Equation 3 is the final form of the ~~Bayesian hierarchical model~~BHM, which was calibrated for each water quality variable across all catchments simultaneously~~ to~~. *BFI_m* and *BFI_range* were each used in separate models to independently assess the ~~impact~~effects of ~~catchment BFI~~these two metrics on C-Q slopes.~~ The effects of *BFI_l* and *BFI_h* were explored with the same model structure.~~

To calibrate the ~~Bayesian model~~BHM, we used the R package *rstan* (Stan Development Team, 2018). The package first sampled parameter values from the Bayesian prior distributions with Markov chain Monte Carlo, and then evaluated candidate models to derive the posterior parameter distributions. Each of the unknown model parameters, β_0, α_s and ~~$\delta BFI_{climate}$~~$\delta_{BFI\_climate}$, was independently derived by sampling from a minimally informative normal prior distribution of *N(0,10)* (Gelman et al., 2013; Stan Development Team, 2018). We used four independent Markov chains in each model run, with a total of 50,000 model iterations for each chain. Convergence of the chains was ensured by checking the *Rhat* value (Sturtz et al., 2005), which is ~~a~~the *rstan* output that ~~summarizes~~summarises the consistency of the four Markov chains used in model calibration. Specifically, we ensured that the *Rhat* value is below 1.1, which ~~suggested~~suggests that the independent Markov chains have been well mixed and converged (Stan Development Team, 2018). The stan codes for both models (with either *BFI_m* or *BFI_range* as the main predictor) are included in Figures S10-11 Supplementary Information.

~~The~~ To interpret the calibrated ~~model interpretation~~ models, we focused on the performance and on the model parameter ~~$\delta BFIclimate$~~$\delta_{BFI\_climate}$, which ~~informed~~informs the climate-specific effects of catchment ~~BFI~~baseflow contributions on C-Q slopes. We specifically assessed the following model outputs ~~(results~~as presented in Section 3.3~~)~~:

1) *Model performance:* ~~We assessed how well~~For each BFI-based model of the C-Q slopes (Eqn. 3~~) reproduced~~ with either *BFI_m* or *BFI_range* as the main predictor), we assessed the model performance with the R^2 calculated between the observed ~~water quality with the Nash Sutcliffe Efficiency (NSE) (Nash & Sutcliffe, 1970). The NSE represents~~and simulated catchment C-Q slopes, which quantifies the proportion of ~~observed variability~~variance in C-Q slopes that is explained by ~~the~~our model. As a benchmark, we also assessed the ~~NSE~~R^2 of a baseline model which ~~uses the classic C-Q relationship (Eqn. 1) observed for individual catchments to predict~~ only allows a single parameter for each baseflow metric (*BFI_m* and *BFI_range*) across all ~~water quality concentrations. This baseline~~ climate zones. Comparison of our climate-specific model ~~represents the best performance that can be achieved to predict concentration using the catchment C-Q slopes together with flow. Therefore, the baseline model provides an informative~~ with this benchmark ~~to assess~~model enabled us to quantify the ~~BFI-based model~~benefit of considering climate-specific effects of baseflow contribution on the C-Q relationships.

Formatted: Font: 9 pt, Font color: Black

2) *Modelled effects:* We extracted the direction, magnitude and significance of the ~~effects of catchment BFI~~model parameter $\delta_{BFI\_climate}$ from the posterior distribution of the calibrated model~~ parameter, $\delta BFI_{climate}$~~, to ~~assess~~infer the impact of ~~catchment BFI on C-Q slope~~baseflow contribution for each climate zone.

3 Results and ~~Discussions~~Discussion

In this section, we first discuss the spatial variation in ~~the median~~ *BFI_m* and *BFI_range* across the study catchments (Section 3.1). We then provide some examples ~~at~~from specific catchments to illustrate how ~~catchment BFI~~baseflow contribution can affect C-Q ~~relationship~~relationships as a proof of concept (Section 3.2). Section 3.3 then presents the inferences made with the BFI-based C-Q model, focusing on the ~~model performance in predicting water quality (Section 3.3.1), and we discuss the modelled effects of catchment BFI on C-Q slopes (Section 3.3.2). Note we focus on the outputs from the model which used the catchment median BFI (*BFI_m*) as the main predictor; the models calibrated using *BFI_l* and *BFI_h* as predictors generally show consistent performance and results with that of *BFI_m*, and are presented in the Supplementary Materials.~~modelled effects of catchment baseflow contribution on C-Q slopes.

3.1 ~~BFI~~Baseflow contribution across catchments

The range of ~~catchment low, median~~*BFI_m, BFI_10th* and ~~high BFIs (*BFI_l, BFI_m* and *BFI_h*)~~*BFI_90th* for all catchments included in this study are ~~summarized~~summarised in Figure ~~3.~~3a). The calculated median BFIs are consistent with previous studies of BFI patterns in Australian catchments (Zhang et al., 2017) and do not seem to correlate with catchment area (Figure S3, Supplementary Material). Generally, temperate catchments have the highest *BFI_m*~~ across all climates~~, while similar ~~ranges of median BFIs~~*BFI_m* values are seen ~~between~~across the other four climate zones~~ (Figure 3-a)). The~~. *BFI_~~l~~10th* and *BFI_~~h~~90th* have ~~consistent~~ distributions consistent with ~~the median *BFI* across~~ *_m* in all climate zones. ~~Considering the~~As different catchments were analysed ~~between~~for each water quality ~~variables, similar catchment~~variable, the same BFI ~~summaries~~metrics were also generated for each water quality variable, and ~~the BFI~~their distributions are generally consistent across different variables (Figure S4, Supplementary Materials).

Formatted: Font: 9 pt, Font color: Black

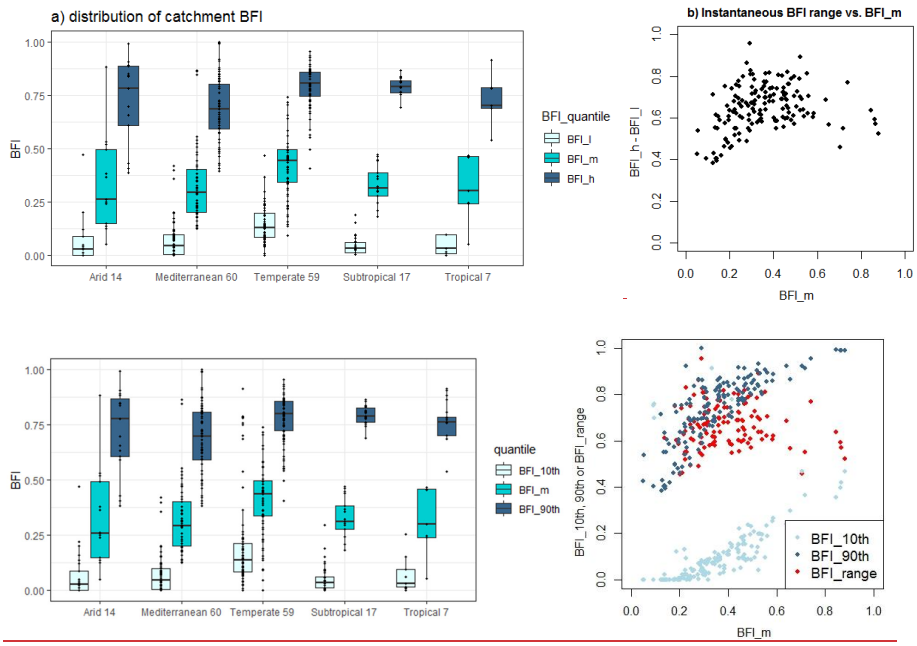


Figure 3. a) Distribution of catchment ~~low,~~ median, and ~~high~~ the 10th and 90th percentiles of daily BFI (*BFI_~~l, BFI~~_m*, *BFI_~~h~~10th*, *BFI_90th*) for each climate zone~~; b) range of instantaneous~~ along with the number of catchments analysed (x-axis); b) the 10th and 90th percentiles of daily BFI (*BFI_~~h~~ 10th* and *BFI_~~l~~90th*), and *BFI_range* (*BFI_90th – BFI_10th*) versus *BFI_m*. Both plots include all 157 catchments across the six water quality variables studied. The corresponding ~~versions of a) and b)~~plots for catchments analysed in individual water quality variables are in ~~Figure S4 and~~ Figures S4 and S5 ~~and S6 (~~in the Supplementary Materials~~).~~.

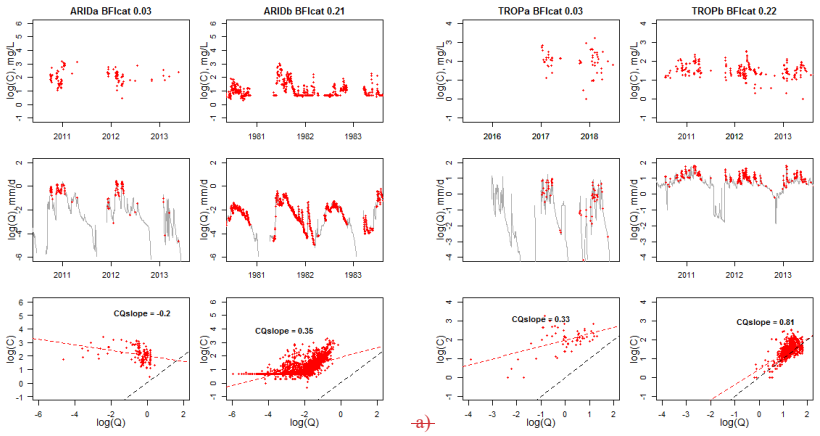
~~It is also worth noting that~~In general, catchments with high median BFI~~_m~~ are likely to have a ~~higher variability~~greater range of ~~instantaneous~~variation of daily BFI, as highlighted by the generally increasing ~~differences between~~ *BFI_~~h~~ and BFI_~~l~~range* with higher *BFI_m* (Figure ~~3 b)).~~3b), Spearman's ρ = 0.33). The link between *BFI_m* and ~~variability of instantaneous BFI~~*BFI_range* suggests ~~potentially different flow pathways for~~that catchments with ~~contrasting~~higher *BFI_m* values are more likely driven by highly variable flow pathways. Specifically, a catchment with a low *BFI_m* tends to be associated with ~~low instantaneous BFIs limited to~~ a small range~~;~~ of daily BFI (low *BFI_range*); thus, the catchment is likely to always have ~~lower~~constantly low contributions of baseflow and higher contributions of ~~surface flow~~quickflow, during both dry and wet conditions. In contrast, a catchment with a high *BFI_m* generally has a large range ~~in instantaneous~~of daily BFIs~~.~~ (high

Formatted: Font: 9 pt, Font color: Black

BFI_range). This means that the catchment is more likely ~~switching~~to switch between groundwater contributions in dry conditions (high ~~instantaneous~~daily BFI) and surface water contributions during wet conditions (low ~~instantaneous BFI). Therefore, catchments with higher~~daily BFI). However, we also note that a small proportion of catchments (9 catchments) with the highest *BFI_m* (>0.6) actually have smaller *BFI_range* compared to other catchments with mid-range BFI values (0.4-0.6). This is a result of *BFI_10th* and *BFI_90th* both increasing with *BFI_m*~~ are more likely dominated by different flow pathways under dry and wet conditions.~~, while the increase in *BFI_90th* plateaus at high *BFI_m*. This nonlinearity suggests that the full distribution of catchment baseflow contributions might not be sufficiently represented by either the *BFI_m* or *BFI_range* alone, providing further justification for the need to explicitly consider both the overall condition and the variation in catchment baseflow contributions when studying their effects on C-Q relationships.

3.2 Impact of ~~BFI~~baseflow contribution on C-Q slope: proof of concept

Before presenting the modelled effects of catchment baseflow contribution on C-Q relationships, we show some examples of individual catchments to illustrate how C-Q relationships vary across catchments with *BFI_m*~~.~~ and *BFI_range*. We focus on the C-Q relationships of TSS for four catchments including two arid catchments (ARIDa, ARIDb) and two tropical catchments (TROPa, TROPb) (Figure 4). For each climate zone, we include one catchment with low *BFI_m* (ARIDa, TROPa) and another one with high *BFI_m* (ARIDb, TROPb), relative to the corresponding range of *BFI_m* for TSS (Figure S4).



~~a)~~ ~~b)~~

Formatted: Font: 9 pt, Font color: Black

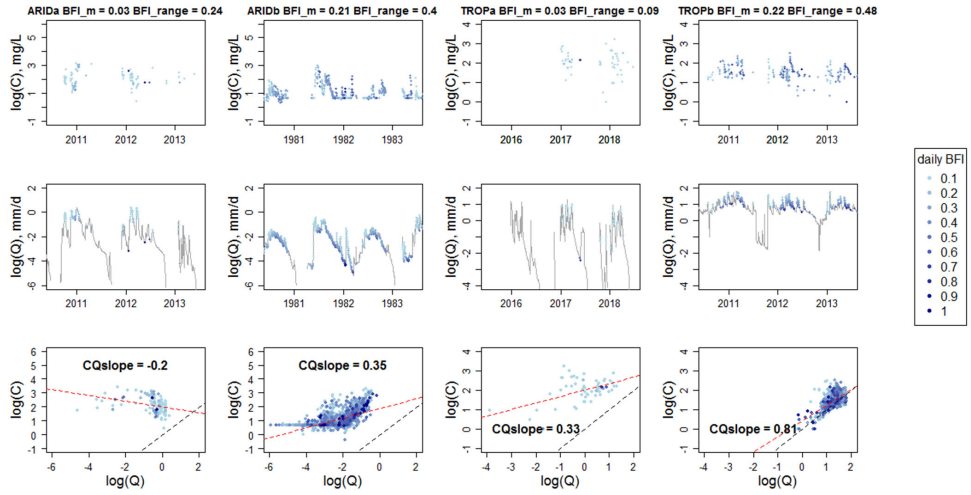


Figure 4. C-Q relationships between TSS and flow for four individual catchments (in columns), including~~: a)~~ two arid catchments (ARIDa, ARIDb~~);~~), and ~~b)~~ two tropical catchments (TROPa, TROPb). Within each climate, two catchments with a low~~ BFI~~ and ~~a~~ high~~-~~ value of *BFI*~~ catchments~~ *m* are included~~.~~. The *BFI_m* along with the corresponding *BFI_~~m~~ range* values for individual catchments are shown in the column titles. The top and middle rows for each catchment show a 3-year ~~timeseries for~~time series within the records of TSS concentrations and the continuous records of flow, with~~ red~~ dots showing the timesteps of water quality samples. The bottom row shows the C-Q relationship with all ~~concentration~~matching TSS and flow data at each catchment~~;~~. All data points are coloured according to the daily BFI and all C-Q values are plotted in log-10 scale. The red dashed lines ~~show~~represent the observed C-Q ~~slope~~relationship, and the black dashed lines show the reference 1:1 line. ~~All values plotted are in log-10 scale.~~

Due to the particulate nature of TSS, we would expect the C-Q relationship to show a strong ~~a~~ mobilisation behaviour that is enhanced during storm events (Musolff et al., 2015). ~~Thus, catchments should have positive C-Q slopes, with a greater slope at a catchment with low *BFI_m*.~~ However, our results show this is not always the case (Figure 4). ~~The low-BFI~~For the arid ~~catchment~~catchments, the low-BFI catchment is largely dominated by quickflow (ARIDa, *BFI_m* = 0.03~~)~~, *BFI_range* = 0.24, most daily BFIs are around 0.1), which has a negative C-Q slope~~, whereas~~. In contrast, the high-BFI catchment ~~(ARIDb, *BFI_m* = 0.21)~~ shows a non-linear C-Q relationship (in log-log space~~).~~) spreading across a much wider range of daily BFIs (ARIDb, *BFI_m* = 0.21, *BFI_range* = 0.4). The overall C-Q slope for ARIDb is positive, which however, consists of a negative slope for lower flows, followed by a positive slope when the flow passes a certain threshold~~.~~ (around log10(Q) = -2). This is similar to the differences in C-Q slopes ~~with~~ across low/high~~ and low~~ flows as seen in previous studies (e.g., Moatar et al., 2017), and suggests that the mobilisation behaviour for TSS ~~is dependent on a threshold flow.~~occurs only during high-flow

Formatted: Font: 9 pt, Font color: Black

events (Thompson et al., 2011). A possible explanation for the negative C-Q slope for TSS during low flows is the dominance of biogeochemical processes rather than hydrological processes (Moatar et al., 2017).

Both tropical catchments (TROPa and TROPb) exhibit positive C-Q slopes that are relatively linear (in log-log space), where seasonal ~~pattern~~patterns in TSS ~~concentration~~ are in phase with those of streamflow. Similar to the patterns seen in the two arid catchments, the catchment with higher *BFI_m* (TROPb) is associated with a wider range of daily BFI values (*BFI_m* = 0.22, *BFI_range* = 0.48). This highlights consistently strong mobilisation behaviours, with a ~~greater~~more positive C-Q slope for the catchment that has ~~a~~ higher ~~baseflow contribution (TROPb, *BFI_m* = 0.22)~~ and *BFI_range*. Overall, this preliminary analysis on a small subset of catchments suggests that ~~BFI~~baseflow contribution may indeed drive differences in C-Q relationships between catchments, and that these effects may vary across climate zones. However, it is difficult to conclude on the individual impact of *BFI_m* and *BFI_range* on the C-Q slopes, from these individual examples. The separate impacts of the two metrics are evaluated over a wide range of catchment conditions across the Australian continent with the model outputs from our BHM (Section 3.3).

3.3 Modelled ~~results from the BFI-based C-Q model~~

~~3.3.1 Model performance in predicting water quality~~

~~**The calibrated BFI-based C-Q model, when using catchment median BFI (*BFI_m*) as the predictor, can generally explain 50%**~~**effects of** ~~**the observed variability for individual water quality variables (Table 1). For TP, TN, SRP and EC, the model can explain 54-93% of the observed variability; the explanatory power is lower for TSS and TN (NSE of 0.50 and 0.47, respectively). Compared to the baseline model that predicts water quality with observed C-Q slopes for individual catchments (see details in Section 2.2), the BFI-based model has only marginally lower performance with baseflow contribution0.01-0.04 decreases in NSE across all water quality variables (Table 1, see Figures S7 and S10 in Supplementary Materials for corresponding plots of the model fit). This suggests that the BFI-based model, while having the capacity to predict C-Q slope across space, can predict water quality almost as well as using the observed C-Q slope. The good performance of the BFI-based model also suggests its suitability to derive inferences of the impacts of catchment BFI**~~ **on C-Q slopes**~~**. Using *BFI_l* and *BFI_h* instead of *BFI_m* as the predictor only has minimal impacts on model performance (Table S3, Supplementary Materials).**~~

~~**Table 1. Performance of the BFI-based model (with *BFI_m* as the main predictor) and the baseline model in predicting across all catchments for individual water quality variables (in rows), summarized as Nash Sutcliffe efficiency (NSE). The corresponding plots of the model fit are in Figures S7 and S10 in Supplementary Materials.**~~

Using catchment-level metrics of baseflow contribution alone (either *BFI_m* or *BFI_range*) can explain up to 22% of the variation in catchment C-Q slopes. Although these results represent limited model predictive capacity, the model does cover a large range of catchment conditions such as contrasting land uses and hydro-climate conditions. Therefore, the amount of variation that can be explained by a single BFI metric highlights baseflow contribution as an important factor that influences catchment C-Q relationships. Further, it is also worth highlighting that incorporating climate-specific impacts of baseflow contribution is highly beneficial in explaining these variations. For all six water quality parameters, the baseline model – which

Formatted: Font: 9 pt, Font color: Black

uses a lumped effect of catchment baseflow contribution across different climate zones – can barely explain any variation in the C-Q slopes (with all $R^2 < 0.08$, i.e., <8% of the variation explained). In contrast, the climate-specific models generally offer up to 20% increase in the variance explained for C-Q slopes, except for EC and SRP, for which performance is equally low regardless of whether the effects of baseflow contribution are separated for individual climates. The low performances for EC and SRP are likely attributed to the smaller magnitudes of C-Q slopes as highlighted in the lower median C-Q slope in Table 1, making it statistically more difficult to explain variations across catchments for these two water quality variables. These results further emphasise that in general, the impacts of catchment baseflow contribution on C-Q slopes are better defined within individual climate zones, which confirms the validity of our BFI-based C-Q models (Eqn. 3).

Table 1. Performance of the BFI-based C-Q models – the columns show four alternative model structures with *BFI_m* or *BFI_range* as the key predictor, and with the impacts of baseflow contribution considered as lumped or specific to individual climate zones. The rows show results for individual water quality parameters. All model performances are summarised by R^2, which quantifies the percentage of variance in C-Q slopes explained by the BFI-based models.

~~Water quality variable~~ WQ parameter	~~BFI-based~~ Median C-Q ~~model~~ slope	Current (climate-specific impacts)		Baseline ~~model~~(lumped impact across climate zones)	
		BFI_m	*BFI_range*	*BFI_m*	*BFI_range*
TSS	0.~~50~~15	0.~~53~~16	0.11	0	0.04
TP	0.~~54~~09	0.~~56~~14	0.17	0	0.08
SRP	0.~~62~~06	0.~~64~~02	0	0.03	0.05
TN	0.~~47~~09	0.~~50~~18	0.12	0.02	0.03
NO_x	0.~~54~~36	0.~~58~~22	0.18	0.03	0
EC	-0.~~93~~07	0.~~94~~	0.01	0	0.01

Inserted Cells

Inserted Cells

Inserted Cells

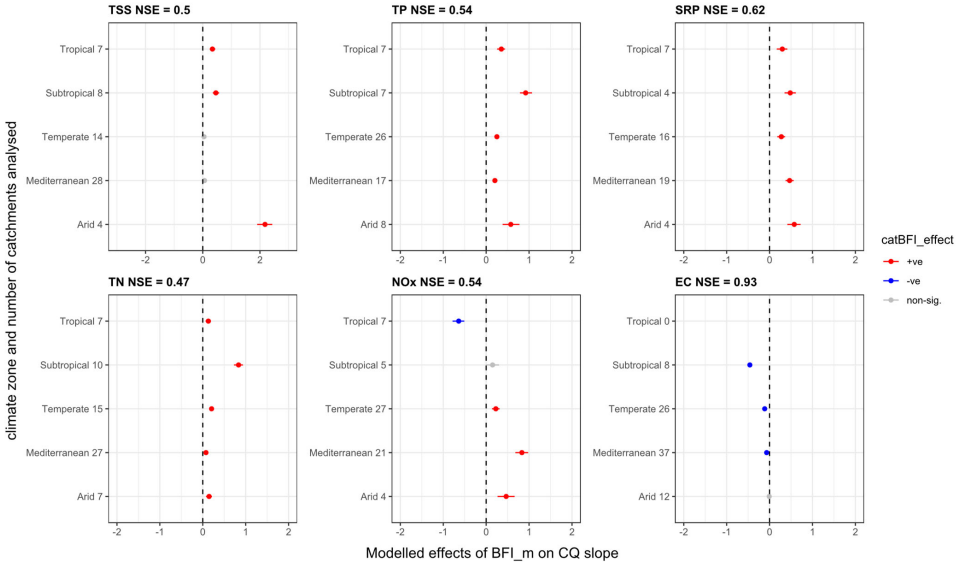
Inserted Cells

~~3.3.2 Modelled effects of BFI on C-Q slope across Australia~~

Our climate-specific, BFI-based C-Q ~~model synthesized~~models synthesised the patterns observed ~~for~~in individual catchments (as illustrated in Section 3.2) across the Australian continent. The ~~model suggests~~models suggest that ~~catchment median BFI,~~both *BFI_m*~~, has~~ and *BFI_range* have a significant influence on the C-Q slope for most climate zones and water quality ~~variables, with some differences~~parameters, and that these influences differ between climate zones~~.~~ for each parameter. Figure 5 presents the median and the ~~95th~~95% credible intervals of these modelled ~~impacts~~effects for each water quality variable~~.~~. The

Formatted: Font: 9 pt, Font color: Black

95% credible interval is the range between the 2.5th and 97.5th percentiles of the posterior distribution of the parameter values , which was derived from the Bayesian posterior estimates of $\delta BFI_{climate}$ ($\delta_{BFI\_climate}$ (Eqn. 3).) to quantify the uncertainty in the modelled effects (Gelman et al., 2013). The effectefferts of catchment median *BFI_m* and *BFI_range* on the C-Q slope isslopes are almost always significant, with the 95th95% credible intervals not crossing over 0 for most combinations of water quality variables and climate zones. An exception is for SRP, for which *BFI_range* always has a non-significant effect on the C-Q slopes.



Formatted: Font: 9 pt, Font color: Black

19

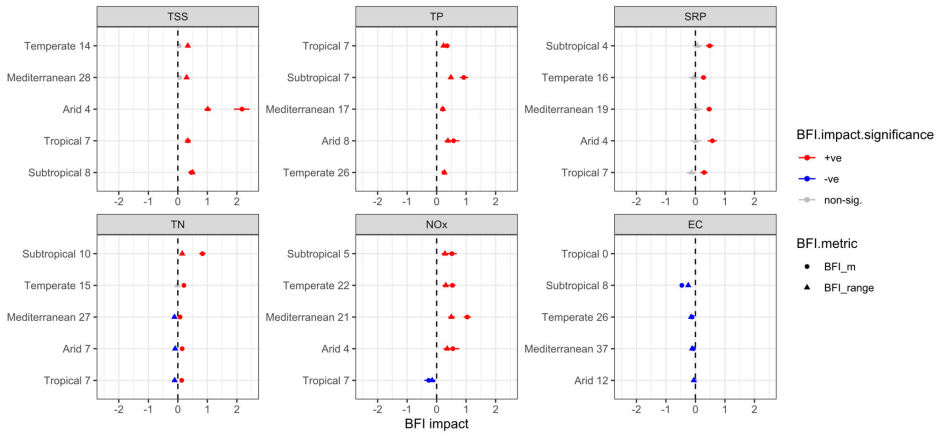
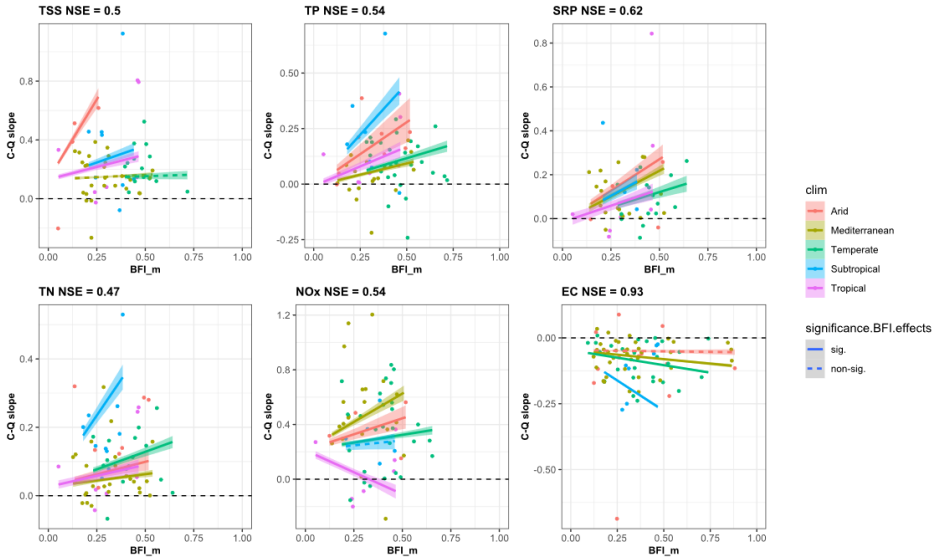


Figure 5. Modelled effects of *BFI_m* and *BFI_range* on catchment C-Q ~~slope for each climate zone. The bars show the 95% credible interval (2.5th to 97.5th percentile) of modelled effects~~slopes for each climate zone ($\delta_{BFI\ climate}$) for each water quality ~~variable~~parameter. The bars show the 95% credible intervals (the range between 2.5th to 97.5th percentiles of Bayesian posterior distribution) of the modelled effects, and the dots indicate the corresponding median levels. The colours indicate whether an effect is significantly positive~~,~~ (red), significantly negative~~,~~ (blue), or non-significant~~;~~ (grey); a positive effect means that the C-Q slope increases with a higher catchment *BFI_m* or *BFI_range*, and vice versa. Black dashed lines show the zero-effect i.e~~.~~., no effect at all. The plot includes results from models with each of *BFI_m* and *BFI_range* as the key predictor, which are differentiated by marker shapes.

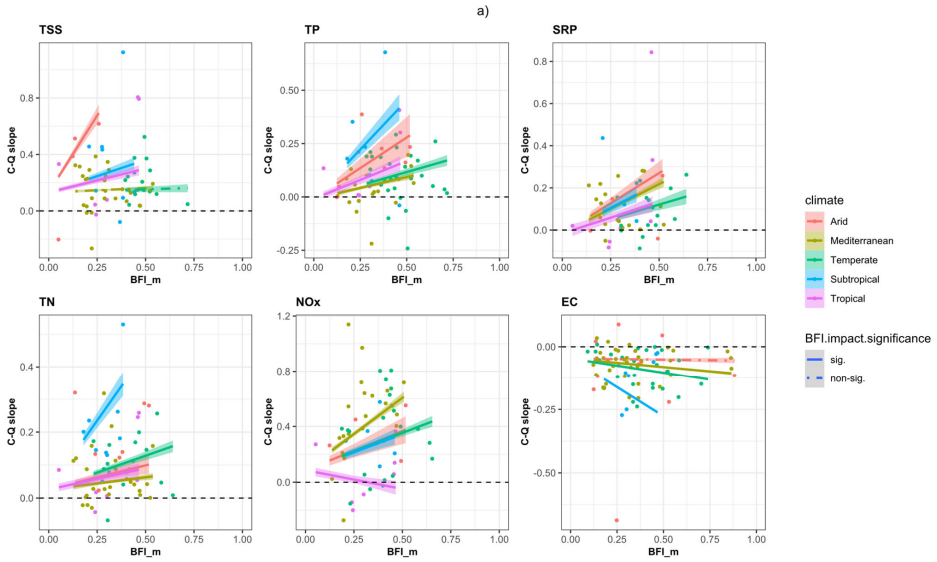
~~Figure 5 shows the directions of the impacts of catchment median BFI (*BFI_m*).~~ To put the impacts of ~~BFI~~ baseflow contribution shown in Figure 5 into context, we ~~show~~present the modelled catchment C-Q slopes against the corresponding *BFI_m* and *BFI_range* values in Figure ~~6.~~6a and b, respectively. Sediment and nutrients are largely dominated by mobilisation, as evidenced by the large proportion of positive C-Q slopes for TSS, TP, SRP, TN and NO_x. In contrast, salts (EC) have largely negative C-Q slopes and are thus dominated by dilution. Regarding the effects of catchment ~~BFI~~baseflow contribution, we first note ~~that~~a common overall pattern for both *BFI_m* and *BFI_range*: for each water quality variable, the fitted relationships between C-Q slopes and ~~BFI~~each BFI metric (either *BFI_m* or *BFI_range*) have a consistent 'diverging' pattern between climate zones. This is a result of our model structure, in which, for each water quality variable, all catchment C-Q slopes share a common 'grand mean' (Section 2.2~~), which represents the~~) – representing a stable export ~~patterns between~~pattern across Australian climate zones ~~as found in our preceding study~~that is specific to the water quality variable (Lintern et al., ~~in review~~2021). The deviation of slopes within each climate zone from the 'grand mean' is dependent on catchment *BFI_m* or *BFI_range* (Eqn. 2). Therefore, for catchments with low *BFI_m*~~,~~ (or low *BFI_range*), the differences in C-Q slopes between climate zones are smaller, and are all close to the 'grand mean'. Conversely, the C-Q slopes of catchments with high *BFI_m*

Formatted: Font: 9 pt, Font color: Black

(*BFI_range*) are affected more strongly by the differences between climate zones. Since these diverging patterns are a result of the model structure, we do not relate these patterns further to any physical interpretation on the impacts of BFI metrics on C-Q slopes.



Formatted: Font: 9 pt, Font color: Black



Formatted: Font: 9 pt, Font color: Black

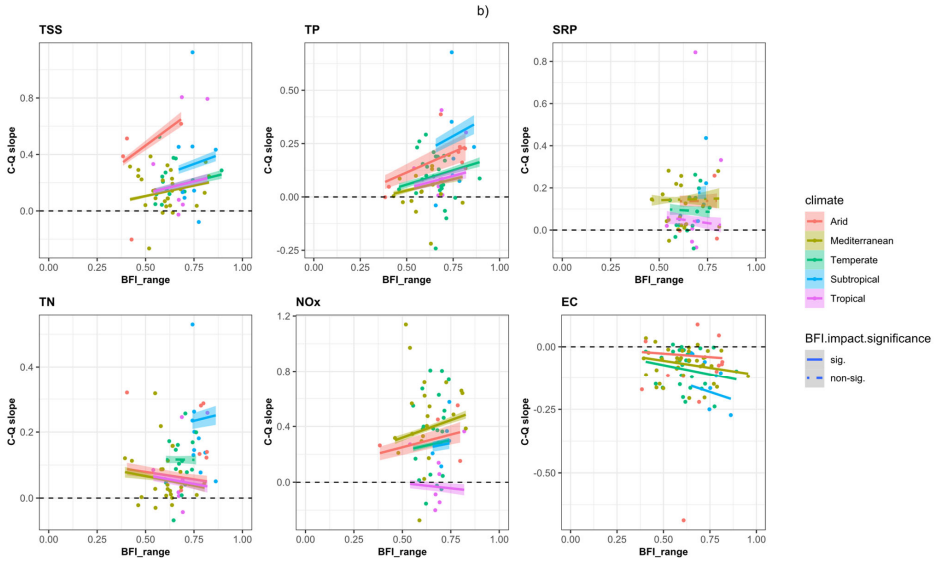


Figure 6. a) Catchment C-Q slope vs. ~~catchment median BFI (*BFI_m*),~~ and b) Catchment C-Q slope vs. *BFI_range*, coloured by climate zones. The lines represent the modelled C-Q slope~*BFI_m* or C-Q slope~*BFI_range* regression lines for individual climate zones~~, where *BFI_m* always has a significant impact on C-Q slope, based on~~ . The bands represent the ~~95th~~95% credible ~~intervals shown in Figure 5.~~interval (the range between 2.5th to 97.5th percentiles of Bayesian posterior distribution) of the modelled C-Q slopes. The dots represent the 'true' C-Q slopes estimated with C-Q observations at individual catchments. The black dashed lines mark a zero C-Q slope which differentiate mobilisation (C-Q slope>0) from dilution (C-Q slope<0).

~~Across all six water quality variables and most climate zones, we found a general pattern that catchments with higher median BFI (*BFI_m*) tend to have steeper C-Q slopes (regardless of direction). This impact of *BFI_m* could be related to the negative correlation between *BFI_m* and the median concentrations combining with the low correlation between *BFI_m* and median flow (Figures S11 and S12, Supplementary Materials). The BFI effects are also unlikely related to longer travel times in larger catchments, as *BFI_m* is not correlated with catchment area (Figure S3). Considering export patterns, this result highlights an overall increase in i) mobilisation for sediment, nitrogen and phosphorus; and ii) dilution for salt, generally at catchments with higher baseflow contribution. In the subsequent discussions, we first detail the modelled effects for individual water quality variables, and then synthesise potential explanations related to catchment processes.~~

~~For both TP and SRP, across all climate zones, most catchments have positive C-Q slopes. This slope is steeper for catchments with higher *BFI_m* for all climates. To further interpret the behaviour of particulate and soluble P, we extracted the SRP:TP~~

Formatted: Font: 9 pt, Font color: Black

ratios for all catchments with both SRP and TP timeseries (Figure S13). The SRP:TP ratios for most catchments are less than 0.4, which suggests that TP is dominated by particulate forms across all catchments and climate zones. Combining this with the positive effects of *BFI_m* seen for both SRP and TP, this suggests an overall mobilisation export pattern for both particulate and soluble P, which is more pronounced at rivers with higher baseflow contributions.

For TN and NOx, the C-Q slopes are largely positive, and the modelling result suggests an increase in C-Q slope with *BFI_m* for most climate zones, except for subtropical (non-significant) and tropical (significantly negative) catchments for NOx. A large proportion of TN is present in particulate forms (Figure S14), with most catchments having NOx:TN ratios lower than 0.25. The particulate-dominated TN and the responses of its C-Q slope to *BFI_m* highlight that particulate N is largely mobilised across all climate zones, which are enhanced with higher contributions of baseflow. For soluble N (NOx), the baseflow-driven mobilisation is also shown as an important pathway for arid, Mediterranean and temperate catchments.

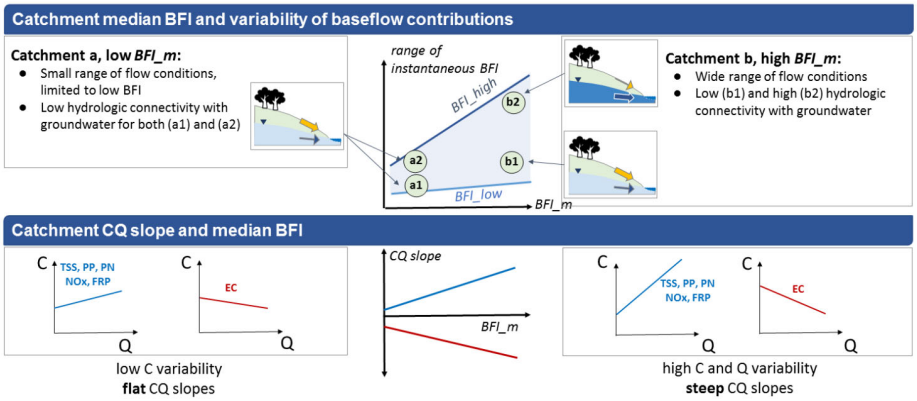
For TSS, most catchments have positive C-Q slopes, which increase with *BFI_m* in arid, subtropical and tropical climates; the effects of *BFI_m* are non-significant for Mediterranean and temperate catchments. This 'enhancing' effect of *BFI_m* on positive C-Q slopes (i.e. mobilisation) is largely consistent with the results for TP and TN, which are both largely particulate-bound.

EC exhibits mostly negative C-Q slopes, indicating an overall dilution export pattern. No tropical catchments were included due to insufficient data. A higher *BFI_m* led to a steeper negative C-Q slope for Mediterranean, subtropical and tropical catchments, but only has non-significant effect on C-Q slope for arid catchments. This result highlights stronger dilution behaviour at catchments with higher baseflow contribution, for Mediterranean, subtropical and tropical climates.

In summary, the above results highlight an overall greater absolute value of C-Q slope at a catchment with higher baseflow contribution. For sediment (TSS) and nutrients (N and P species), we see an overall mobilisation behaviour across Australian catchments, which is stronger in catchments with higher baseflow contribution. For salts (EC), we see an overall dilution behaviour, which is also enhanced at baseflow dominated catchments. The potential processes are discussed subsequently and summarized in Figure 7.

24

Formatted: Font: 9 pt, Font color: Black



~~**Figure 7. Conceptual diagram of the modelled effect of baseflow contribution on C-Q slopes, for a catchment with low *BFI_m* (catchment a) and a catchment with high *BFI_m* (catchment b).**~~

~~For particulate water quality variables (TSS, and the largely particulate-bound part of TP and TN), our model result suggests that enhanced mobilisation in catchments with high *BFI_m*. This is a rather surprising result considering the dominance of surface flow in transporting particulates (Lintern et al., 2018). One potential explanation relates to the higher variability of instantaneous BFI seen in catchments with high *BFI_m*, as seen~~Figure 6 highlights the overall impacts of baseflow contribution on the C-Q slopes of individual water quality variables. For TSS, TP and NO_x, we generally see stronger mobilisation in catchments with higher values in both *BFI_m* and *BFI_range*. For TN, the mobilisation is stronger with higher *BFI_m*, while *BFI_range* generally has slightly negative effects. The detailed model results for each water quality parameter and potential interpretation are discussed in the following paragraphs; we do not further interpret the modelled results for SRP and EC due to limited ability to explain variation in their C-Q slopes (Table 1).

TSS and TP both show consistently strong positive effects of the baseflow contribution on the C-Q relationships, which both have increasing positive C-Q slopes with a higher value in either *BFI_m* or *BFI_range*, for most climate types. For TP, both *BFI_m* and *BFI_range* have significant positive impacts on the C-Q slopes for catchments across all climate zones, while for TSS, *BFI_range* always has a significant positive impact on the C-Q slopes and *BFI_m* has consistent impacts for arid, subtropical and tropical catchments. These positive effects of both *BFI_m* and *BFI_range* on the largely positive C-Q slopes of TSS highlight that particulate transport may be enhanced by higher overall baseflow contributions, as well as by greater variability in baseflow conditions. TP is largely particulate-bound, as evidenced by SRP:TP ratios lower than 0.4 for most catchments across all climate zones (Figure S8). Therefore, the transport of TP is likely also enhanced by variations in baseflow

Formatted: Font: 9 pt, Font color: Black

conditions in the same manner as for TSS. Note that the overall positive effect of *BFI_m* in enhancing mobilisation is generally significant despite that catchments with higher *BFI_m* generally have lower median concentrations of TSS and TP (Figure S6), suggesting relatively limited sources in catchments with high *BFI_m.*

The enhanced mobilisation of particulates (TSS and TP) with higher *BFI_m* is consistent with previous studies in European catchments, which also reported positive effects of BFI on the C-Q slopes of TSS (Moatar et al., 2017; Musolff et al., 2015). However, no physical interpretation of this result was discussed previously. Combining our modelled results of *BFI_m* together with those of *BFI_range*, we are able to draw a plausible explanation that links particulate mobilisation with the two highly correlated baseflow metrics (Figure 3b~~.~~). Specifically, catchments with lower *BFI_m* generally have narrower ranges of variation in instantaneous BFI~~,~~ (low *BFI_range*), which thus tend to always ~~have low baseflow contributions (i.e.~~ be dominated by surface flow ~~dominated)~~ regardless of dry or wet conditions (Catchment ~~a~~A, Figure 7). This can lead to a limited range of water sources with small variation of flow pathways ~~to~~that transport ~~water chemistry~~chemical species to rivers, resulting in a ~~relative~~relatively stable export pattern across low and high flows ~~at~~in these catchments. In contrast, catchments with higher *BFI_m* generally have higher variability in instantaneous BFI. This suggests higher variations in flow pathways, including surface ~~flows~~flow dominance during wet ~~period~~periods and subsurface ~~flows~~flow dominance during dry ~~period at these catchments~~ periods (Catchment ~~b~~B, Figure 7). Consequently, ~~these~~we contend that catchments with high *BFI_m* and *BFI_range* can have a higher diversity of flow pathways and water sources ~~and~~, potentially leading to larger chemical gradients between groundwater-driven concentrations at low flow and ~~runoff-driven~~surface flow-riven concentrations at high flow.

Formatted: Font: 9 pt, Font color: Black

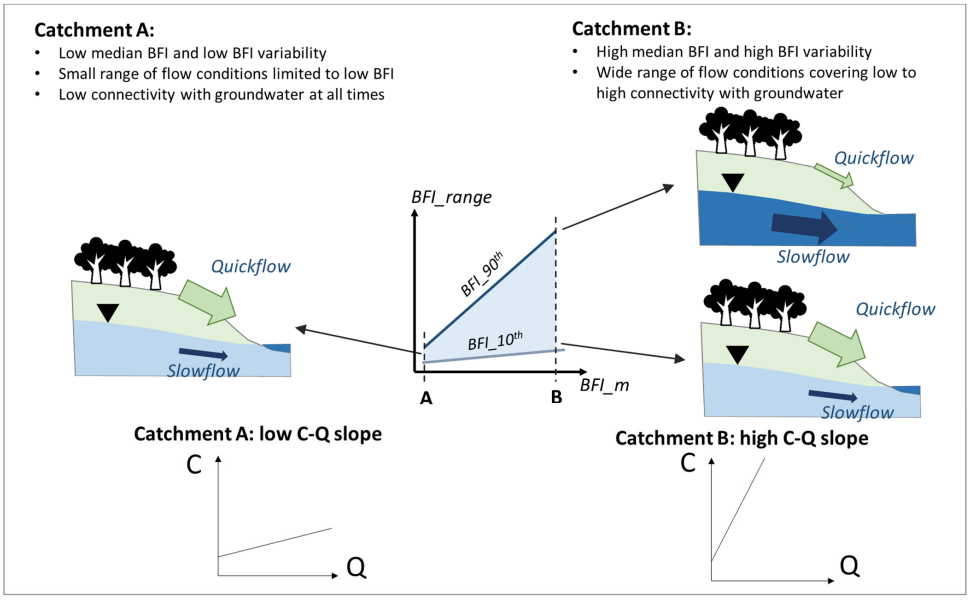


Figure 7. Conceptual diagram of the expected hydrological conditions in catchments with low ~~For soluble N~~ and ~~P (NOx~~high median and ~~SRP),~~variability in baseflow contribution (*BFI_m* and *BFI_range*), as Catchments A and B, respectively. The contrasting hydrological conditions can help explain our modelled results of the impacts of baseflow contributions on C-Q slopes. Note that the C-Q intercepts in the plots are not indicative since we do not investigate the variation in C-Q intercepts in this study.

For NO_x, the modelled effects are also ~~suggest~~ largely consistent between models with *BFI_m* and *BFI_range* as the key predictor. The C-Q slopes increase (become more positive) with an increase in either *BFI_m* or *BFI_range*, for catchments within arid, Mediterranean, temperate, and subtropical climates, while they decrease for the tropics. This suggests enhanced mobilisation ~~in catchments with high *BFI_m*. In Australian catchments, soluble~~of NO_x in most catchments when baseflow contributions and their temporal variations are higher. We note that tropical catchments generally have the lowest positive C-Q slopes, or even slightly negative slopes suggesting weak dilution export patterns. Therefore, higher values in either *BFI_m* or *BFI_range* may actually enhance the dilution effects in tropical catchments, as opposed to mobilisation in other climate zones.

Soluble N and P concentrations in ~~the~~shallow groundwater are generally low in Australia (Cartwright, 2020). ~~This discards the case of rich~~ This contrasts with agricultural catchments in Europe and North America, where high nutrient ~~inputs~~levels are

Formatted: Font: 9 pt, Font color: Black

often observed in groundwater due to the legacy of long-term agricultural practices~~, which is often observed in agricultural catchments in Europe and North America~~ (Van Meter et al., 2017; Stackpoole et al., 2019; Ehrhardt et al., 2018). ~~Thus, steeper C-Q slopes in Australian catchments with higher *BFI_m* could be interpreted as the result of a larger connectivity between the stream and the vadose zone. However, as the case of TSS and particulate N and P~~Thus, it is also plausible that the enhanced mobilisation pattern seen in high *BFI_m* catchments is rather ~~results from~~ the ~~larger range~~effect of ~~instantaneous~~a high *BFI* ~~and thus more frequent mobilisation events. As discussed above, catchments~~ *_range*. Catchments with a greater variability in ~~the instantaneous BFI~~baseflow contribution (Catchment B, Figure 7) are likely ~~having~~to have greater gradients of concentrations for soluble N~~ and P~~, between low groundwater-fed concentrations at low flow and high concentrations from surface~~/subsurface contributions at high flow. For the specific case of SRP, large oscillations of the groundwater table (~~ runoff and/or interflow at high flow (e.g., via leaching), resulting in a stronger mobilisation pattern as illustrated with a higher C-Q slope. Further, a typical temporal pattern of nitrate leaching in Australian catchments is the accumulation of N in soils during periods of low soil water drainage, followed by strong export during high drainage (Drewry et al., 2006), which is also more likely to occur in catchments with greater variation in baseflow contributions.

BFI_m and *BFI_range* show opposite impacts on the C-Q slopes of TN for all climate zones other than subtropical. A large proportion of TN in Australia is present in particulate forms (Figure S9) with most catchments having NO_X:TN ratios lower than 0.25, which ~~corresponds to large ranges of instantaneous BFI) were also shown to generate soil rewetting conditions favouring the release of soluble reactive P (Dupas et al., 2015; Gu~~contrasts with many other catchments in the United States and Europe (Ator et al~~. 2017).~~., 2011; Durand et al., 2011). The particulate-dominated TN and the responses of C-Q slopes to *BFI_m* highlight that particulate N is largely mobilised across all climate zones, which are enhanced with higher contributions of baseflow. A stronger mobilisation is seen for high *BFI_m* across all climate zones, while a weaker mobilisation is observed for high *BFI_range* across all climates other than the subtropical catchments.

~~The enhanced dilution export for EC (e.g. steeper negative C-Q slopes) in catchments with high *BFI_m* suggests the key role of deep flow pathways, which were found in catchments that have high groundwater concentrations of major ions (e.g., Zhi et al., 2019). The weaker effect of baseflow contribution for the arid and Mediterranean catchments can be the result of the overall less pronounced dilution patterns. Previous studies have found that in semi-arid areas, high evapotranspiration can lead to higher concentration of major ions in soil water or shallow groundwater compared with surface water, resulting in C-Q slopes close to 0 (e.g., Herczeg et al., 2001; Li et al., 2017).~~

For the largely particulate-bound TN, one would expect the effects of *BFI_m* and *BFI_range* to be similar to TSS. This brings a question for the interpretation of the weaker mobilisation for a higher *BFI_range*. This unexpected result might suggest that the export patterns for particulate N are different to those for TSS and TP at various baseflow conditions. Therefore, further

Formatted: Font: 9 pt, Font color: Black

investigation is required on the impact of the variability in baseflow contribution on the export patterns of individual N constituents such as particulate N.

Besides the ~~abovementioned~~above-mentioned processes, another potential explanation for the modelled effects of *BFI_m* on C-Q relationships ~~hypothesis~~ is related to flow seasonality, which needs to be further explored. High baseflow contribution is generally found in more perennial catchments in Australia (Kennard et al., 2010), which might be associated with more clearly defined seasonal patterns in transporting water quality variables. These conditions are likely leading to well-defined C-Q relationships (Minaudo et al. 2019) and could result in steeper slopes compared to other catchments. In contrast, catchments with lower baseflow contribution are more likely driven by intermittent flow while lacking clear seasonal patterns, which leads to more scattered C-Q relationships. In this case, the absolute values of C-Q slopes tend to be close to 0 and these catchments often fall in the category of chemostatic with unclear export regimes (e.g~~.~~., Godsey et al., 2009). However, ~~we acknowledge that~~ this hypothesis should be further tested~~, preferably~~ beyond the current study, ideally with a subset of study catchments where high-frequency observations have been collected~~.~~. Such future studies should also consider more broadly the temporal variations in flow regime and baseflow condition and their influences on C-Q relationships. For example, seasonality can play a big role in shaping the C-Q relationships for nutrients, as these relationships over time during the build-up of pollutant sources, and during the flushing of readily available sources at the onset of high flow periods (Bende-Michl et al., 2013). Besides, anthropogenic disturbances and/or management actions in the catchment can cause changes in C-Q relationships over time (Zhang, 2018). Flow flashiness is also shown to influence the C-Q relationships, which differ across particulates and solutes, and across natural and highly regulated catchments (Moatar et al., 2020).

In summary, our results highlight the potential to improve understanding of transport processes via the relationships between water quality and baseflow contributions. Our model ~~proved~~ highlighted that the impacts of both *BFI_m* ~~useful in predicting~~and *BFI_range* on catchment C-Q slopes ~~across space (Section 3.3.1), but also indicated that *BFI_m* may not be a suitable indicator to differentiate key flow pathways between catchments. Indeed, a high *BFI_m* may be associated with~~are highly ~~variable~~similar, which are both likely linked to the variability of baseflow contributions ~~involving both~~and thus the range of surface and subsurface sources and flow pathways~~, as illustrated in Figure 3 b)~~. Therefore, ~~a valuable avenue for~~to better understand the spatial variation of C-Q slopes, future research ~~would be to identify suitable BFI~~should seek alternative metrics to better ~~represent~~capture the variability of baseflow conditions and the temporal dynamics of flow pathways ~~to further improve the understanding of baseflow impacts on transport processes of water quality constituents~~within individual catchments.

4 Conclusions

In this study, a Bayesian hierarchical model was developed to understand the impacts of catchment baseflow contribution on C-Q slopes for six water quality parameters across Australia. ~~These BFI based models show good performances, which can~~

Formatted: Font: 9 pt, Font color: Black

~~explain the majority of the observed variability in EC, SRP, TP, NOx and TSS (93, 62, 54, 54 and 50% explained, respectively) and almost half the observed variability for TN (47% explained). This highlights a potential parsimonious model that can be useful for predicting i) the C-Q slope across space; and ii) water quality for individual catchments, where flow data is available.~~

Our model suggests significant influences of catchment baseflow contributions ~~- as represented by catchment median BFI -~~ on C-Q slopes across most water quality variables and climate zones. ~~One of the important findings is that~~Across the nation, the median and range of BFIs are also positively correlated for most studied catchments, while the C-Q slopes are largely positive for sediments (TSS) and both ~~particular~~particulate and soluble N and P (NO_x, TN~~, SRP~~ and TP). For TSS, NO_x and TP~~), and are steeper for~~ we generally see stronger mobilisation in catchments with higher values in either the median ~~BFI across all climate zones (for TN, SRP and TP).~~or the range of catchment BFIs. The enhanced mobilisation ~~at~~in catchments with higher median BFI (and/or BFI range) is likely a result of more variable flow pathways over time, which introduces higher gradients of concentration ~~gradients~~ between low and high flows~~ that~~. These low and high flows are likely dominated ~~differently~~ by different groundwater and surface water sources, each mobilising different pools of solutes and particulates. This result highlights the crucial role of flow pathways in determining catchment exports of water quality constituents, and the need ~~of~~for further studies to identify suitable ~~baseflow~~hydrological metrics in differentiating flow pathways to improve the prediction and understanding of C-Q relationships. The results also suggest a priority for managing and monitoring stream P and N, which should focus on catchments with the greater fluctuations in baseflow contributions. To this end, it would be worth establishing explicit links between C-Q relationships and water age with high-frequency samples collected at select catchments (e.g., Cartwright, 2020).

~~This study complements our preceding study on the impacts of other catchment characteristics - including land use, land cover, geology and climate - on C-Q slopes across Australia (Liu et al, in preparation). Further work should aim to synthesize the impacts of baseflow contribution and other spatial drivers by considering their interactions and establishing relative importance on influencing C-Q relationships.~~

This study used catchment-level metrics of baseflow contribution as the only predictor of C-Q slopes. The baseflow contribution alone can explain up to 22% variance in the C-Q slopes across the Australian continent. This highlights a substantial role in baseflow contribution in shaping the C-Q relationships, while also suggesting the need of further work to synthesise the impacts of baseflow contribution together with other spatial drivers (e.g., climate, land use, land cover and geology) to include their interactions and establishing their relative importance on influencing C-Q relationships. Further, this study used a linear model structure to synthesise large-scale patterns of the impacts of baseflow contribution on the C-Q relationships across different climate zones. Although this model structure is limited and likely to be influenced by outliers, we believe it is suitable for the study purpose, as we are able to demonstrate the ability of the model to identify significant effects of catchment baseflow contribution on C-Q slopes, with statistically significant modelled effects for most climates and

Formatted: Font: 9 pt, Font color: Black

water quality parameters (Figures 5 and 6). Further studies can build on the learning from the current study to explore alternative model structures, to improve our ability to predict C-Q slopes within individual climate zones.

This study also highlights the effectiveness of Bayesian hierarchical models in interpreting water quality data across large spatial scales. Such a model is ideal to analyse water quality data over a large number of catchments, with high heterogeneity in temporal coverage and sampling frequency. This is particularly relevant for Australia, as water quality monitoring is often undertaken under different local/regional programs, and thus limited to certain timeframes and focusing on specific management ~~interests~~interests.

Data availability

Water quality and flow data used in this study are available upon request from seven Australian state agencies. These include: the Department of Land, Water and Planning (VIC DELWP, Victoria); WaterNSW (New South Wales); Department of Resources and Department of Environment and Science (QLD DNRME, Queensland); Department for Water and Environment (SA DEW, South Australia); Department of Water and Environmental Regulation (WA DER, Western Australia); Department of Primary Industries, Parks, Water and Environment (TAS DPIPWE, Tasmania) and Department of Environment, Parks and Water Security (NT DEPWS, Northern Territory). Sources of data are detailed in Section 2.1.1.

Author contribution

All authors contributed to the design of the research. Danlu Guo carried out data collation, performed the simulations and prepared the manuscript with contributions from all co-authors. All authors contributed to the interpretation of the results and provided feedback.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgement

We would like to acknowledge that all water quality and flow data used in this study were accessed from the monitoring data collected by state agencies across Australia. In collecting these data, we were assisted by: Steve Tickell and Yuchun Chou (Department of Environment, Parks and Water Security, Northern Territory), Erinna Colton and Ashley Webb (WaterNSW, New South Wales), Christine Webb (The Department of Water and Environmental Regulation, Western Australia), David

Formatted: Font: 9 pt, Font color: Black

Waters, Belinda Thomson, Ryan Turner, Rae Huggins (Department of Resources and Department of Environment and Science, Queensland), Bryce Graham (Department of Primary Industries, Parks, Water and Environment, Tasmania), Matt Gibbs (Department of for Water and Environment, South Australia), Paul Wilson (Department of Land, Water and Planning, Victoria). We also thank Professor Andrew Western, Ms Natalie Kho and Dr Rémi Dupas for their generous assistance in guiding this work and in data processing. Clément Duvert thanks Charles Darwin University for supporting a research visit to the University of Melbourne in March 2020. We also acknowledge the Traditional Owners who were the first custodians of Australian waterways.

Formatted: Font: 9 pt, Font color: Black

References

Ator, S. W., Brakebill, J. W., & Blomquist, J. D. (2011). Sources, fate, and transport of nitrogen and phosphorus in the Chesapeake Bay watershed: An empirical model (Vol. 5167): US Department of the Interior, US Geological Survey.

Beck, H. E., van Dijk, A. I. J. M., Miralles, D. G., de Jeu, R. A. M., Bruijnzeel, L. A., McVicar, T. R., & Schellekens, J. (2013). Global patterns in base flow index and recession based on streamflow observations from 3394 catchments. Water Resources Research, 49(12), 7843-7863. doi:https://doi.org/10.1002/2013WR013918

Bende-Michl, U., Verburg, K., & Cresswell, H. P. (2013). High-frequency nutrient monitoring to infer seasonal patterns in catchment source availability, mobilisation and delivery. Environmental Monitoring and Assessment, 185(11), 9191-9219. doi:10.1007/s10661-013-324

Cartwright, I. (2020). Concentration vs. streamflow (C-Q) relationships of major ions in south-eastern Australian rivers: Sources and fluxes of inorganic ions and nutrients. Applied Geochemistry, 120, 104680. doi:https://doi.org/10.1016/j.apgeochem.2020.104680 6-8

Dupas, R., Gruau, G., Gu, S., Humbert, G., Jaffrézic, A., & Gascuel-Odoux, C. (2015). Groundwater control of biogeochemical processes causing phosphorus release from riparian wetlands. Water Research, 84, 307-314. doi:https://doi.org/10.1016/j.watres.2015.07.048

Dupas, R., Abbott, B. W., Minaudo, C., ,, & Fovet, O. (2019). Distribution of Landscape Units Within Catchments Influences Nutrient Export Dynamics. Frontiers in Environmental Science, 7(43). doi:10.3389/fenvs.2019.00043

Dupas, R., Causse, J., Jaffrezic, A., Aquilina, L., & Durand, P. (2021). Flowpath controls on high-spatial-resolution water-chemistry profiles in headwater streams. Hydrological Processes, 35(6), e14247. doi:https://doi.org/10.1002/hyp.14247

Dupas, R., Minaudo, C., & Abbott, B. W. (2019). Stability of spatial patterns in water chemistry across temperate ecoregions. Environmental Research Letters, 14(7), 074015. doi:10.1088/1748-9326/ab24f4

Durand, P., Breuer, L., Johnes, P. J., Billen, G., Butturini, A., Pinay, G., Van Grinsven, H., Garnier, J., Rivett, M., Reay, D. S. (2011). Nitrogen processes in aquatic ecosystems. In *European Nitrogen Assessment*. Cambridge University Press, Cambridge, pp. 126-146. ISBN 9781107006126 Available at http://centaur.reading.ac.uk/20855/.

Drewry, J., Newham, L., Greene, R., Jakeman, A., & Croke, B. (2006). A review of nitrogen and phosphorus export to waterways: context for catchment modelling. Marine and Freshwater Research, 57(8), 757-774.

Ebeling, P., Kumar, R., Weber, M., Knoll, L., Fleckenstein, J. H., & Musolff, A. (2021). Archetypes and Controls of Riverine Nutrient Export Across German Catchments. Water Resources Research, 57(4), e2020WR028134. doi:https://doi.org/10.1029/2020WR028134

Formatted: Font: 9 pt, Font color: Black

Eckhardt, K. (2008). A comparison of baseflow indices, which were calculated with seven different baseflow separation methods. Journal of Hydrology, 352(1), 168-173. doi:https://doi.org/10.1016/j.jhydrol.2008.01.005

Ehrhardt, S.; Kumar, R.; Fleckenstein, J. H.; Attinger, S.; Musolff, A. (2018). Decadal Trajectories of Nitrate Input and Output in Three Nested Catchments along a Land Use Gradient. Hydrol. Earth Syst. Sci. Discuss., 1–36. https://doi.org/10.5194/hess-2018-475.

Frost, A. J., Ramchurn, A., & Smith, A. (2016). The bureau's operational AWRA landscape (AWRA-L) Model. Retrieved from http://www.bom.gov.au/water/landscape/assets/static/publications/Frost__Model_Description_Report.pdf

Gelman, A., Carlin, J. B., Stern, H. S., Dunson, D. B., Vehtari, A., & Rubin, D. B. (2013). Bayesian Data Analysis, Third Edition: Taylor & Francis.

Godsey, S. E., Hartmann, J., & Kirchner, J. W. (2019). Catchment chemostasis revisited: Water quality responds differently to variations in weather and climate. Hydrological Processes, 33(24), 3056-3069. doi:https://doi.org/10.1002/hyp.13554

Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration–discharge relationships reflect chemostatic characteristics of US catchments. Hydrological Processes, 23(13), 1844-1864. doi:https://doi.org/10.1002/hyp.7315

Gorski, G., & Zimmer, M. A. (2021). Hydrologic regimes drive nitrate export behavior in human-impacted watersheds. Hydrol. Earth Syst. Sci., 25(3), 1333-1345. doi:10.5194/hess-25-1333-2021

Gu, S.; Gruau, G.; Dupas, R.; Rumpel, C.; Crème, A.; Fovet, O.; Gascuel-Odoux, C.; Jeanneau, L.; Humbert, G.; Petitjean, P. (2017). Release of Dissolved Phosphorus from Riparian Wetlands: Evidence for Complex Interactions among Hydroclimate Variability, Topography and Soil Properties. Sci. Total Environ., 598, 421–431. https://doi.org/10.1016/j.scitotenv.2017.04.028.

Guo, D., Lintern, A., Webb, J. A., Ryu, D., Liu, S., Bende-Michl, U., Leahy, P., Wilson, P., Western, A. W. (2019). Key Factors Affecting Temporal Variability in Stream Water Quality. Water Resources Research, 55(1), 112-129. doi:10.1029/2018wr023370

Guo, D., Lintern, A., Webb, J. A., Ryu, D., Bende-Michl, U., Liu, S. & Western, A. W. (2020). A data-based predictive model for spatiotemporal variability in stream water quality. *Hydrology and Earth System Sciences*, 24(2), pp. 827-847. doi:10.5194/hess-24-827-2020

Heiner M., Heaton M., Abbott B.W., White P., Minaudo C., & R., D. Model-based clustering of trends and cycles of nitrate concentrations in Rivers across France. Submitted to Journal of the Royal Statistical Society.

Herczeg, A., Dogramaci, S., & Leaney, F. (2001). Origin of dissolved salts in a large, semi-arid groundwater system: Murray Basin, Australia. Marine and Freshwater Research, 52(1), 41-52.

Field Code Changed

Formatted: Font: 9 pt, Font color: Black

Jensen, C. K., McGuire, K. J., McLaughlin, D. L., & Scott, D. T. (2019). Quantifying spatiotemporal variation in headwater stream length using flow intermittency sensors. Environmental Monitoring and Assessment, 191(4), 226. doi:10.1007/s10661-019-7373-8

Kennard, M. J., Pusey, B. J., Olden, J. D., Mackay, S. J., Stein, J. L., & Marsh, N. (2010). Classification of natural flow regimes in Australia to support environmental flow management. Freshwater Biology, 55(1), 171-193. doi:https://doi.org/10.1111/j.1365-2427.2009.02307.x

Kirchner, J. W., Feng, X., Neal, C., & Robson, A. J. (2004). The fine structure of water-quality dynamics: the (high-frequency) wave of the future. Hydrological Processes, 18(7), 1353-1359. doi:10.1002/hyp.5537

Knapp, J. L. A., von Freyberg, J., Studer, B., Kiewiet, L., & Kirchner, J. W. (2020). Concentration–discharge relationships vary among hydrological events, reflecting differences in event characteristics. Hydrol. Earth Syst. Sci., 24(5), 2561-2576. doi:10.5194/hess-24-2561-2020

Ladson, A. R., Brown, R., Neal, B., & Nathan, R. (2013). A standard approach to baseflow separation using the Lyne and Hollick filter. Australasian Journal of Water Resources, 17(1), 25-34.

Li, L., Bao, C., Sullivan, P. L., Brantley, S., Shi, Y., & Duffy, C. (2017). Understanding watershed hydrogeochemistry: 2. Synchronized hydrological and geochemical processes drive stream chemostatic behavior. Water Resources Research, 53(3), 2346-2367. doi:https://doi.org/10.1002/2016WR018935

Lintern, A., Webb, J.A., Ryu, D., Liu, S., Bende-Michl, U., Waters, D., Leahy, P., Wilson, P., Western, A.W., (2018). Key factors influencing differences in stream water quality across space. Wires Water 51, e1260.

Lintern, A., Liu, S., Minaudo, C., Dupas, R., Guo, D., Zhang, K., Bende-Michl, U., Duvert, C. (~~in review). Climate controls~~2021). The influence of climate on water chemistry states and dynamics in rivers across Australia. ~~Submitted to~~ Hydrological Processes, e14423. doi:https://doi.org/10.1002/hyp.14423

Liu, S., Ryu, D., Webb, J. A., Lintern, A., Guo, D., Waters, D. & Western, A. W. (2021). A Bayesian approach to understanding the key factors influencing temporal variability in stream water quality - a case study in the Great Barrier Reef catchments. *Hydrology and Earth System Sciences*, 25(5), pp. 2663-2683. doi:10.5194/hess-25-2663-2021

~~Liu, S., Lintern, A., Minaudo, C., Dupas, R., Guo, D., Zhang, K., Bende-Michl, U., Duvert, C. (in preparation). Key factors affecting differences in spatial differences in water quality across Australian continent.~~

Lyne, V., & Hollick, M. (1979). Stochastic time-variable rainfall-runoff modelling. Paper presented at the Institute of Engineers Australia National Conference.

Formatted: Font: 9 pt, Font color: Black

McGuire, K. J., Torgersen, C. E., Likens, G. E., Buso, D. C., Lowe, W. H., & Bailey, S. W. (2014). Network analysis reveals multiscale controls on streamwater chemistry. Proceedings of the National Academy of Sciences, 111(19), 7030-7035. doi:10.1073/pnas.1404820111

Minaudo, C., Dupas, R., Gascuel-Odoux, C., Roubeix, V., Danis, P.-A., & Moatar, F. (2019). Seasonal and event-based concentration-discharge relationships to identify catchment controls on nutrient export regimes. Advances in Water Resources, 131, 103379. doi:https://doi.org/10.1016/j.advwatres.2019.103379

Moatar, F., Abbott, B. W., Minaudo, C., Curie, F., & Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. Water Resources Research, 53(2), 1270-1287. doi:10.1002/2016wr019635

Moatar, F., Floury, M., Gold, A. J., Meybeck, M., Renard, B., Ferréol, M., et al. (2020). Stream Solutes and Particulates Export Regimes: A New Framework to Optimize Their Monitoring. Frontiers in Ecology and Evolution, 7(516). doi:10.3389/fevo.2019.00516

Musolff, A., Schmidt, C., Selle, B., & Fleckenstein, J. H. (2015). Catchment controls on solute export. Advances in Water Resources, 86, 133-146. doi:https://doi.org/10.1016/j.advwatres.2015.09.026

Musolff A:, Q. Zhan, R. Dupas, C. Minaudo, J. H. Fleckenstein, M. Rode, ~~et al.~~J. Dehaspe, K. Rinke, Spatio-temporal Variability in Concentration-Discharge Relationships at the Event Scale. ~~Under review in~~ Water Resources Research~~.~~, 57(10), e2020WR029442. doi:https://doi.org/10.1029/2020WR029442

Nash, J. E., & Sutcliffe, J. V. (1970). River flow forecasting through conceptual models part I — A discussion of principles. Journal of Hydrology, 10(3), 282-290. doi:https://doi.org/10.1016/0022-1694(70)90255-6

Nathan, R. J., & McMahon, T. A. (1990). Evaluation of automated techniques for base flow and recession analyses. Water Resources Research, 26(7), 1465-1473. doi:https://doi.org/10.1029/WR026i007p01465

Rode, M., Wade, A. J., Cohen, M. J., Hensley, R. T., Bowes, M. J., Kirchner, J. W., et al. (2016). Sensors in the Stream: The High-Frequency Wave of the Present. Environmental Science & Technology, 50(19), 10297-10307. doi:10.1021/acs.est.6b02155

Rusjan, S., Brilly, M., & Mikoš, M. (2008). Flushing of nitrate from a forested watershed: An insight into hydrological nitrate mobilization mechanisms through seasonal high-frequency stream nitrate dynamics. Journal of Hydrology, 354(1), 187-202. doi:https://doi.org/10.1016/j.jhydrol.2008.03.009

Stackpoole, S. M.; Stets, E. G.; Sprague, L. A. (2019). Variable Impacts of Contemporary versus Legacy Agricultural Phosphorus on US River Water Quality. Proc. Natl. Acad. Sci., 201903226. https://doi.org/10.1073/pnas.1903226116.

Formatted: Font: 9 pt, Font color: Black

Stan Development Team. (2018). RStan: the R interface to Stan. R package version 2.18.1.

Sturtz, S., Ligges, U., & Gelman, A. E. (2005). R2WinBUGS: a package for running WinBUGS from R.

Thompson, S. E., Basu, N. B., Lascurain Jr., J., Aubeneau, A., & Rao, P. S. C. (2011). Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. Water Resources Research, 47(10). doi:https://doi.org/10.1029/2010WR009605

Tunqui Neira, J. M., Andréassian, V., Tallec, G., & Mouchel, J. M. (2020a). Technical note: A two-sided affine power scaling relationship to represent the concentration–discharge relationship. Hydrol. Earth Syst. Sci., 24(4), 1823-1830. doi:10.5194/hess-24-1823-2020

Tunqui Neira, J. M., Tallec, G., Andréassian, V., & Mouchel, J.-M. (2020b). A combined mixing model for high-frequency concentration–discharge relationships. Journal of Hydrology, 591, 125559. ~~doi:https://doi.org/10.1016/j.jhydrol.2020.125559~~doi:https://doi.org/10.1016/j.jhydrol.2020.125559

von Freyberg, J., Allen, S. T., Seeger, S., Weiler, M., & Kirchner, J. W. (2018). Sensitivity of young water fractions to hydro-climatic forcing and landscape properties across 22 Swiss catchments. Hydrol. Earth Syst. Sci., 22(7), 3841-3861. doi:10.5194/hess-22-3841-2018

Van Meter, K. J.; Basu, N. B.; Van Cappellen, P. (2017). Two Centuries of Nitrogen Dynamics: Legacy Sources and Sinks in the Mississippi and Susquehanna River Basins. Global Biogeochem. Cycles, 31 (1), 2–23. https://doi.org/10.1002/2016GB005498.

Webb, J. A., & King, L. E. (2009). A Bayesian hierarchical trend analysis finds strong evidence for large-scale temporal declines in stream ecological condition around Melbourne, Australia. Ecography, 32(2), 215-225. doi:doi:10.1111/j.1600-0587.2008.05686.x

Zhang, J., Zhang, Y., Song, J., & Cheng, L. (2017). Evaluating relative merits of four baseflow separation methods in Eastern Australia. Journal of Hydrology, 549, 252-263. ~~doi:https://doi.org/10.1016/j.jhydrol.2017.04.004~~doi:https://doi.org/10.1016/j.jhydrol.2017.04.004

Zhang, Q. (2018). Synthesis of nutrient and sediment export patterns in the Chesapeake Bay watershed: Complex and non-stationary concentration-discharge relationships. Science of The Total Environment, 618, 1268-1283. doi:https://doi.org/10.1016/j.scitotenv.2017.09.221

Zhi, W., Li, L., Dong, W., Brown, W., Kaye, J., Steefel, C., et al. (2019). Distinct Source Water Chemistry Shapes Contrasting Concentration-Discharge Patterns. Water Resources Research, 55(5), 4233-4251. doi:https://doi.org/10.1029/2018WR024257

Formatted: Font: 9 pt, Font color: Black