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The influence of climate on water chemistry states and dynamics in rivers across Australia

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Abstract

For effective water quality management and policy development, spatial variability in the mean concentrations and dynamics of riverine water quality needs to be understood. Using water chemistry (calcium, electrical conductivity, nitrate-nitrite, soluble reactive phosphorus, total nitrogen, total phosphorus and total suspended solids) data for up to 578 locations across the Australian continent, we assessed the impact of climate zones (arid, Mediterranean, temperate, subtropical, tropical) on (i) inter-annual mean concentration and (ii) water chemistry dynamics as represented by constituent export regimes (ratio of the coefficients of variation of concentration and discharge) and export patterns (slope of the concentration-discharge relationship). We found that inter-annual mean concentrations vary significantly by climate zones and that spatial variability in water chemistry generally exceeds temporal variability. However, export regimes and patterns are generally consistent across climate zones. This suggests that intrinsic properties of individual constituents rather than catchment properties determine export regimes and patterns. The spatially consistent water chemistry dynamics highlights the potential to predict riverine water quality across the Australian continent, which can support national riverine water quality management and policy development.

Highlights

- Continental scale analysis of water chemistry across 5 climate zones in Australia
- Significantly different mean concentrations across climate zones
- No clear variation of water chemistry dynamics across climate zones
- Spatial variability in water chemistry generally exceeds temporal variability

1. Introduction

Surface water quality can degrade due to both local human activities and global climate change (Michalak, 2016; Schwarzenbach et al., 2010). Degradation of surface water quality poses risks on aquatic ecosystem health, and often affects social and economic development (Jiang, 2009; Vörösmarty et al., 2010). Monitoring and management of surface water quality is critical for maintaining and improving healthy ecosystems as well as supporting human life and sustainable economies.

Surface water quality varies greatly across both space and time (Chang, 2008; Guo et al., 2020, 2019). This variability can pose a fundamental challenge to developing and implementing effective water quality management policies and strategies. It is therefore crucial to understand principles and changes in average water quality and dynamics across large spatial scales. Water quality dynamics can be represented by quantifying the relationship between constituent concentrations (C) and discharge (Q). Several metrics can be used to represent constituent dynamics. Two examples are: (i) the coefficients of variation of concentration divided by that of discharge (CV ratio) (Thompson et al., 2011), which informs constituent export regimes; and (ii) the rate of change in the constituent concentration compared to the rate of change in discharge (C-Q slope) (Godsey et al., 2009), which informs constituent export patterns.

Previous studies of CV ratios suggested that most constituents exhibit chemostatic export regimes (Musolff et al., 2015). Chemostatic export regimes are those where concentrations vary less than discharge over time. For geogenic constituents, it has been suggested that their chemostatic export regimes are due to large stores of constituents in the catchment (Godsey et al., 2009; Thompson et al., 2011). The chemostatic export regime for anthropogenic nutrients in intensively managed catchments is hypothesised to be due to the presence of legacy nutrient stores in the catchment (Basu et al., 2010; Van Meter et al., 2016). Some constituents exhibit chemodynamic export regimes. Chemodynamic export regimes of nutrients and sediments have been attributed to catchments with point sources, large temporal variability in dilution capacity, agricultural activities that lead to nutrient accumulation in topsoils and human activities that result in increased erosion (Mellander et al., 2015; Ockenden et al., 2016).

The C-Q slope of constituents can be impacted by: (i) the spatial distribution of constituent sources within a catchment, and (ii) the transport process (flow path) of that constituent (Fazekas et al., 2020;

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Zhi et al., 2019). The C-Q slope is positive when concentration increases with increasing flows, indicating 'flushing' behaviour. This generally occurs when there are non-point constituent sources originating from 'shallow' sources (Abbott et al., 2018; Botter et al., 2020; Musolff et al., 2017). When the C-Q slope is negative, concentration decreases with increasing flows, indicating 'diluting' behaviour (Godsey et al., 2009). This is commonly observed for constituents originating from point sources (Bowes et al., 2015; Greene et al., 2011), or for 'deep' non-point constituent sources (Abbott et al., 2018; Botter et al., 2020; Musolff et al., 2017). C-Q slopes need to be interpreted with some caution because in-stream biogeochemical transformations can also affect the magnitude and direction of C-Q slopes. For example, in-stream biogeochemical transformations during low flows have been found to result in positive C-Q slopes, particularly for nutrients because processes such as nutrient uptake and denitrification often occur under low flow conditions (Casquin et al., 2020; Minaudo et al., 2019; Moatar et al., 2017).

It is relatively straight-forward to investigate spatial variability in average constituent concentrations over catchments or drainage divisions. However, investigations of spatial variability of constituent dynamics across large spatial scales (e.g., continental-scale) are less common. Such assessments are needed to provide critical information for managing water quality across large administrative jurisdictions. Previous studies and monitoring programs have addressed spatial variability in constituent concentrations and constituent dynamics over large geographical areas, including regional and national scales (Botter et al., 2020; Ebeling et al., 2021; Godsey et al., 2019; Guillemot et al., 2020; Lintern et al., 2018; Liu et al., 2021, 2018; Minaudo et al., 2019). We add to this growing body of work by examining constituent concentrations and dynamics consistently across a wide range of latitudes and climates.

In this study, we investigate the relationship between a range of climate zones and water chemistry states and dynamics in rivers across the entire Australian continent. We focus on calcium, electrical conductivity, nitrate-nitrite, soluble reactive phosphorus, total nitrogen, total phosphorus and total suspended solids. Our key objectives are to (i) identify the spatial variability in mean water chemistry concentrations at a continental scale and across climate zones; and (ii) identify the variability in export regimes and export patterns at a continental scale using C-Q relationships (CV ratios and C-Q slopes). We hypothesise that there will be strong variability in both mean concentrations and water chemistry dynamics across climate zones.

In addition, there are challenges with using large datasets to investigate spatial variability in constituent concentrations and dynamics over large spatial scales. Analyses that consider a large variety of correlated variables (e.g., strong correlations between land use and topography) sometimes lead to difficulty in identifying the key drivers of water quality variability. Integrative variables such as climate indices could be adopted as an alternative to using multiple correlated variables when studying the key drivers underlying spatial variability in water quality. This is because other possible direct drivers of water quality such as land use or population density are highly influenced by climate properties (Abbott et al., 2016; Lintern et al., 2018; Mellander et al., 2018; Thomas et al., 2016). Furthermore, climate indices can be a strong indicator of rainfall patterns, which drive the rainfall-runoff processes that underpin constituent mobilisation and transport (Lintern et al., 2018).

Australia contains most of the Earth's climate zones. Therefore, conclusions from a continental-scale analysis of Australia may have implications for other regions of the world. This continental-scale analysis will reveal how mean water quality states and dynamics change across such a wide range of

climate zones. We envisage that this work can add significant new knowledge to catchment water quality both within Australia and internationally.

2. Methods

2.1 Water quality and flow data collation

Water chemistry (concentration) and discharge (Q) data were obtained from publicly available water monitoring databases managed by seven state and territory agencies across Australia. These included: the Department of Land, Water and Planning (Victoria) (Department of Environment, Land, Water & Planning, 2021); WaterNSW (New South Wales) (WaterNSW, 2021); Department of Resources and Department of Environment and Science (Queensland) (Queensland Government, 2021); Department for Water and Environment (South Australia) (Government of South Australia, 2021); Department of Water and Environmental Regulation (Western Australia) (Government of Western Australia Department of Water and Environmental Regulation, 2021); Department of Primary Industries, Parks, Water and Environment (Tasmania) (DPIPWE, 2021) and Department of Environment, Parks and Water Security (Northern Territory) (Government of Northern Territory, 2021). Details on monitoring and analytical methods for each state are available in the Supplementary Materials (File S2). For all states, water chemistry was analysed by National Association of Testing Authorities (NATA) accredited laboratories following standard methods.

This paper focuses on seven major water quality constituents. The seven constituents are: calcium (Ca^{2+} in mg/L (referred to as Ca from hereon in); 253 sites), electrical conductivity in μS/cm (EC; 515 sites), the sum of nitrate (NO_3^-) with nitrite (NO_2^-) in terms of mg/L nitrogen (NO_x; 197 sites), soluble reactive phosphorus in mg/L (SRP; 183 sites), total nitrogen in mg/L (TN; 234 sites), total phosphorus in mg/L (TP; 328 sites), and total suspended solids in mg/L (TSS; 408 sites). These constituents were selected because: (i) they are constituents of concern for the Australian environment (Bartley et al., 2012; Prosser, 2011; Sarker et al., 2008; Water Quality Australia, 2018); and/or (ii) they have a sufficient number of sites with at least 50 pairs of water quality and discharge data (referred to as 'C-Q pairs' from hereon in) and a reasonably good coverage across all climate zones. Only sites with at least 50 pairs of water quality and discharge data were selected based on an assessment of the effect of sample size on the robustness of our estimates (see further details in Supplementary Text S1). In selecting the constituents, we also made sure that both dissolved and particulate constituents were included, representing different sources and pathways (i.e. nutrients, sediment, ions). For each monitoring site for the abovementioned seven variables, we also obtained the corresponding available daily streamflow data from the same seven state agencies as listed above.

The mean number of C-Q pairs used for each constituent and the mean length of the time series are provided in Table S2 (Supplementary Materials). We did not set a minimum or maximum length of the water quality time series in the selection of data, and the length of the time series ranges from 4 to 47 years (Table S2, Supplementary Materials). Figure 1a shows the locations of the sites included for EC, which is the constituent for which we have the largest number of sites.

Figure 1: Map showing the location of sampling sites for EC in Australia included in data analysis on a map of the Köppen-Geiger Climate Classification (a). Map showing mean constituent concentrations for each site for Ca mg/L (b), EC μS/cm (c), NO_x -N mg/L (d), SRP mg/L, (e), TN mg/L (f), TP mg/L (g), TSS mg/L (h). In (a), 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. Maps showing site locations, mean concentrations, C-Q slopes and CV ratios for all seven constituents are provided in Figures S1 to S7 in Supplementary Materials.

For the water chemistry and discharge database we masked all discharge and concentration data associated with poor quality codes, following recommendations from the state-based data collection agencies (Table S1 of the Supplementary Materials). This included removal of both concentration and discharge data with high uncertainty (typically >20%) and of any water quality records at missing flows. All concentration data below the limit of detection for a given constituent were assigned values of half of the limit of detection (Helsel, 1990). The proportion of water quality samples below the limit of detection were: 0.2% for Ca, 0% for EC, 8% for NO_x, 28% for SRP, 2% for TN, 6% for TP and 20% for TSS.

2.2 Catchment delineation and climate zones

Catchment boundaries for each of the monitoring sites were determined using the Australian Bureau of Meteorology's Geofabric and the Geofabric toolset (Bureau of Meteorology, 2012). For each site we identified the dominant climate class of the catchment based on the Köppen-Geiger Climate Classification (Beck et al., 2018). The dominant climate class was found by aggregating gridded climate data for each catchment and then selecting the major climate class within the catchment, as shown in Figure 1a). We then grouped climate classes into five broad climate zones, i.e. arid (*Bwh*, *Bwk*, *Bsh* and *Bsk*), Mediterranean (*Csa* and *Csb*), temperate (*Cfb* and *Cfc*), subtropical (*Cfa* and *Cwa*) and tropical (*Af*, *Am* and *Aw*). Catchment areas ranged from 0.9 km^2 to 888,682 km^2. The percentage agriculture land use of the catchments range from 0 to 100% with a median of 0.7% (Geoscience Australia, 2011). The percentage urbanisation of the catchments range from 0 to 71% with a median of 0.07% (Geoscience Australia, 2011).

2.3 Data analysis

For the 578 sites included in this study and for each of the seven constituents, we extracted three key measures of water chemistry. These were: mean concentration, the ratio of the coefficients of variation of concentration and discharge to characterise export regimes (referred to as the CV ratio from hereon in), and the C-Q slope to characterise export patterns. The C-Q slopes were calculated using a linear regression of the log-transformed concentration and discharge data (Equation 1), following Godsey et al. (2009) and Musolff et al. (2015).

$$\ln(C) = a + b \ln(Q) \hspace{3cm} \text{Equation 1}$$

The parameter *b* from Equation 1 was then adopted as the C-Q slope for each site and for each constituent. Following the method proposed by Musolff et al. (2015), we plotted the C-Q slopes against the CV ratio (e.g., Figure 2) to better understand the interaction between discharge and water quality, and the spatial variability in these relationships. CV ratios below 0.5 indicate 'chemostatic' export regimes, where the variability in water chemistry is less than half the variability in flow. CV ratios above 0.5 indicate 'chemodynamic' regimes (Figure 2) (Ebeling et al., 2021; Musolff et al., 2017).

Figure 2: Relationship between CV ratios (export regimes) and CQ slopes (export patterns). Adapted from Musolff et al. (2015).

To assess whether climate is an important driver of water quality across Australian rivers, we explored the relationship between climate zones and the mean concentration, CV ratios and C-Q slopes using the Kruskal-Wallis test ($\alpha=0.05$) (Kruskal and Wallis, 1952). This non-parametric test was used to assess the differences in the distributions of water quality data from different climate zones because the data did not satisfy the assumptions of normality (assessed using the Shapiro-Wilk test) (Shapiro and Wilk, 1965) and homoscedasticity (assessed using Levene's Test) (Levene, 1960). A Dunn's post-hoc test (Dunn, 1964) ($\alpha=0.05$) was conducted for pairwise comparisons between climate zones. Studying the relationship between climate and water quality is important not only to identify spatial patterns in water quality processes, but also because climate determines many other key catchment attributes that impact water quality such as land use and population density.

3. Results and discussion

3.1 Spatial variability in mean water quality concentrations across Australia

Mean constituent concentrations vary substantially across the Australian continent. Higher concentrations are generally found in the central east coast, inland eastern Australia and the west coast (Figure 1). This spatial variability appears to follow the climate zones (Figure 3), with statistically significant ($p<0.05$) differences in mean concentrations between climate zones for all constituents (Figure 3, Table 1). In addition, there are strong negative Spearman correlations ($|\rho|>0.5$) between the mean constituent concentration and catchment slope (EC, SRP and TN) and catchment average rainfall (TN, EC and Ca); and strong positive Spearman correlations ($|\rho|>0.5$) between the mean constituent concentration and catchment average temperature (TSS, TP, SRP, Figure S11 in the Supplementary Materials). These catchment characteristics have strong cross-correlations (Spearman rank correlations), with the catchment slope being cross-correlated with catchment rainfall ($|\rho|>0.5$). These results justify our focus on climate zones as a key driver governing spatial water quality variability.

Ca and EC concentrations tend to be higher in catchments within a Mediterranean climate zone (means of 43.2 mg/L and 3819 µS/cm) (Figure 3). Indeed, there are generally significant pairwise differences for Ca and EC between Mediterranean catchments and other climate zones. The higher concentrations of Ca and EC in the Mediterranean catchments could be a result of lower rainfall and thus less flow to dilute constituents. Mediterranean climates have the second lowest rainfall levels, with a mean of 779 mm (Figure S8, Supplementary Materials). The higher relative proportion of subsurface flows could mobilise salts and bedrock-derived constituents such as Ca into streams (Caruso, 2002; Tomaz et al., 2020).

For Ca and EC, the tropical zones of northern Australia tend to have lower concentrations compared to the other climate zones (Figure 3, Table 1). This is likely related to the high rainfall rates in the tropics that may result in significant dilution of constituents in rivers (Liu et al., 2021, 2018). Mean rainfall across tropical catchments is higher than the other climate zones at approximately 1,444 mm (2.5th percentile of 857 mm and 97.5th percentile of 2,674 mm). In addition to the likely dilution of constituents due to high river flow, the lower constituent concentrations observed in tropical rivers might also be related to lower availability in the subsurface. Intensely weathered soils are typical of the tropics and particularly of tropical savannahs (Pellegrini, 2016; Reich and Oleksyn, 2004; Wright et al., 2011).

TSS and TP concentrations are highest in arid regions, with mean concentrations of 193 mg/L and 0.20 mg/L, respectively (Figure 3, Table 1). The high TSS concentration is likely due to the high levels of erosion and particulate transport during the occasional, high-intensity rainfall events occurring in these regions. The low vegetation cover of arid regions may further explain these high rates of erosion (Green et al., 2007). It is also important to note that in the arid region, a significant part of the water quality measurements were obtained during high flow events due to the highly intermittent nature of these systems (Sheldon et al., 2010) (Figure S9 in the Supplementary Materials), potentially biasing our analysis towards higher concentrations due to enhanced flushing during event periods. The high TP in arid regions could be indicating that the TP is of geogenic origin and as a result of erosion (Lintern et al., 2018; Nhiwatiwa and Dalu, 2017). Indeed, the SRP:TP ratio is less than 0.5 for arid climates (Figure S10 in the Supplementary Materials), indicating that a large proportion of TP is particulate-bound. In addition, mean TSS and mean TP at each site are strongly correlated (Spearman) with each other in the arid catchments ($\rho=0.81$, $p<0.05$).

Subtropical catchments have relatively higher levels of TSS and TP (means of 63 mg/L and 0.18 mg/L, respectively) compared to the other non-arid climate zones (Figure 3). Subtropical catchments can appear to have high levels of agricultural activities (mean of 4.6% of the catchment used for agricultural activities and 2.5th and 97.5th percentiles of 9 and 26%) (Figure S8, Supplementary Materials). They also have higher levels of total P in the soil (mean of 0.46 %) (Viscarra Rossel et al., 2014) (Figure S8, Supplementary Materials).

TSS and TP are low in streams in temperate regions (means of 16.8 mg/L and 0.09 mg/L, respectively) (Figure 3). Most of the temperate catchments included in the analysis are clustered around the high-elevation areas of the Australian Alps (Victoria) and Tasmania. These catchments are less impacted by agricultural activities (average of 1.9%; 2.5th and 97.5th percentiles of 0 and 11.1%) and appear to have lower levels of soil TP (mean of 0.035%) (Viscarra Rossel et al., 2014). Dunn's pairwise comparisons show that there are statistically significant differences in mean SRP concentrations between the temperate climate zone and the others (Table 1), with the lowest levels of SRP in the temperate zone (Figure 3). This is likely due to mechanisms similar to those responsible for the low TSS and TP concentrations in temperate streams - the low level of agricultural activities and lower levels of soil TP (Figure S8, Supplementary Materials).

There are higher NO_x and TN concentrations in catchments within a Mediterranean climate zone (means of 0.41 mg/L and 1.13 mg/L) (Figure 3). Mean NO_x and TN concentrations in Mediterranean catchments differ statistically significantly from all other climate zones (Table 1). This could be due to the importance of agricultural land use in these catchments (average of 9.5%; 2.5th percentile of 0% and 97.5th percentile of 97.6%). The lowest TN concentrations appear to be occurring in the temperate catchments, with statistically significant differences between TN concentrations in the temperate catchments and arid, Mediterranean and subtropical catchments. This is likely due to the low level of agricultural activities in temperate catchments (Figure S8, Supplementary Materials).

Figure 3: Variability in mean constituent concentrations for each climate zone. Results of Kruskal-Wallis test (p-values) to identify statistically significant variability in mean constituent concentrations across climate zones shown above each boxplot. n in x axis denotes the number of monitoring sites included in each boxplot. Abbreviations are: Arid (arid), Med (Mediterranean), Tem (temperate), Sub (subtropical), Tro (tropical). Boxes represent the interquartile range, whiskers represent 1.5 times

the interquartile range, the dots represent outliers, the black line represents the median and the black dots represent the mean.

Table 1: Pairwise comparison of catchment mean concentration between climate zones using Dunn's post-hoc test. Statistically significantly different catchment mean concentrations between specific climate zone pairs are indicated by grey shading (p<0.05).

Climate Zone Pair	Constituent						
	Ca	EC	NO$_x$	SRP	TN	TP	TSS
Arid-Mediterranean		▓				▓	▓
Arid-Subtropical		▓			▓	▓	▓
Arid-Temperate	▓	▓		▓	▓	▓	▓
Arid-Tropical	▓	▓			▓		▓
Mediterranean-Subtropical		▓	▓			▓	▓
Mediterranean-Temperate	▓	▓	▓	▓	▓	▓	
Mediterranean-Tropical	▓	▓	▓		▓	▓	▓
Subtropical-Temperate	▓	▓		▓	▓	▓	
Subtropical-Tropical	▓	▓					▓
Temperate-Tropical	▓	▓				▓	▓

The comparison of mean constituent concentrations across the climate zones indicates that there appear to be systematic differences between climate zones. This may be driven not just by the rainfall and temperature in these climatic zones, but also catchment characteristics that cross-correlate with climate. For example, climate can impact human activities in catchments as well as soil properties (Figure S8, Supplementary materials).

In terms of overall findings, Mediterranean catchments have the highest concentrations of four out of the seven investigated constituents: Ca, EC, NO$_x$ and TN. This is likely driven by low rainfall (for Ca and EC), with the likely transport of weathered Ca and salts via subsurface flow paths (Godsey et al., 2019). In addition, arid catchments have high TP and TSS concentrations. Previous studies have hypothesised that the lack of vegetation in arid areas results in high erosion rates, and the transport of

sediments and particulate phosphorus to receiving waters (Green et al., 2007). The high concentrations of TN and NO$_x$ in Mediterranean catchments may be driven by the relatively high agricultural activity in these catchments (Figure S8, Supplementary Materials). Similarly, temperate catchments tend to have lower concentrations of TSS, TP, SRP, NO$_x$ and TN. This is likely due to the low level of agricultural activities in this region, a result of the high slopes and colder climate (Figure S8, Supplementary materials). This indicates that at the national scale, Mediterranean catchments may be key areas of risk of high constituent concentrations. In fact, it appears that two of the climate zones with the least number of monitoring sites (arid and Mediterranean catchments) have the highest mean constituent concentrations, indicating that resources may need to be shifted to focus future monitoring efforts on these catchments.

These findings are in line with previous studies of national-scale spatial variability in water quality. These studies have found that in general, land use and lithology most strongly correlate to long-term means in water chemistry (Ebeling et al., 2021; Godsey et al., 2019; Guillemot et al., 2020). In addition, a study of 787 catchments in Germany, Ebeling et al., (2021) found correlations between climate and long-term means in NO$_x$ concentrations. As such, it appears that previous studies have identified both land use and climate as key drivers of spatial variability in water quality. In our study, we find that there appear to be systematic differences in long-term mean water chemistry across climate zones, which is likely driven by land use and land cover differences.

3.2 Spatial variability in export regimes and patterns across the Australian continent
3.2.1: Export regimes
The variability in constituent concentrations appears to be greater over space than over time (Figure 4). This is consistent with previous findings, which also identified greater variability across space in constituent concentrations (Botter et al., 2020; Dupas et al., 2019; Gu et al., 2021). The greater variability in water chemistry across space suggests that implementing a larger number of routine water quality monitoring stations would allow us to understand water quality processes and trends better than increasing the number of samples taken at a single site. Further work is required to explore the relative importance of spatial versus temporal variability at different spatial and temporal scales to better understand optimal water quality monitoring strategies to capture inherent variability.

Figure 4: Comparison between variability in constituent concentrations over time and space. 'Spatial CV' indicates the spatial coefficient of variation determined monthly across all sites located in a given climate zone, and 'Temporal CV' represents the coefficient of variations determined for each site. Markers represent the mean, and error bars represent the interquartile range.

Whilst there is some variability in CV ratios within each climate zone, the export regime of constituents (chemostatic vs chemodynamic) is the same regardless of the climate (Table 2, Figure S12). Solutes (EC and Ca) exhibit chemostatic behaviour (CV ratio<0.5) across all climate zones, indicating that the variability in constituent concentration is less than the variability in Q (Table 2, Figure S12). Previous studies have also observed chemostatic behaviour for constituents such as Ca (Botter et al., 2020; Duncan et al., 2017; Foks et al., 2018; Rose et al., 2018). This has been attributed to large stores of these constituents available for transport in the aquifer or bedrock (Godsey et al., 2019, 2009; Hunsaker and Johnson, 2017; Musolff et al., 2015). These previous studies have all been

conducted in largely temperate climates, and our study confirms that these chemostatic export regimes for these constituents also occur in other climate zones.

Some nutrients (TP, TN, SRP) also have a chemostatic export regime in either temperate, Mediterranean or subtropical climate zones. High levels of anthropogenic activities such as agriculture and urbanisation can lead to large nutrient stores in the catchment (Basu et al., 2010; Van Meter et al., 2016). Indeed, the temperate, Mediterranean and subtropical catchments that we studied have high levels of soil nutrients (TP), agriculture and urbanisation (Figure S8, Supplementary Materials).

Previous studies have found that chemodynamic behaviour occurs in catchments when the hydrologic connection between constituent stores and rivers vary over time (Hoagland et al., 2017). TSS and NO_x show chemodynamic export regimes across all climate zones (Table 2, Figure S12). This is a export regime for TSS identified in previous European studies (Mellander et al., 2015; Musolff et al., 2015; Ockenden et al., 2016). Previous studies have found that NO_x can demonstrate chemostatic properties (e.g., Long et al., 2014), however our study found that NO_x has chemodynamic export regimes in Australia. The chemodynamic behaviour of NO_x may be indicating that the agricultural land uses in Australia are not as intensely managed as in other countries. In addition, Australia has a shorter history of agricultural intensification and this may be resulting in less legacy stores of NO_x in the soils and groundwater. With less consistent NO_x stores throughout the catchments, NO_x export can vary from storm to storm, depending on spatial rainfall patterns of a particular storm and the flow pathways that are activated during specific events.

Table 2: Percentage of sites exhibiting dilution behaviour (C-Q slope<0) and chemostatic behaviour (CV ratio <0.5) within each constituent-climate zone category for each constituent (bold and italic text indicates where this occurs for over 50% monitoring sites within a constituent-climate zone category). Total number of sites for each climate zone-constituent category provided in parentheses.

EXPORT REGIME Chemostatic behaviour (CV ratio < 0.5)					
	Climate Zone				
Constituent	**Arid**	**Mediterranean**	**Temperate**	**Subtropical**	**Tropical**
Ca	*96% (24)*	*97% (29)*	*82% (39)*	*95% (128)*	*94% (33)*
EC	*88% (52)*	*97% (117)*	*89% (149)*	*95% (257)*	*90% (49)*
NO$_x$	7% (15)	27% (39)	38% (98)	29% (35)	11% (19)
SRP	40% (10)	29% (42)	34% (116)	*80% (20)*	0% (18)
TN	47% (43)	*79% (61)*	*79% (66)*	*88% (65)*	*56% (18)*
TP	*50% (24)*	23% (48)	*56% (170)*	*64% (67)*	26% (19)
TSS	38% (24)	19% (52)	25% (138)	33% (132)	38% (47)
EXPORT PATTERN Dilution behaviour (C-Q slope < 0)					
	Climate Zone				
Constituent	**Arid**	**Mediterranean**	**Temperate**	**Subtropical**	**Tropical**
Ca	*96% (24)*	*66% (29)*	*90% (39)*	*92% (128)*	*97% (33)*
EC	*98% (53)*	*92% (117)*	*90% (149)*	*96% (257)*	*98% (49)*
NO$_x$	20% (15)	15% (39)	8% (98)	11% (35)	26% (19)
SRP	10% (10)	29% (42)	20% (116)	0% (18)	0% (18)
TN	13% (24)	10% (61)	8% (66)	6% (65)	11% (18)
TP	13% (24)	19% (48)	23% (170)	6% (67)	5% (19)
TSS	29% (24)	15% (52)	9% (138)	4% (132)	0% (47)

3.2.2: Export patterns

There are statistically significant differences in C-Q slopes across climate zones for four out of the seven constituents (NO_x, SRP, TP and TSS) (Figure 5, Table S3 in Supplementary materials). For example, there appears to be a trend of increasing C-Q slopes for SRP from arid to tropical catchments (Figure 5). This suggests that the shift from drier to wetter catchments is leading to a change in SRP transport to be more flushing dominated. In a study of over 2000 catchments, Godsey et al. (2019) found that CQ slopes for solutes were steeper in humid catchments compared to arid catchments, which was attributed to the fact that arid catchments have greater 'buffering capacity' and are able to retain constituents within the catchments more readily due to the lower rainfall. Previous studies have also suggested that export patterns of solutes, particulates and nutrients may be driven by changes in constituent transport by shallow flow pathways compared to deeper flow pathways (Botter et al., 2020; Ebeling et al., 2021). This is largely due to the fact that the constituent concentrations on the surface, in shallow soils or deeper soils can vary depending on modern and historical land use. This may explain the statistically significant differences seen in the CQ slopes across climate zones for NO_x and TSS.

However, the signs of the C-Q slopes for all constituents do not appear to be climate-related (Figure 5). Indeed, individual constituents do not shift from dilution (C-Q slope <0) to flushing behaviour (C-Q slope >0) across climate zones (Table 2), indicating that the export pattern of a constituent is consistent across all climate zones. This suggests that for a given particulate or dissolved constituent, the fundamental sources and transport processes are consistent across the continent. This is in contrast to previous studies in other parts of the world that have found that C-Q slopes of constituents can vary across space, with this variability largely driven by land use (Fazekas et al., 2020; Musolff et al., 2015; Zhi and Li, 2020). We hypothesise however that we may see relationships between C-Q slopes and catchment characteristics such as land use within each of the climate zones. As such, further work is required to untangle the key catchment drivers that lead to the spatial variability in C-Q slopes seen within each climate zone.

C-Q slopes are negative for Ca and EC for over 80% of sites in all climate zones (except for Mediterranean climates) (Figure 5 and Table 2). This indicates that these constituents exhibit dilution patterns at most of the monitoring sites across Australia. Previous studies have found that Ca and EC typically have higher concentrations at low flow (Li et al., 2017; Moatar et al., 2017; Zhi et al., 2019) and that this dilution behaviour is consistent across space and time for these constituents (Li et al., 2017). According to Zhi and Li (2020) a negative C-Q slope indicates a dominance of deep groundwater flow pathways of these constituents. The lower percentage of dilution patterns observed in Mediterranean catchments for Ca and EC may be related to high evapotranspiration rates that can lead to high solute concentration in the shallow soil, as commonly reported in low rainfall areas of southern Australia (Cartwright et al., 2006; Herczeg et al., 2001).

Suspended sediments and nutrients (NO_x, SRP, TN, TP and TSS) have positive C-Q slopes for more than 70% of the Australian monitoring sites, across all climate zones (Figure 5 and Table 2). A positive C-Q slope is hypothesised to be a result of constituents being mobilised and transported by shallow (either surface or shallow subsurface) flow pathways (Li et al., 2021; Zhi and Li, 2020). Our findings from the Australian catchments are consistent with these previous studies. Previous studies at

both catchment and larger spatial scales have generally found that constituents that are largely associated with particulate matter (e.g., TSS, TP) exhibit positive C-Q slopes because they are transported to rivers via shallow flow pathways (Bieroza et al., 2018; Musolff et al., 2015). However, in contrast to our finding, some of these studies have also found negative C-Q slopes for soluble nutrients such as SRP and NO_x (Bieroza et al., 2018; Dupas et al., 2015). The positive C-Q slopes for SRP and NO_x at the Australian sites, as also observed by Cartwright (2020) in Victorian catchments, suggest that these compounds are (i) largely transport-limited and (ii) largely transported by shallow flow pathways rather than deeper flow pathways (Musolff et al., 2015; Winter et al., 2021).

It is important to note that this study also demonstrates a lack of correlation between the CV ratios and C-Q slopes (Figure S12, Supplementary Materials). It therefore appears that the C-Q slope cannot be used to characterise the export regime of catchments (chemodynamic vs chemostatic) and should only be used to characterise export patterns (flushing vs dilution pattern). This is a result of the fact that when the constituent C is highly variable (chemodynamic export regime), the C-Q slope can still be close to zero if the change in constituent concentration is largely independent of changes in Q. This can be observed for example when the constituent is being discharged from a point source into the river (Musolff et al., 2015).

Further work is however required to further understand the temporal variability in export patterns. Previous studies have found that export patterns can change over time - within events and seasonally (Knapp et al., 2020; Minaudo et al., 2019). Whilst this study used a simple aggregated C-Q slope and CV ratio to determine the export regime and export patterns, future work should seek to understand temporal variations in these metrics. In particular, one solution may be to identify C-Q metrics separately for different hydrological regimes, differentiating for instance, the observations under dominant groundwater contribution from the ones when surface runoff dominates (Minaudo et al., 2019; Tunqui Neira et al., 2020).

Figure 5: Variations in C-Q slope for each climate zone. Results of Kruskal-Wallis test (p-values) to identify statistically significant variability in C-Q slopes across climate zones shown above each boxplot. Boxes represent the interquartile range, whiskers represent 1.5 times the interquartile range, the dots represent outliers, the black line represents the median and the black dots represent the mean.

3.3 Implications of the variability in water chemistry on future water quality management, monitoring and water policies

Bringing together water quality and streamflow data from a number of state-based organisations, our national-scale water quality study revealed a general pattern of constituent behaviour in Australia. The pattern that was identified in this study also helps inform future approaches to management and monitoring of water quality as well as informing water policies. Our study showed positive C-Q slopes for constituents of concern such as reactive, dissolved nutrient compounds (SRP and NO_x) at most of the Australian sites, suggesting that these constituents are largely transport-limited and/or largely transported by shallow flow pathways rather than deeper groundwater flows (Musolff et al., 2015; Winter et al., 2021). As these constituents demonstrate similar export regimes and patterns, they could be managed using similar types of strategies that target sources that interact with shallow flow pathways. TP, TSS and TN also appear to be transport-limited and largely affected by shallow flow

paths in most parts of the country, indicating that measures targeting these shallow flow paths would be useful strategies. Generally avoiding and reducing the build-up of nutrients and sediments sources should be targeted as a management strategy. EC and Ca, which inform management of salinity, on the other hand, appears to be dominated by deeper groundwater flows and are source-limited across the country. Thus, understanding and managing surface water-groundwater interactions, using EC and Ca as a proxy for salinity, will be critical for managing surface water salinity (e.g., Banks et al., 2011).

Our study has also highlighted key gaps in the current monitoring programs across Australia. Figure 1 indicates that monitoring is concentrated in Mediterranean, temperate and subtropical regions. This is despite the fact that monitoring sites in arid catchments have the highest TSS and TP concentrations. Whilst the lack of monitoring in arid catchments is likely due to its remoteness, our analyses suggest that more efforts are required to closely monitor rivers in arid regions, and gather samples of higher frequency to avoid the bias towards high flows and to obtain an understanding of baseline conditions (Figure S9, Supplementary materials). Previous studies have also noted the lack of water quality data in arid or semi-arid regions (Koci et al., 2020). Although it is unclear whether this is due to a bias in sampling, further investigation will be required to determine the underlying cause of the higher TSS and TP concentrations in arid regions. A systematic approach that distributes resources more evenly across multiple climate zones within the framework of a state-wide or national-scale monitoring programs may be needed for enhancing our understanding of water chemistry and for monitoring risks and vulnerabilities faced by human communities and ecosystems.

In Australia, water quality monitoring and management is administered and legislated through complex interactions at a sub-national (state and territory or local government) level and supported through water quality policies such as the National Water Quality Management Strategy (NWQMS) at the federal level. While this strategy is a nationally agreed approach to manage water quality, for example to share information across borders and jurisdictions, this process is currently not supported by a national scale water quality data inventory. Our analysis provided a first picture of national-scale water quality trends and demonstrated how our understanding of the water chemistry patterns across a national scale can be improved through the analysis of a national-scale dataset. The study identified for example where previously undetected water quality hotspots across the country occur and explained how anthropogenic and natural factors affect the quality of surface water. Further assessments can be undertaken to expand this picture and to improve the understanding of specific drivers of changes in the behaviour of water chemistry across the Australian continent, e.g., land use and hydrological regimes. Ongoing assessments and understanding whether the status of Australia's surface water quality improves or deteriorates will also inform and guide further improvements to Australia's water policies.

4. Conclusion

A national-scale assessment of water quality and its drivers is needed to further inform future water policy development. Through this work we have gathered available historical water quality and flow data from seven Australian states and territories and collated them into a single nationwide repository. By analysing this dataset, this study provides preliminary insights into the continental-scale variability of three key water quality indices (mean C, CV ratio, C-Q slope).

We have shown that there is significant variability in mean constituent concentrations across the Australian continent for Ca, EC, SRP, NO$_x$, TP, TN and TSS. These differences in water chemistry appear to vary according to climate zones. The relationship between climate zones and water chemistry is likely driven by differences in the interplay between land use, soil characteristics and rainfall-runoff processes affecting the extent of source and flow pathways across these climate zones.

CV ratios and C-Q slopes also vary spatially. However, export regimes and patterns are consistent regardless of climate zone. These results suggest that intrinsic properties of individual constituents determine export regimes and patterns, rather than catchment properties and climate controls. We hypothesise that this is a result of individual constituents originating from similar sources and being transported along similar pathways, in all climate zones.

This study has provided some insight into Australian water chemistry, and further work is required to understand the processes affecting water chemistry across the continent. In this study, we identified large variability in water chemistry within each climate zone, and the drivers of this variability need to be further identified. Additionally, there is a need to determine the seasonality and trends in water chemistry across the Australian continent. Of particular importance is understanding the impact of changes in flow regime on water chemistry.

Systematic national-scale assessments of water quality conditions are crucial for the development and implementation of successful water management policies and strategies. The findings from this study demonstrate the value in synthesising the data collected by state and territory-based agencies. These syntheses would enable future use in regular national-scale water quality assessments (e.g., UN Sustainable Development Goal (UN SDG) 3.6.2 reporting) and water quality trend analyses (e.g., State of the Environment (SoE) reporting). They can target further development of evidence-based federal water quality policies, such as Australia's National Water Quality Management Strategy (NWQMS) as well as tracing its successes.

Data availability statement

Data used for this study are derived from public domain resources. They include the following:
- WaterNSW (https://realtimedata.waternsw.com.au/)
- Water Measurement Information System (https://data.water.vic.gov.au/)
- Water Monitoring Information Portal (https://water-monitoring.information.qld.gov.au/)
- Water information reporting (http://wir.water.wa.gov.au/Pages/Water-Information-Reporting.aspx)
- Surface Water Data (https://www.waterconnect.sa.gov.au/Systems/SWD/Pages/Default.aspx)
- Water Data Portal (https://nt.gov.au/environment/water/water-information-systems/water-data-portal)
- DPIPWE Water Data Portal (https://portal.wrt.tas.gov.au/)

References

Abbott, B.W., Baranov, V., Mendoza-Lera, C., Nikolakopoulou, M., Harjung, A., Kolbe, T., Balasubramanian, M.N., Vaessen, T.N., Ciocca, F., Campeau, A., Wallin, M.B., Romeijn, P., Antonelli, M., Gonçalves, J., Datry, T., Laverman, A.M., de Dreuzy, J.-R., Hannah, D.M., Krause, S., Oldham, C., Pinay, G., 2016. Using multi-tracer inference to move beyond single-catchment ecohydrology. Earth-Science Reviews 160, 19–42. https://doi.org/10.1016/j.earscirev.2016.06.014

Abbott, B.W., Gruau, G., Zarnetske, J.P., Moatar, F., Barbe, L., Thomas, Z., Fovet, O., Kolbe, T., Gu, S., Pierson-Wickmann, A. -C., Davy, P., Pinay, G., 2018. Unexpected spatial stability of water chemistry in headwater stream networks. Ecology Letters 21, 296–308. https://doi.org/10.1111/ele.12897

Banks, E.W., Simmons, C.T., Love, A.J., Shand, P., 2011. Assessing spatial and temporal connectivity between surface water and groundwater in a regional catchment: Implications for regional scale water quantity and quality. Journal of Hydrology 404, 30–49. https://doi.org/10.1016/j.jhydrol.2011.04.017

Bartley, R., Speirs, W.J., Ellis, T.W., Waters, D.K., 2012. A review of sediment and nutrient concentration data from Australia for use in catchment water quality models. Marine Pollution Bulletin, The Catchment to Reef Continuum: Case studies from the Great Barrier Reef 65, 101–116. https://doi.org/10.1016/j.marpolbul.2011.08.009

Basu, N.B., Destouni, G., Jawitz, J.W., Thompson, S.E., Loukinova, N.V., Darracq, A., Zanardo, S., Yaeger, M., Sivapalan, M., Rinaldo, A., Rao, P.S.C., 2010. Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. Geophysical Research Letters 37. https://doi.org/10.1029/2010GL045168

Beck, H.E., Zimmermann, N.E., McVicar, T.R., Vergopolan, N., Berg, A., Wood, E.F., 2018. Present and future Köppen-Geiger climate classification maps at 1-km resolution. Scientific Data 5, 180214. https://doi.org/10.1038/sdata.2018.214

Bieroza, M.Z., Heathwaite, A.L., Bechmann, M., Kyllmar, K., Jordan, P., 2018. The concentration-discharge slope as a tool for water quality management. Science of The Total Environment 630, 738–749. https://doi.org/10.1016/j.scitotenv.2018.02.256

Botter, M., Li, L., Hartmann, J., Burlando, P., Fatichi, S., 2020. Depth of Solute Generation Is a Dominant Control on Concentration-Discharge Relations. Water Resources Research 56, e2019WR026695. https://doi.org/10.1029/2019WR026695

Bowes, M.J., Jarvie, H.P., Halliday, S.J., Skeffington, R.A., Wade, A.J., Loewenthal, M., Gozzard, E., Newman, J.R., Palmer-Felgate, E.J., 2015. Characterising phosphorus and nitrate inputs to a rural

river using high-frequency concentration–flow relationships. Science of The Total Environment 511, 608–620. https://doi.org/10.1016/j.scitotenv.2014.12.086

Bureau of Meteorology, 2012. Geofabric V2.

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. https://doi.org/10.1016/j.apgeochem.2020.104680

Cartwright, I., Weaver, T.R., Fifield, L.K., 2006. Cl/Br ratios and environmental isotopes as indicators of recharge variability and groundwater flow: An example from the southeast Murray Basin, Australia. Chemical Geology 231, 38–56. https://doi.org/10.1016/j.chemgeo.2005.12.009

Caruso, B.S., 2002. Temporal and spatial patterns of extreme low flows and effects on stream ecosystems in Otago, New Zealand. Journal of Hydrology 257, 115–133. https://doi.org/10.1016/S0022-1694(01)00546-7

Casquin, A., Gu, S., Dupas, R., Petitjean, P., Gruau, G., Durand, P., 2020. River network alteration of C-N-P dynamics in a mesoscale agricultural catchment. Science of The Total Environment 749, 141551. https://doi.org/10.1016/j.scitotenv.2020.141551

Chang, H., 2008. Spatial analysis of water quality trends in the Han River basin, South Korea. Water Research 42, 3285–3304. https://doi.org/10.1016/j.watres.2008.04.006

Department of Environment, Land, Water & Planning, 2021. Water Measurement Information System [WWW Document]. URL https://data.water.vic.gov.au/ (accessed 5.23.21).

DPIPWE, 2021. Data - DPIPWE Water Data Portal [WWW Document]. URL https://portal.wrt.tas.gov.au/ (accessed 5.23.21).

Duncan, J.M., Welty, C., Kemper, J.T., Groffman, P.M., Band, L.E., 2017. Dynamics of nitrate concentration-discharge patterns in an urban watershed. Water Resources Research 53, 7349–7365. https://doi.org/10.1002/2017WR020500

Dunn, O.J., 1964. Multiple Comparisons Using Rank Sums. Technometrics 6, 241–252. https://doi.org/10.2307/1266041

Dupas, R., Delmas, M., Dorioz, J.-M., Garnier, J., Moatar, F., Gascuel-Odoux, C., 2015. Assessing the impact of agricultural pressures on N and P loads and eutrophication risk. Ecological Indicators 48, 396–407. https://doi.org/10.1016/j.ecolind.2014.08.007

Dupas, R., Minaudo, C., Abbott, B.W., 2019. Stability of spatial patterns in water chemistry across temperate ecoregions. Environ. Res. Lett. 14, 074015. https://doi.org/10.1088/1748-9326/ab24f4

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, e2020WR028134. https://doi.org/10.1029/2020WR028134

Fazekas, H.M., Wymore, A.S., McDowell, W.H., 2020. Dissolved Organic Carbon and Nitrate Concentration-Discharge Behavior Across Scales: Land Use, Excursions, and Misclassification. Water Resources Research 56, e2019WR027028. https://doi.org/10.1029/2019WR027028

Foks, S.S., Stets, E.G., Singha, K., Clow, D.W., 2018. Influence of climate on alpine stream chemistry and water sources. Hydrological Processes 32, 1993–2008. https://doi.org/10.1002/hyp.13124

Geoscience Australia, 2011. Environmental Attributes Database.

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, 3056–3069. 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, 1844–1864. https://doi.org/10.1002/hyp.7315

Government of Northern Territory, 2021. Water data portal [WWW Document]. URL https://nt.gov.au/environment/water/water-information-systems/water-data-portal (accessed 5.23.21).

Government of South Australia, 2021. Surface Water Data [WWW Document]. URL
https://www.waterconnect.sa.gov.au/Systems/SWD/Pages/Default.aspx (accessed 5.23.21).

Government of Western Australia Department of Water and Environmental Regulation, 2021. Water
Information Reporting [WWW Document]. URL http://wir.water.wa.gov.au/Pages/Water-
Information-Reporting.aspx (accessed 5.23.21).

Green, M.B., Nieber, J.L., Johnson, G., Magner, J., Schaefer, B., 2007. Flow path influence on an N:P
ratio in two headwater streams: A paired watershed study. Journal of Geophysical Research:
Biogeosciences 112. https://doi.org/10.1029/2007JG000403

Greene, S., Taylor, D., McElarney, Y.R., Foy, R.H., Jordan, P., 2011. An evaluation of catchment-
scale phosphorus mitigation using load apportionment modelling. Science of The Total Environment
409, 2211–2221. https://doi.org/10.1016/j.scitotenv.2011.02.016

Gu, S., Casquin, A., Dupas, R., Abbott, B.W., Petitjean, P., Durand, P., Gruau, G., 2021. Spatial
Persistence of Water Chemistry Patterns Across Flow Conditions in a Mesoscale Agricultural
Catchment. Water Resources Research 57, e2020WR029053. https://doi.org/10.1029/2020WR029053

Guillemot, S., Fovet, O., Gascuel-Odoux, C., Gruau, G., Casquin, A., Curie, F., Minaudo, C.,
Strohmenger, L., Moatar, F., 2020. Spatio-temporal controls of C-N-P dynamics across headwater
catchments of a temperate agricultural region from public data analysis. Hydrology and Earth System
Sciences Discussions 1–31. https://doi.org/10.5194/hess-2020-257

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, 827–847. https://doi.org/10.5194/hess-24-827-2020

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, 112–129. https://doi.org/10.1029/2018WR023370

Helsel, D.R., 1990. Less than obvious - statistical treatment of data below the detection limit. Environ.
Sci. Technol. 24, 1766–1774. https://doi.org/10.1021/es00082a001

Herczeg, A.L., Dogramaci, S.S., Leaney, F.W.J., 2001. Origin of dissolved salts in a large, semi-arid
groundwater system: Murray Basin, Australia. Mar. Freshwater Res. 52, 41–52.
https://doi.org/10.1071/mf00040

Hoagland, B., Russo, T.A., Gu, X., Hill, L., Kaye, J., Forsythe, B., Brantley, S.L., 2017. Hyporheic
zone influences on concentration-discharge relationships in a headwater sandstone stream. Water
Resources Research 53, 4643–4667. https://doi.org/10.1002/2016WR019717

Hunsaker, C.T., Johnson, D.W., 2017. Concentration-discharge relationships in headwater streams of
the Sierra Nevada, California. Water Resources Research 53, 7869–7884.
https://doi.org/10.1002/2016WR019693

Jiang, Y., 2009. China's water scarcity. Journal of Environmental Management 90, 3185–3196.
https://doi.org/10.1016/j.jenvman.2009.04.016

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.
Hydrology and Earth System Sciences 24, 2561–2576. https://doi.org/10.5194/hess-24-2561-2020

Koci, J., Sidle, R.C., Kinsey-Henderson, A.E., Bartley, R., Wilkinson, S.N., Hawdon, A.A., Jarihani,
B., Roth, C.H., Hogarth, L., 2020. Effect of reduced grazing pressure on sediment and nutrient yields
in savanna rangeland streams draining to the Great Barrier Reef. Journal of Hydrology 582, 124520.
https://doi.org/10.1016/j.jhydrol.2019.124520

Kruskal, W.H., Wallis, W.A., 1952. Use of Ranks in One-Criterion Variance Analysis. Journal of the
American Statistical Association 47, 583–621. https://doi.org/10.1080/01621459.1952.10483441

Levene, H., 1960. Robust tests for equality of variances, in: Contributions to Probability and
Statistics: Essays in Honor of Harold Hotelling. Stanford University Press, pp. 278–292.

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, 2346–2367. https://doi.org/10.1002/2016WR018935

Li, L., Sullivan, P.L., Benettin, P., Cirpka, O.A., Bishop, K., Brantley, S.L., Knapp, J.L.A., Meerveld, I. van, Rinaldo, A., Seibert, J., Wen, H., Kirchner, J.W., 2021. Toward catchment hydro-biogeochemical theories. WIREs Water 8, e1495. https://doi.org/10.1002/wat2.1495

Lintern, A., Webb, J.A., Ryu, D., Liu, S., Waters, D., Leahy, P., Bende‐Michl, U., Western, A.W., 2018. What Are the Key Catchment Characteristics Affecting Spatial Differences in Riverine Water Quality? Water Resources Research 54, 7252–7272. https://doi.org/10.1029/2017WR022172

Liu, S., Ryu, D., Webb, J.A., Lintern, A., Guo, D., Waters, D., Western, A.W., 2021. A multi-model approach to assessing the impacts of catchment characteristics on spatial water quality in the Great Barrier Reef catchments. Environmental Pollution 117337. https://doi.org/10.1016/j.envpol.2021.117337

Liu, S., Ryu, D., Webb, J.A., Lintern, A., Waters, D., Guo, D., Western, A.W., 2018. Characterisation of spatial variability in water quality in the Great Barrier Reef catchments using multivariate statistical analysis. Marine Pollution Bulletin 137, 137–151. https://doi.org/10.1016/j.marpolbul.2018.10.019

Long, T., Wellen, C., Arhonditsis, G., Boyd, D., 2014. Evaluation of stormwater and snowmelt inputs, land use and seasonality on nutrient dynamics in the watersheds of Hamilton Harbour, Ontario, Canada. Journal of Great Lakes Research 40, 964–979. https://doi.org/10.1016/j.jglr.2014.09.017

Mellander, P.-E., Jordan, P., Bechmann, M., Fovet, O., Shore, M.M., McDonald, N.T., Gascuel-Odoux, C., 2018. Integrated climate-chemical indicators of diffuse pollution from land to water. Scientific Reports 8, 944. https://doi.org/10.1038/s41598-018-19143-1

Mellander, P.-E., Jordan, P., Shore, M., Melland, A.R., Shortle, G., 2015. Flow paths and phosphorus transfer pathways in two agricultural streams with contrasting flow controls. Hydrological Processes 29, 3504–3518. https://doi.org/10.1002/hyp.10415

Michalak, A.M., 2016. Study role of climate change in extreme threats to water quality. Nature News 535, 349. https://doi.org/10.1038/535349a

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. 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. https://doi.org/10.1002/2016WR019635

Musolff, A., Fleckenstein, J.H., Rao, P.S.C., Jawitz, J.W., 2017. Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. Geophysical Research Letters 44, 4143–4151. https://doi.org/10.1002/2017GL072630

Musolff, A., Schmidt, C., Selle, B., Fleckenstein, J.H., 2015. Catchment controls on solute export. Advances in Water Resources 86, Part A, 133–146. http://dx.doi.org/10.1016/j.advwatres.2015.09.026

Nhiwatiwa, T., Dalu, T., 2017. Seasonal variation in pans in relation to limno-chemistry, size, hydroperiod, and river connectivity in a semi-arid subtropical region. Physics and Chemistry of the Earth, Parts A/B/C, Biogeochemical Processes in the Changing Wetland Environment 97, 37–45. https://doi.org/10.1016/j.pce.2016.11.003

Ockenden, M.C., Deasy, C.E., Benskin, C.McW.H., Beven, K.J., Burke, S., Collins, A.L., Evans, R., Falloon, P.D., Forber, K.J., Hiscock, K.M., Hollaway, M.J., Kahana, R., Macleod, C.J.A., Reaney, S.M., Snell, M.A., Villamizar, M.L., Wearing, C., Withers, P.J.A., Zhou, J.G., Haygarth, P.M., 2016.

Changing climate and nutrient transfers: Evidence from high temporal resolution concentration-flow dynamics in headwater catchments. Science of The Total Environment 548–549, 325–339. https://doi.org/10.1016/j.scitotenv.2015.12.086

Pellegrini, A.F.A., 2016. Nutrient limitation in tropical savannas across multiple scales and mechanisms. Ecology 97, 313–324. https://doi.org/10.1890/15-0869.1

Prosser, I.P., 2011. Water : science and solutions for Australia, Science and solutions for Australia : water. Collingwood, Vic. : CSIRO Publishing, Collingwood, Vic.

Queensland Government, 2021. WMIP [WWW Document]. URL https://water-monitoring.information.qld.gov.au/ (accessed 5.23.21).

Reich, P.B., Oleksyn, J., 2004. Global patterns of plant leaf N and P in relation to temperature and latitude. PNAS 101, 11001–11006. https://doi.org/10.1073/pnas.0403588101

Rose, L.A., Karwan, D.L., Godsey, S.E., 2018. Concentration–discharge relationships describe solute and sediment mobilization, reaction, and transport at event and longer timescales. Hydrological Processes 32, 2829–2844. https://doi.org/10.1002/hyp.13235

Sarker, A., Ross, H., Shrestha, K.K., 2008. A common-pool resource approach for water quality management: An Australian case study. Ecological Economics 68, 461–471. https://doi.org/10.1016/j.ecolecon.2008.05.001

Schwarzenbach, R.P., Egli, T., Hofstetter, T.B., von Gunten, U., Wehrli, B., 2010. Global Water Pollution and Human Health. Annual Review of Environment and Resources 35, 109–136. https://doi.org/10.1146/annurev-environ-100809-125342

Shapiro, S.S., Wilk, M.B., 1965. An analysis of variance test for normality (complete samples)†. Biometrika 52, 591–611. https://doi.org/10.1093/biomet/52.3-4.591

Sheldon, F., Fellows, C.S., Sheldon, F., Fellows, C.S., 2010. Water quality in two Australian dryland rivers: spatial and temporal variability and the role of flow. Mar. Freshwater Res. 61, 864–874. https://doi.org/10.1071/MF09289

Thomas, Z., Abbott, B.W., Troccaz, O., Baudry, J., Pinay, G., 2016. Proximate and ultimate controls on carbon and nutrient dynamics of small agricultural catchments. Biogeosciences 13, 1863–1875. https://doi.org/10.5194/bg-13-1863-2016

Thompson, S.E., Basu, N.B., Lascurain, 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, n/a-n/a. https://doi.org/10.1029/2010WR009605

Tomaz, A., Palma, P., Fialho, S., Lima, A., Alvarenga, P., Potes, M., Salgado, R., 2020. Spatial and temporal dynamics of irrigation water quality under drought conditions in a large reservoir in Southern Portugal. Environ Monit Assess 192, 93. https://doi.org/10.1007/s10661-019-8048-1

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

Van Meter, K.J., Basu, N.B., Veenstra, J.J., Burras, C.L., 2016. The nitrogen legacy: emerging evidence of nitrogen accumulation in anthropogenic landscapes. Environ. Res. Lett. 11, 035014. https://doi.org/10.1088/1748-9326/11/3/035014

Viscarra Rossel, R., Chen, C., Grundy, M., Searle, R., Clifford, D., Odgers, N., Holmes, K., Griffin, T., Liddicoat, C., Kidd, D., 2014. Soil and Landscape Grid National Soil Attribute Maps - Total Phosphorus (3" resolution) - Release 1. v5. CSIRO. Data Collection.

Vörösmarty, C.J., McIntyre, P.B., Gessner, M.O., Dudgeon, D., Prusevich, A., Green, P., Glidden, S., Bunn, S.E., Sullivan, C.A., Liermann, C.R., Davies, P.M., 2010. Global threats to human water security and river biodiversity. Nature 467, 555–561. https://doi.org/10.1038/nature09440

Water Quality Australia, 2018. Water Quality Guidelines.

WaterNSW, 2021. Real-time water data [WWW Document]. URL
https://realtimedata.waternsw.com.au/ (accessed 5.23.21).

Winter, C., Lutz, S.R., Musolff, A., Kumar, R., Weber, M., Fleckenstein, J.H., 2021. Disentangling
the Impact of Catchment Heterogeneity on Nitrate Export Dynamics From Event to Long-Term Time
Scales. Water Resources Research 57, e2020WR027992. https://doi.org/10.1029/2020WR027992

Wright, S.J., Yavitt, J.B., Wurzburger, N., Turner, B.L., Tanner, E.V.J., Sayer, E.J., Santiago, L.S.,
Kaspari, M., Hedin, L.O., Harms, K.E., Garcia, M.N., Corre, M.D., 2011. Potassium, phosphorus, or
nitrogen limit root allocation, tree growth, or litter production in a lowland tropical forest. Ecology 92,
1616–1625. https://doi.org/10.1890/10-1558.1

Zhi, W., Li, L., 2020. The Shallow and Deep Hypothesis: Subsurface Vertical Chemical Contrasts
Shape Nitrate Export Patterns from Different Land Uses. Environ. Sci. Technol. 54, 11915–11928.
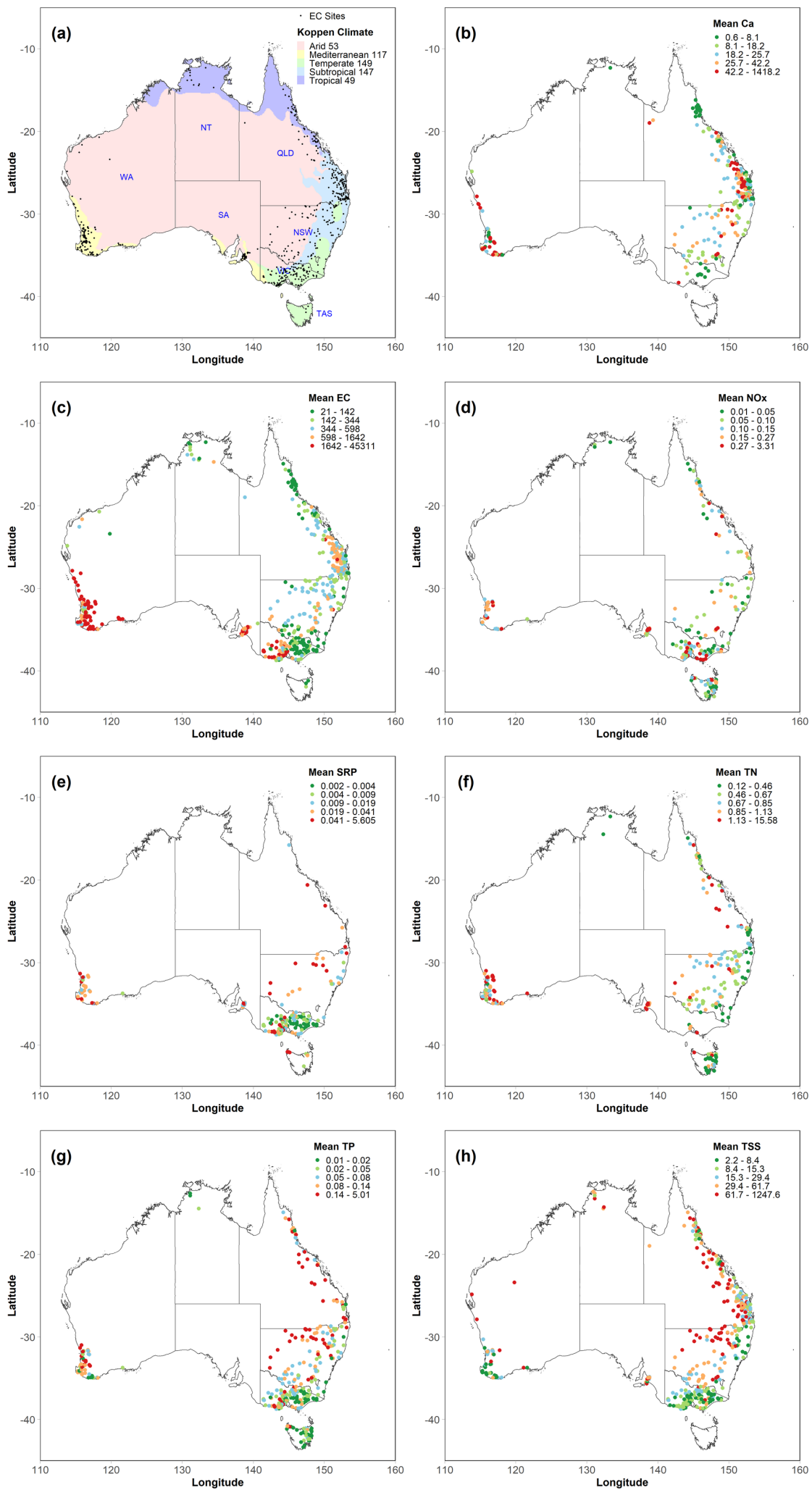https://doi.org/10.1021/acs.est.0c01340

Zhi, W., Li, L., Dong, W., Brown, W., Kaye, J., Steefel, C., Williams, K.H., 2019. Distinct Source
Water Chemistry Shapes Contrasting Concentration-Discharge Patterns. Water Resources Research
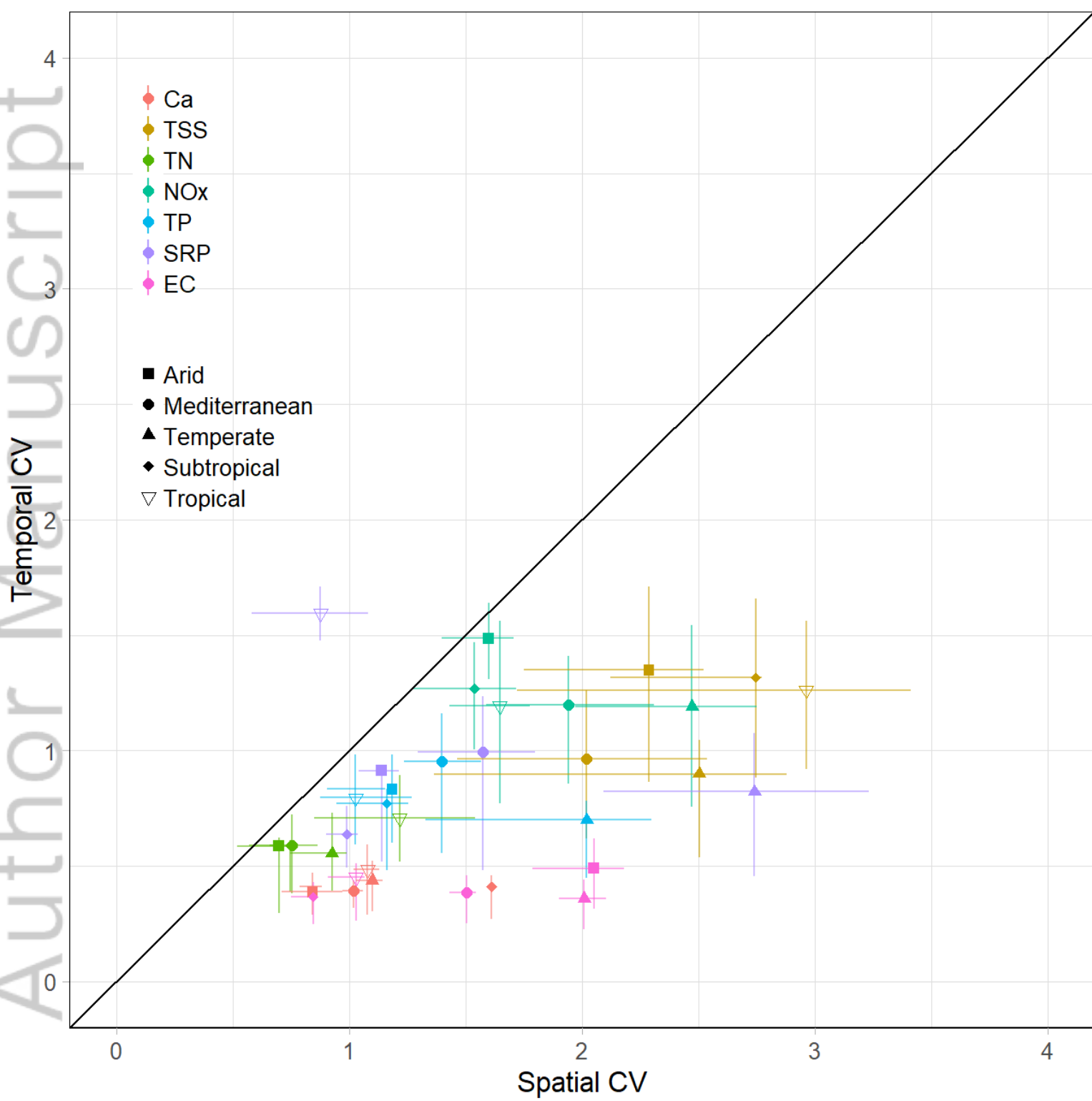55, 4233–4251. https://doi.org/10.1029/2018WR024257
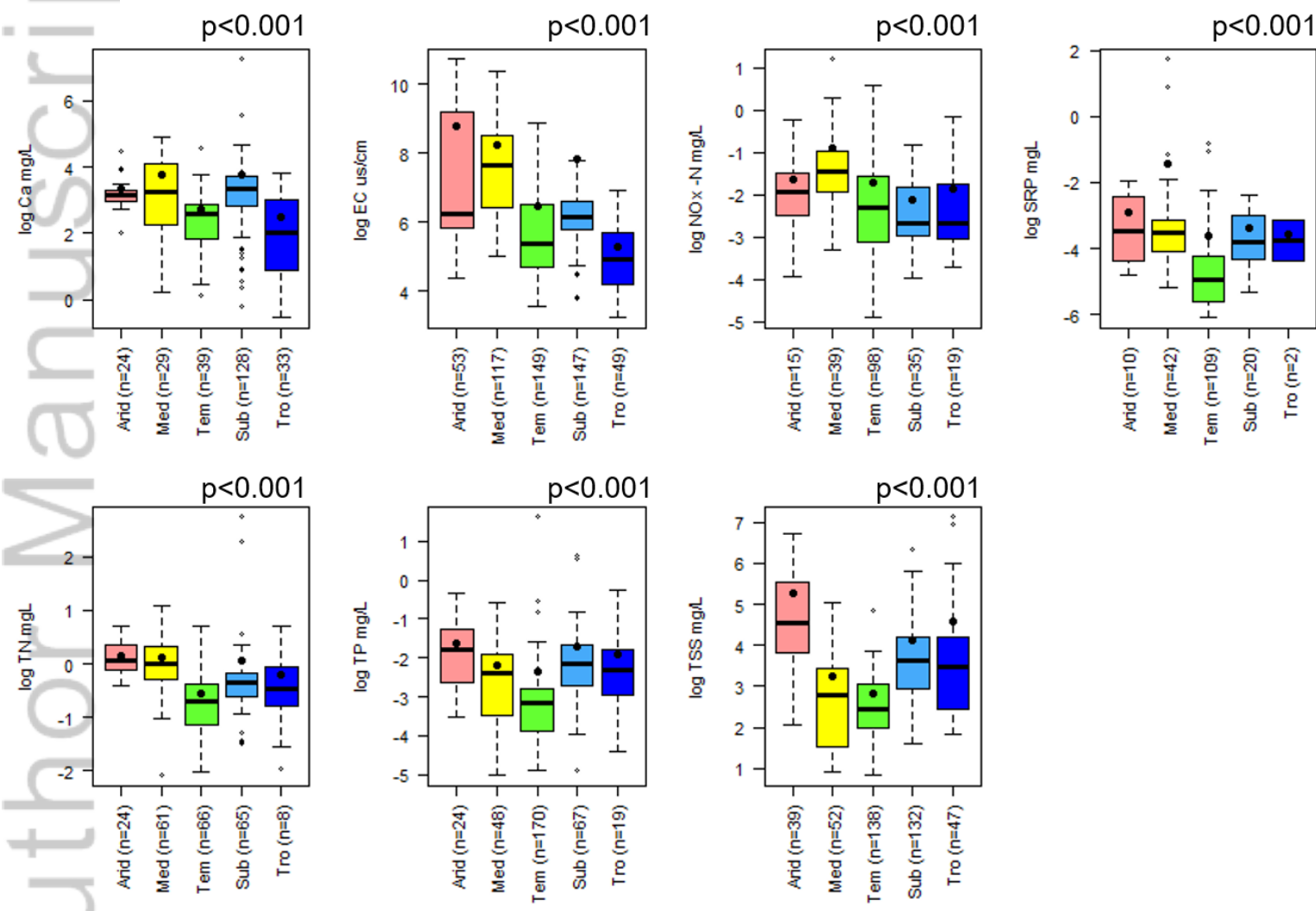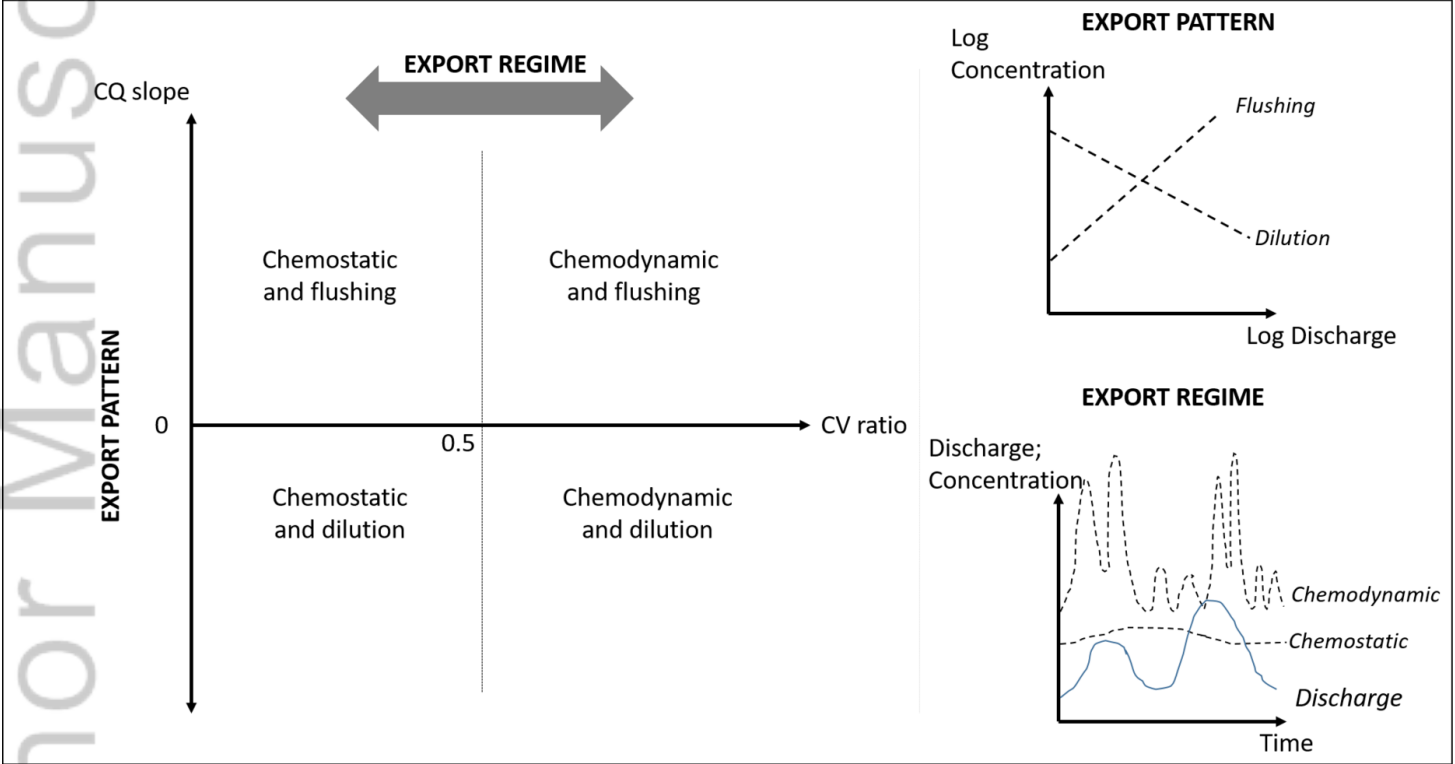
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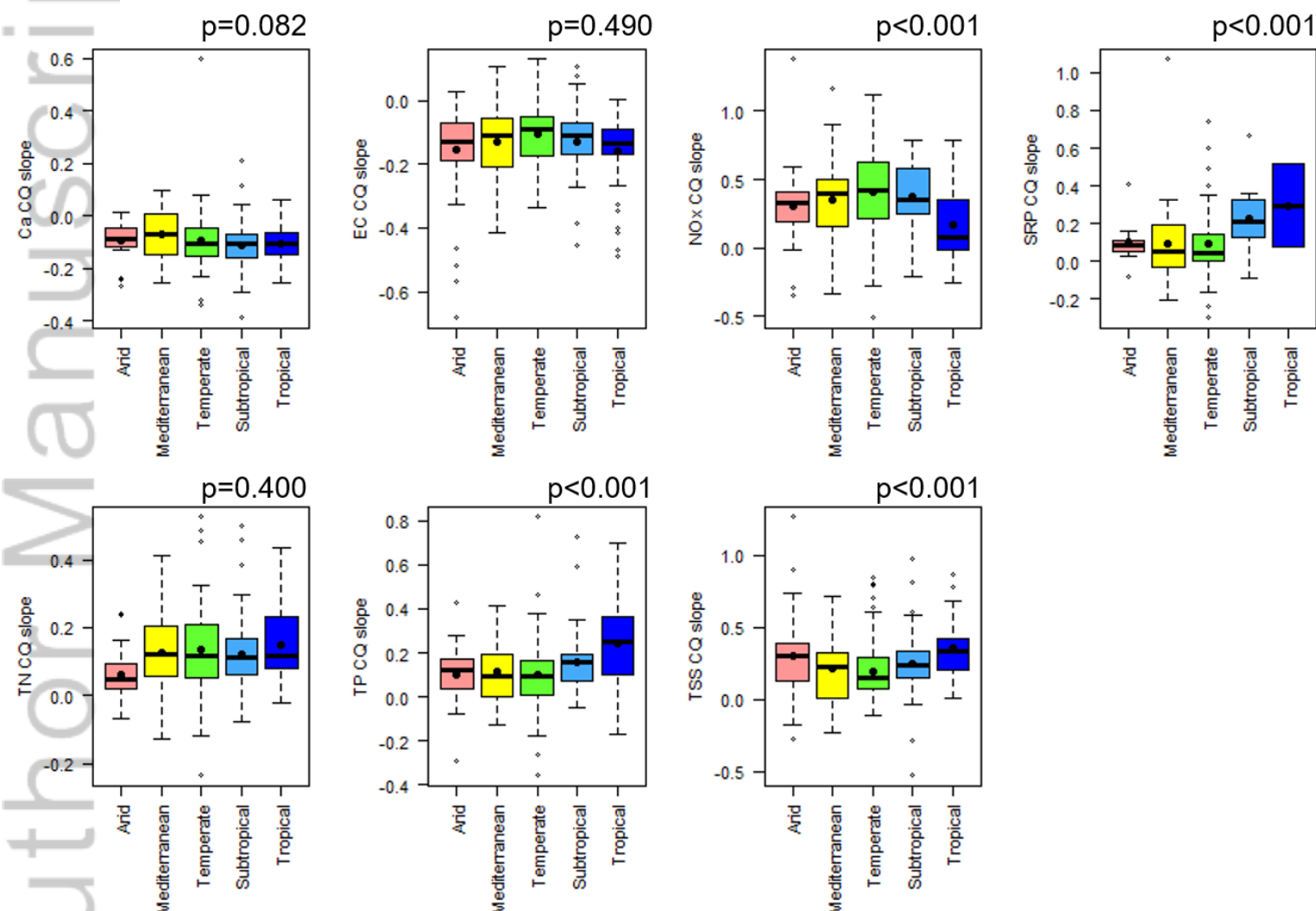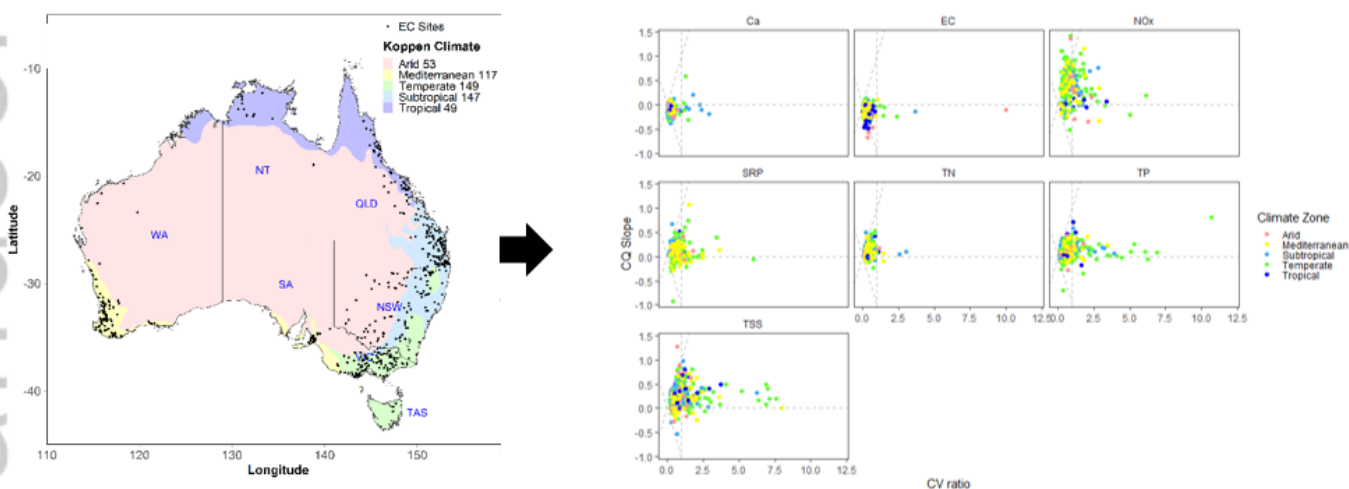
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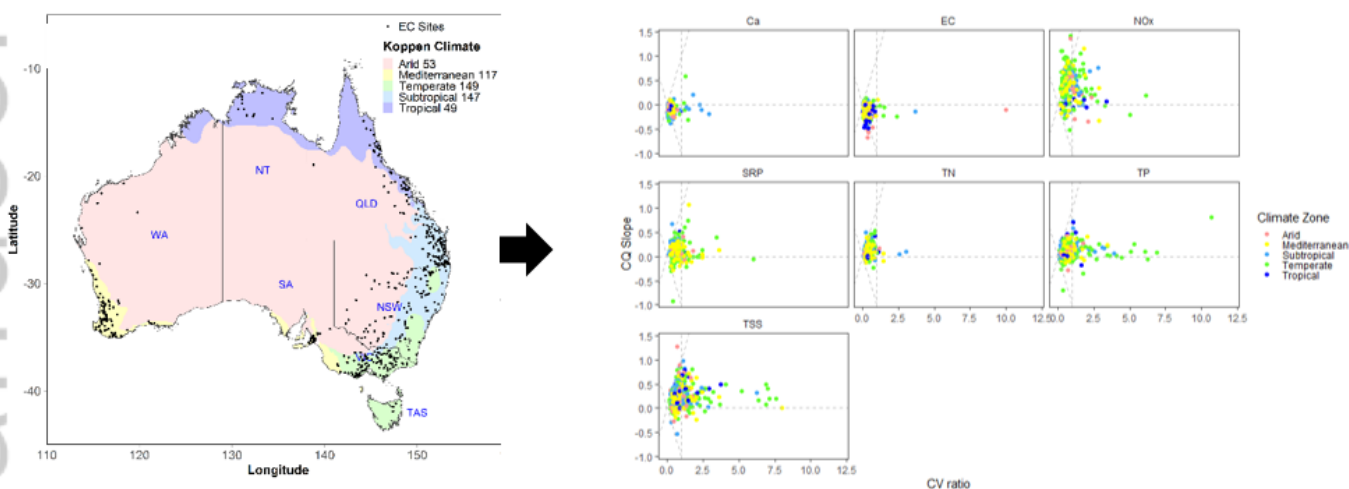
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HYP_14423_Figure 2.png

- Significantly different mean concentrations across climate zones

BUT

- Export patterns and regimes driven by instrinsic constituent properties (not climate zones)

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

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Abstract. The spatial and temporal variation of concentration-discharge (C-Q) relationships inform 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 patterns have not yet been investigated across large spatial scales. To address

20 this, the study aims to assess how baseflow contributions, as defined by the median catchment baseflow index (BFI_m), 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), nitrate–nitrite (NOx) and total nitrogen (TN). The impact of baseflow contribution is explored with a novel Bayesian hierarchical model.

25 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

30 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.

1 Introduction

Understanding the causes of spatiotemporal variability in riverine chemistry is critical to support water quality management 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 are determined by (i) the spatial distribution of constituent sources within the catchment; and (ii) the interplay between the

40 biogeochemical and hydrological processes, which controls constituent mobilisation and transport through the 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 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

45 multiple spatial scales, from small headwater catchments (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 critical drivers for these spatial variations (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 temporal changes are driven by a series of mechanisms such as chemical build-up and flushing under varying flow magnitudes, and contrasting baseflow contributions during different stages of runoff events (Bende-Michl et al., 2013; Knapp et al., 2020; Musolff A: et al.; Rusjan et al., 2008; Tunqui Neira et al., 2020).

In the existing studies that explore the variation of C-Q relationships, hydrological characteristics of catchments have been highlighted as a key influencing factor, as it defines the flow pathways and magnitudes that are critical to the transport processes (Tunqui Neira et al., 2020a, 2020b). Several studies have highlighted that, within a particular catchment, the C-Q relationship (and thus export behaviour) is dependent on whether streamflow is dominated by baseflow or quickflow (Gorski & Zimmer, 2021; Knapp et al., 2020; Minaudo et al., 2019). However, there is little understanding of how the overall 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 the impact of baseflow contribution on C-Q relationships focused on catchments in temperate climates in Europe and North America (e.g., Gorski & Zimmer, 2021; Minaudo et al., 2019; Musolff et al., 2015). This leads to a limitation in transferring and systematically comparing findings to other climate zones and other parts of the world.

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), 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 water quality variables and suggested that the inherent properties of each water quality variable determine its C-Q relationships. However, the role of different baseflow contributions on C-Q relationships has not yet been examined.

This study aims to assess the impact of catchment baseflow contribution on C-Q relationships of sediment, nutrients and salts 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 baseflow contributions, leading to contrasted responses in terms of catchment export patterns, as represented by C-Q slopes. With this analysis we also hypothesise that the C-Q slopes in Australian catchments can be predicted across space by baseflow contribution. We test these hypotheses with a Bayesian hierarchical modelling approach, which will i) add new understanding to the sources and export patterns of water quality variables; ii) improve the predictive capacity of water quality variables by better prediction of C-Q relationships over space.

2 Method

2.1 Data and study catchments

80 ### 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

85 Primary Industries, Parks, Water and Environment (TAS DPIPWE, Tasmania) and Department of Environment, Parks and Water Security (NT DEPWS, Northern Territory).

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). Quality control of the data was performed using quality codes, flags and detection limits provided by individual state agencies. The dataset consists of a mixture of grab samples and high-

90 frequency (continuously measured) water quality data; a daily average is taken if more than one water quality sample was collected for any day at any site. This study focuses on six water quality variables: total suspended solids (TSS), total phosphorus (TP), soluble reactive phosphorus (SRP), total nitrogen (TN), nitrate–nitrite (NOx) 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).

95 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 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 missing or erroneous data for individual water quality variables (Table S2, Supplementary Materials). These gaps and low-quality samples

100 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:

105 1) Having over 50 pairs of corresponding concentration and flow data points; this is to ensure that the C-Q relationships observed are unaffected by outliers (Lintern et al., in review).

2) Having water quality time-series that spans 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).

4

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

110   quality samples; this ensures that C-Q relationships are not biased by samples obtained at high or low flows for

individual catchments.

We 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 50-83 catchments used to investigate each variable. These

catchments are distributed across five main Australian climate zones as defined by Lintern et al. (in review): arid,

115   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.
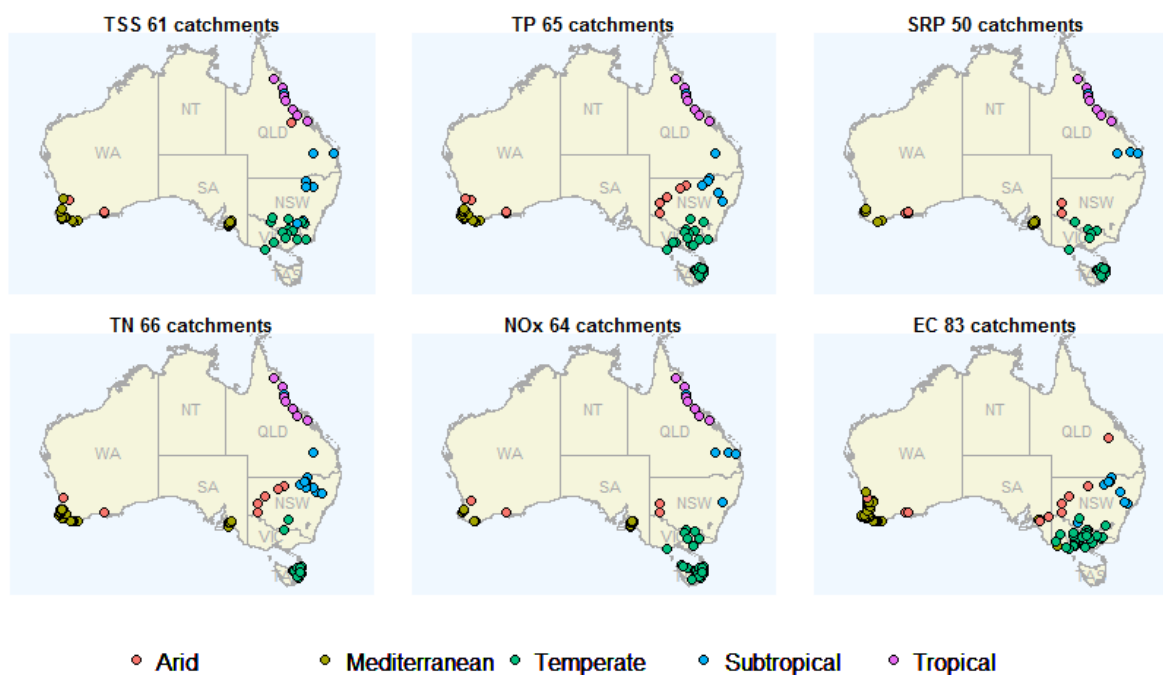
Figure 1. Catchments included in study for each water quality variable (total number of catchments shown in panel titles). The colours denote five key climate zones in Australia. States and territories of Australia on the map are: New South Wales - NSW, Queensland - QLD, South Australia - SA, Tasmania - TAS, Victoria -VIC, Western Australia -WA, and Northern Territory - NT.

2.1.2 Representing catchment baseflow contribution with baseflow index

125   To represent the overall contribution of baseflow to total streamflow in each catchment and explore how this impacts the C-Q

relationships across space, we used catchment baseflow index (BFI). BFI represents the proportion of discharge that occurs as

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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. 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

130   series, as recommended for 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 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

135   explore how the distribution of BFI of each catchment can affect C-Q relationships.

2.2 Modelling the impacts of catchment baseflow contribution on concentration

We developed a Bayesian hierarchical model (BHM) to explore the effect of catchment BFI on C-Q slope. The BHM is advantageous in its 'borrowing power' across space (Gelman et al., 2013; Webb & King, 2009), which is highly effective to explain variability in spatial-temporal data under data-limited situations. Bayesian modelling is also effective for incorporating

140   uncertainty, which is necessary when analysing water quality data, as they are often associated with high uncertainty due to incomplete sampling of its natural variability (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):

$$\log(C_{s,t}) = \alpha_s + \beta_s \log(Q_{s,t}) \tag{1}$$

145   Our model used a modified version of Eqn. 1 based on previous literature on the effects of baseflow contribution on C-Q slopes within individual catchments (Gorski & Zimmer, 2021; Minaudo et al., 2019). We assume that for each water quality variable, the C-Q slopes of all catchments are following a normal distribution with a 'grand mean', β_0. Then the variation of C-Q slopes between catchments, away from β_0, are explained by changes in catchment BFI. The use of a mean C-Q slope is based on our preceding study, which suggested that for each water quality variable, export patterns (as represented by C-Q slopes) did not

150   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 the 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.
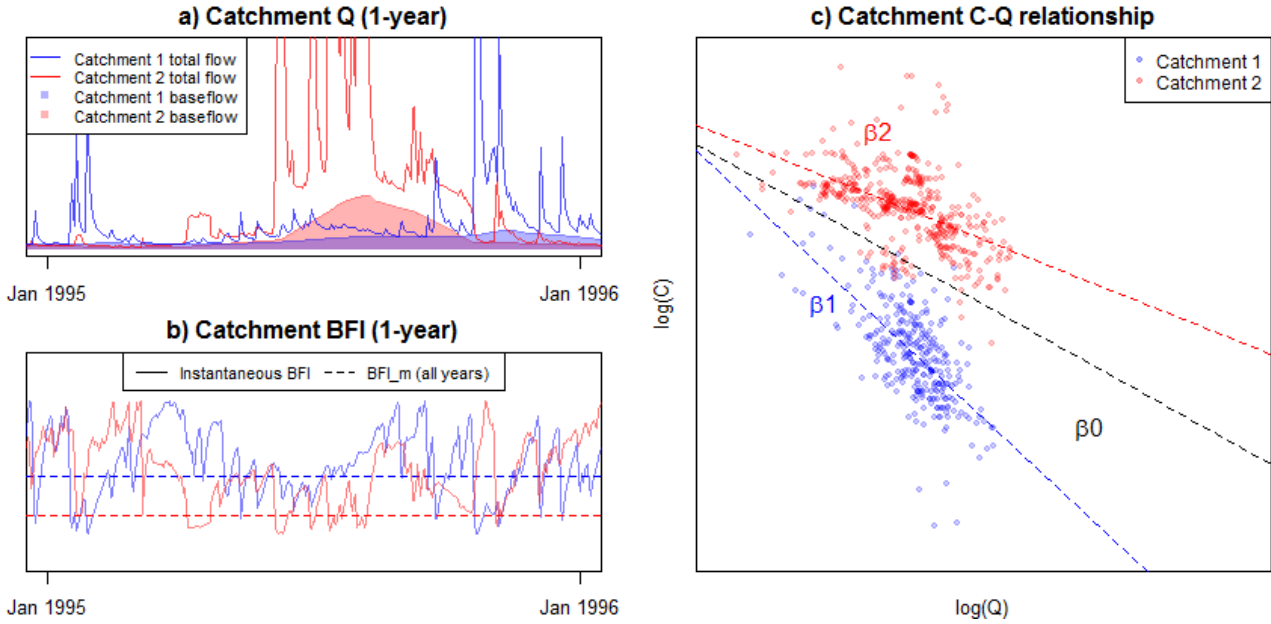
Figure 2. Illustration of conceptualization of the BFI-based C-Q models with two catchments, with the catchment median BFI (*BFI_m*) as the main predictor of C-Q slope. a) flow time-series with shaded regions showing the baseflow contribution; b) BFI time-series and the corresponding *BFI_m*; and c) 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 one year for visualisation.

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

$$\beta_s = \beta_0 + BFI\_m_s \times \delta BFI_{climate} \tag{2}$$

In Eqn. 2, the model parameter, $\delta BFI_{climate}$, represents the effect of *BFI_m* on C-Q slope. This effect is considered as a climate-specific parameter to assess whether the catchment BFI effects differ between climate. Such conceptualization of the BFI effects would then lead to a modified C-Q relationship for each catchment as:

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

Equation 3 is the final form of the Bayesian hierarchical model, which was calibrated for each water quality variable across all catchments simultaneously to assess the impact of catchment BFI on C-Q slopes. The effects of *BFI_l* and *BFI_h* were explored with the same model structure.

To calibrate the Bayesian model, 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 $\delta BFI_{climate}$, 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

7

for each chain. Convergence of the chains was ensured by checking the *Rhat* value (Sturtz et al., 2005), which is a *rstan* output
that summarizes the consistency of the four Markov chains used in model calibration. Specifically, we ensured that the *Rhat*
value is below 1.1, which suggested that the independent Markov chains have been well mixed and converged (Stan
Development Team, 2018).

The calibrated model interpretation focused on the performance and the model parameter *δBFIclimate,* which informed the
climate-specific effects of catchment BFI on C-Q slopes. We specifically assessed the following model outputs (results
presented in Section 3.3):

1) *Model performance:* We assessed how well each BFI-based model (Eqn. 3) reproduced observed water quality with
   the Nash Sutcliffe Efficiency (NSE) (Nash & Sutcliffe, 1970). The NSE represents the proportion of observed
   variability that is explained by the model. As a benchmark, we also assessed the NSE of a baseline model which uses
   the classic C-Q relationship (Eqn. 1) observed for individual catchments to predict all water quality concentrations.
   This baseline 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 benchmark to assess the BFI-
   based model.

2) *Modelled effects:* We extracted the direction, magnitude and significance of the effects of catchment BFI from the
   posterior distribution of the calibrated model parameter, *δBFI_{climate}*, to assess the impact of catchment BFI on C-Q
   slope for each climate zone.

3 Results and Discussions

In this section, we first discuss the spatial variation in the median BFI across the study catchments (Section 3.1). We then
provide some examples at specific catchments to illustrate how catchment BFI can affect C-Q relationship 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.

3.1 BFI across catchments

The range of catchment low, median and high BFIs (*BFI_l, BFI_m* and *BFI_h*) for all catchments included in this study are
summarized in Figure 3. The calculated 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 are seen between the

other four climate zones (Figure 3 a)). The *BFI_l* and *BFI_h* have consistent distributions with the median BFI across climate

205 zones. Considering the different catchments analysed between water quality variables, similar catchment BFI summaries were

also generated for each water quality variable, and the BFI distributions are generally consistent across different variables
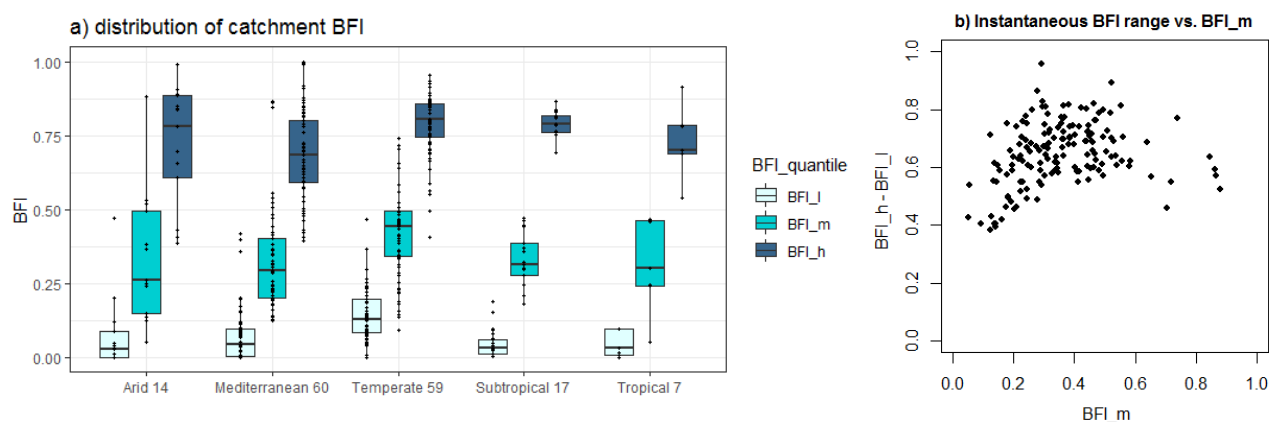
(Figure S4, Supplementary Materials).

Figure 3. a) Distribution of catchment low, median and high BFI (*BFI_l, BFI_m, BFI_h*) for each climate zone; b) range of
210 **instantaneous BFI (*BFI_h − BFI_l*) versus *BFI_m*. Both plots include all 157 catchments across six water quality variables studied.**
The corresponding versions of a) and b) for individual water quality variables are in Figure S4 and Figures S5 and S6
(Supplementary Materials).

It is also worth noting that catchments with high *BFI_m* are likely to have a higher variability of instantaneous BFI, as

highlighted by the generally increasing differences between *BFI_h* and *BFI_l* with higher *BFI_m* (Figure 3 b)). The link

215 between *BFI_m* and variability of instantaneous BFI suggests potentially different flow pathways for catchments with

contrasting *BFI_m*. Specifically, a catchment with a low *BFI_m* tends to be associated with low instantaneous BFIs limited to

a small range; thus, the catchment is likely to always have lower contributions of baseflow and higher contributions of surface

flow, during both dry and wet conditions. In contrast, a catchment with a high *BFI_m* generally has a large range in

instantaneous BFIs. This means that the catchment is more likely switching between groundwater contributions in dry

220 conditions (high instantaneous BFI) and surface water contributions during wet conditions (low instantaneous BFI). Therefore,

catchments with higher *BFI_m* are more likely dominated by different flow pathways under dry and wet conditions.

3.2 Impact of BFI 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*. We focus on the C-Q

225 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).
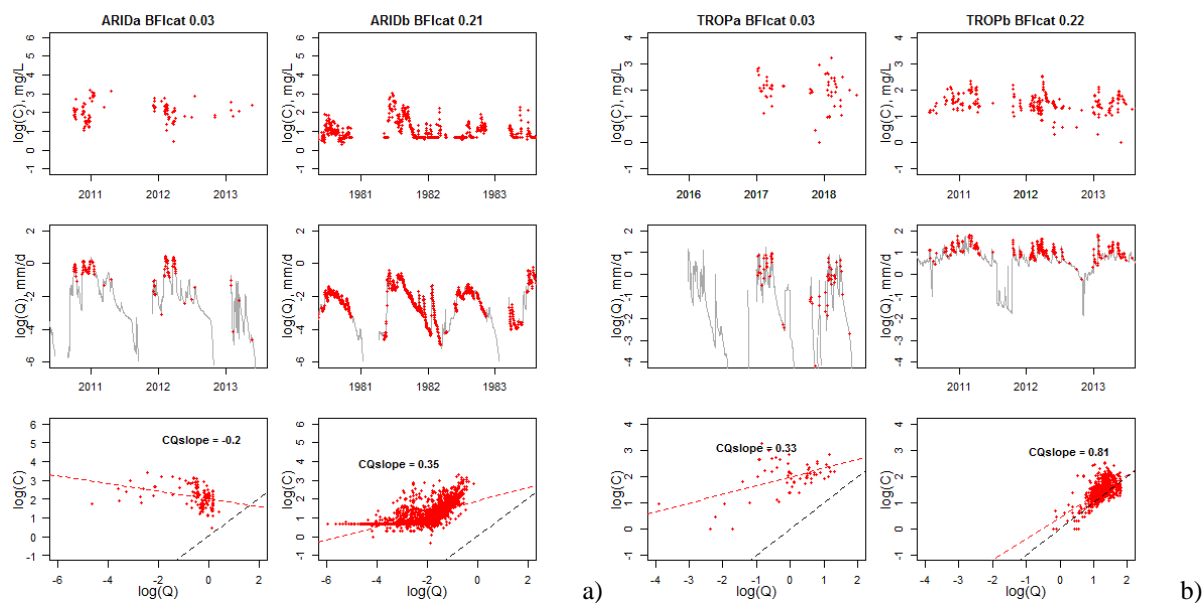
Figure 4. C-Q relationships between TSS and flow for four individual catchments (in columns), including: a) two arid catchments (ARIDa, ARIDb); and b) two tropical catchments (TROPa, TROPb). Within each climate, a low-BFI and a high-BFI catchments are included, with the corresponding *BFI_m* shown in column titles. The top and middle rows for each catchment show a 3-year timeseries for 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 and flow data at each catchment; the red dashed lines show the observed C-Q slope 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 strong a mobilisation behaviour that is enhanced during 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 arid catchment (ARIDa, *BFI_m* = 0.03) has a negative C-Q slope, whereas the high-BFI catchment (ARIDb, *BFI_m* = 0.21) shows a non-linear C-Q relationship (in log-log space). The overall C-Q slope is positive, which however, consists of a negative slope for lower flows, followed by a positive slope when the flow passes a certain threshold. This is similar to the differences in C-Q slopes with 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.

Both tropical catchments (TROPa and TROPb) exhibit positive C-Q slopes that are relatively linear (in log-log space), where seasonal pattern in TSS concentration are in phase with those of streamflow. This highlights consistently strong mobilisation behaviours, with a greater positive C-Q slope for the catchment that has a higher baseflow contribution (TROPb, *BFI_m* = 0.22). Overall, this preliminary analysis on a small subset of catchments suggests that BFI may indeed drive differences in C-Q relationships between catchments, and that these effects may vary across climate zones.

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

3.3.1 Model performance in predicting water quality

250 The calibrated BFI-based C-Q model, when using catchment median BFI (BFI_m) as the predictor, can generally explain 50% 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 0.01-0.04 decreases in NSE across all water

255 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).

260 **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.**

Water quality variable	BFI-based C-Q model	Baseline model
TSS	0.50	0.53
TP	0.54	0.56
SRP	0.62	0.64
TN	0.47	0.50
NOx	0.54	0.58
EC	0.93	0.94

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

265 Our BFI-based C-Q model synthesized the patterns observed for individual catchments (as illustrated in Section 3.2) across the Australian continent. The model suggests that catchment median BFI, BFI_m, has significant influence on the C-Q slope for most climate zones and water quality variables, with some differences between climate zones. Figure 5 presents the median and the 95th credible intervals of these modelled impacts for each water quality variable, derived from the Bayesian posterior estimates of $\delta BFI_{climate}$ (Eqn. 3). The effect of catchment median BFI on C-Q slope is almost always significant, with the

270 95th credible intervals not crossing over 0 for most combinations of water quality variables and climate zones.
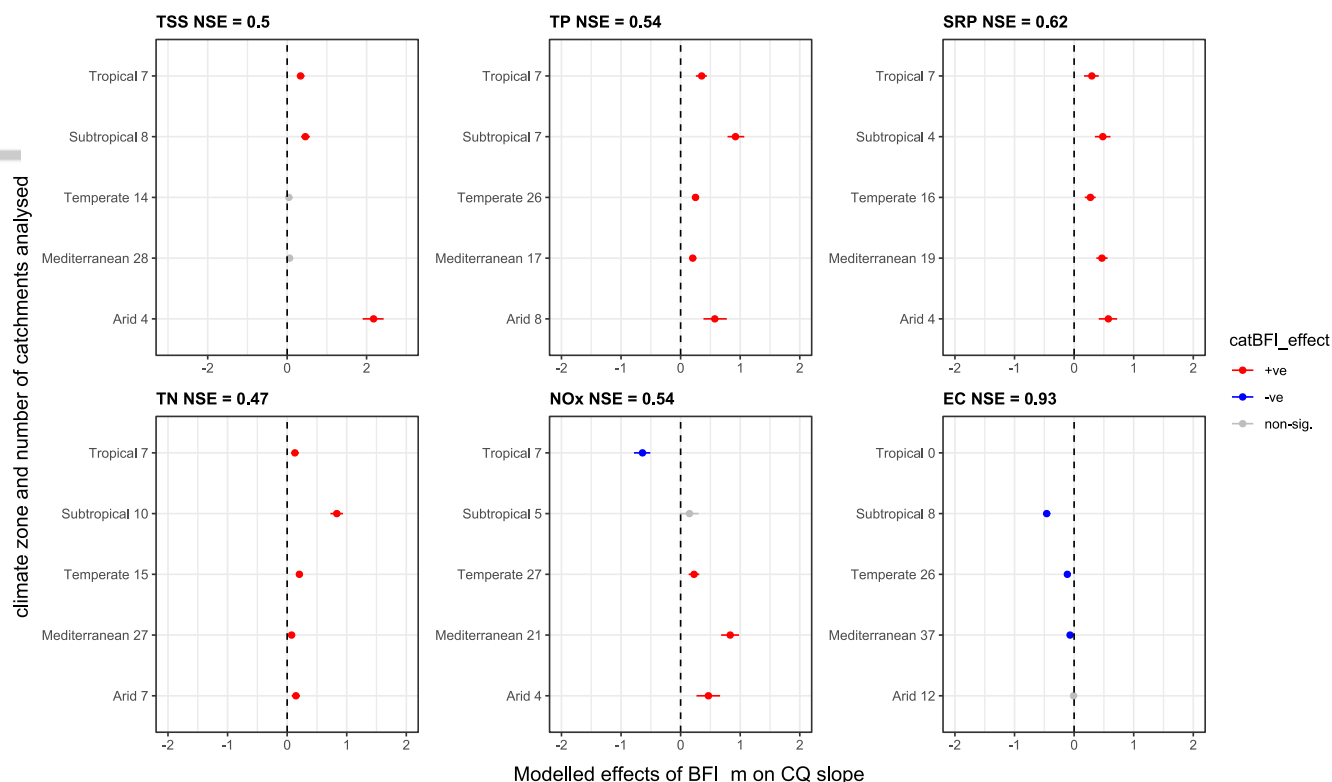
Figure 5. Modelled effects of *BFI_m* on C-Q slope for each climate zone. The bars show the 95% credible interval (2.5th to 97.5th percentile) of modelled effect for each climate zone for each water quality variable, and the dots indicate the corresponding median levels. The colours indicate whether an effect is significantly positive, significantly negative, or non-significant; a positive effect means that C-Q slope increases with higher catchment BFI, and vice versa. Black dashed lines show zero-effect i.e. no effect at all.

Figure 5 shows the directions of the impacts of catchment median BFI (*BFI_m*). To put the impacts of BFI into context, we show the modelled catchment C-Q slopes against the corresponding *BFI_m* values in Figure 6. 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 NOx. In contrast, salts (EC) have largely negative C-Q slopes and are thus dominated by dilution. Regarding the effects of catchment BFI, we first note that for each water quality variable, the fitted relationships between C-Q slopes and BFI 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 stable export patterns between climate zones as found in our preceding study (Lintern et al., in review). The deviation of slopes within each climate zone from the 'grand mean' is dependent on catchment *BFI_m* (Eqn. 2). Therefore, for catchments with low *BFI_m*, 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* are affected more strongly by the differences between climate zones.

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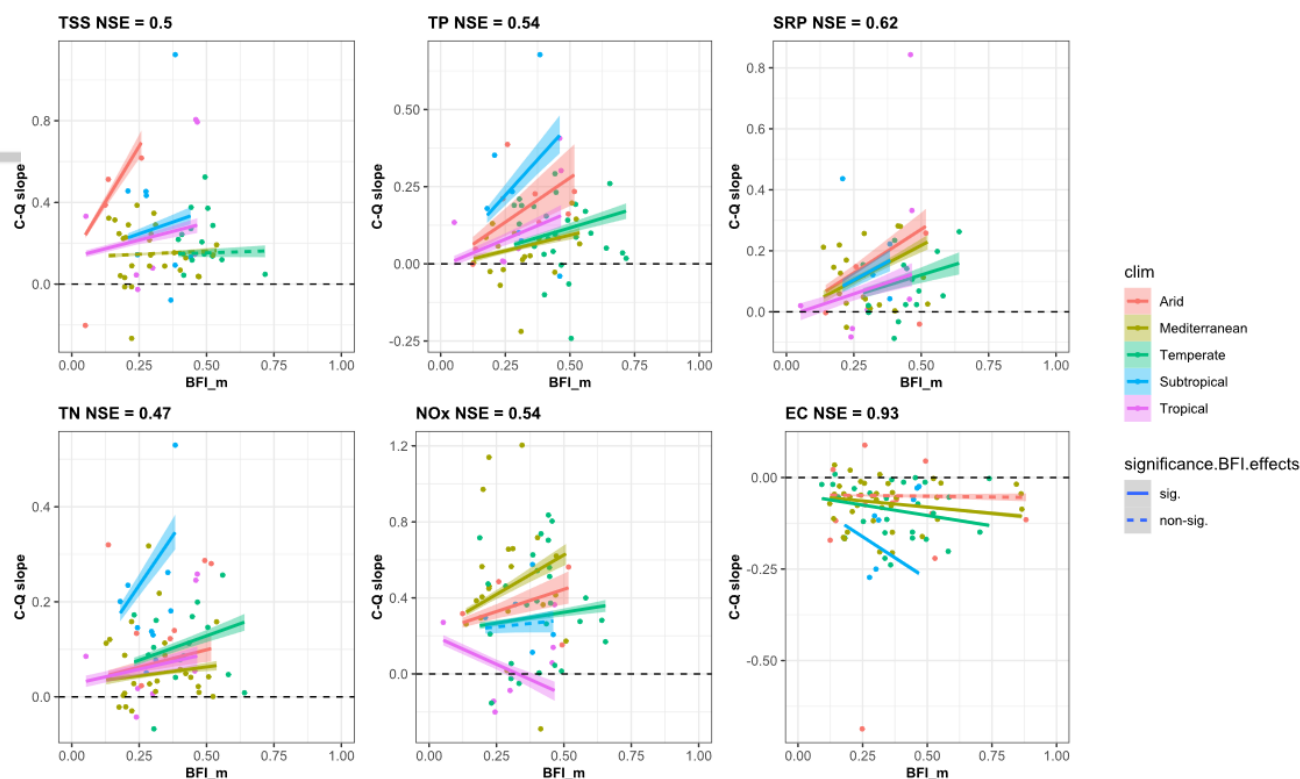
Figure 6. Catchment C-Q slope vs. catchment median BFI (*BFI_m*), coloured by climate zones. The lines represent the modelled C-Q slope~*BFI_m* regression lines for individual climate zones, where *BFI_m* always has a significant impact on C-Q slope, based on the 95th credible intervals shown in Figure 5. The dots represent 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 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

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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.

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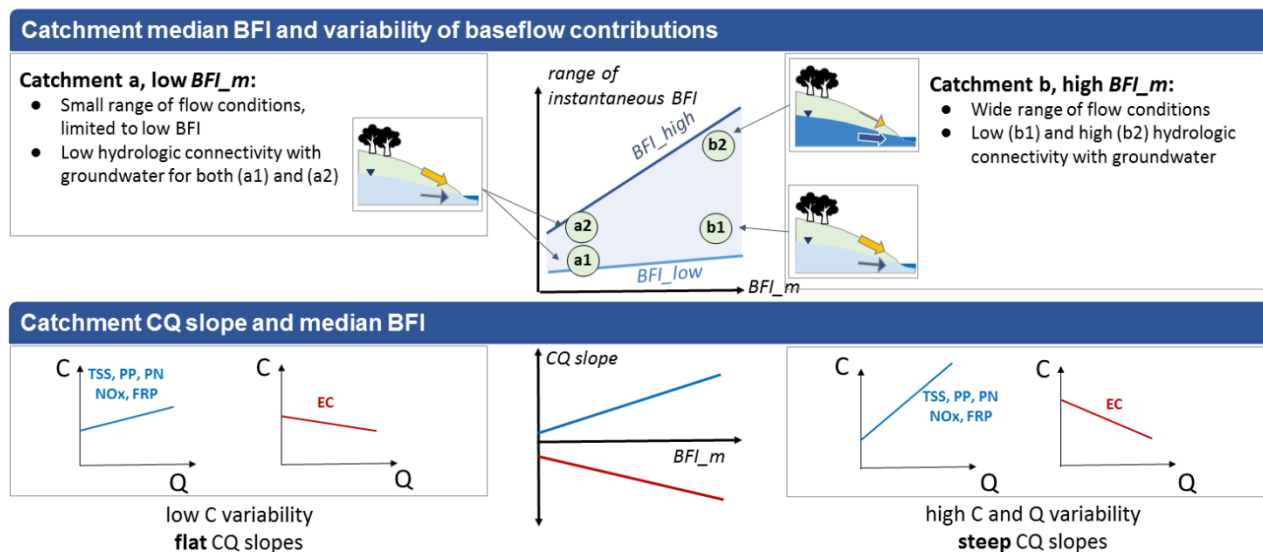
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Figure 7. Conceptual diagram of the modelled effect of baseflow contribution on C-Q slopes, for a catchment with low _BFI_m_ (catchment a) and a catchment with high _BFI_m_ (catchment b).

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

330   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 in Figure 3b. Specifically, catchments with lower _BFI_m_ generally have narrower ranges of instantaneous BFI, which thus tend to always have low baseflow contributions (i.e. surface flow dominated) regardless of dry or wet conditions (Catchment a, Figure 7). This can lead to a limited range of water sources with small variation of flow pathways to transport water chemistry to rivers, resulting in a relative stable export pattern across

335   low and high flows at 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 dominance during wet period and subsurface flows dominance during dry period at these catchments (Catchment b, Figure 7). Consequently, these catchments can have a higher diversity of water sources and potentially larger gradients between groundwater-driven concentrations at low flow and runoff-driven concentrations at high flow.

340   For soluble N and P (NOx and SRP), our results also suggest enhanced mobilisation in catchments with high _BFI_m_. In Australian catchments, soluble N and P concentrations in the groundwater are generally low (Cartwright, 2020). This discards the case of rich nutrient inputs 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

345   between the stream and the vadose zone. However, as the case of TSS and particulate N and P, it is also plausible that the

enhanced mobilisation pattern seen in high *BFI_m* catchments rather results from the larger range of instantaneous BFI and thus more frequent mobilisation events. As discussed above, catchments with a greater variability in the instantaneous BFI are likely having 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 (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 et al. 2017).

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).

Besides the abovementioned 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 with a subset of study catchments where high-frequency observations have been collected.

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 *BFI_m* useful in predicting 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 highly variable baseflow contributions involving both the surface and subsurface pathways, as illustrated in Figure 3 b). Therefore, a valuable avenue for future research would be to identify suitable BFI metrics to better represent the temporal dynamics of flow pathways to further improve the understanding of baseflow impacts on transport processes of water quality constituents.

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

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.

380 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 the C-Q slopes are largely positive for both particular and soluble N and P (NOx, TN, SRP and TP), and are steeper for catchments with higher median BFI across all climate zones (for TN, SRP and TP). The enhanced mobilisation at catchments with higher median BFI is likely a result of more variable flow pathways, which introduces higher concentration gradients between low and high flows
385 that are dominated differently by groundwater and surface water sources. This result highlights the crucial role of flow pathways in determining catchment exports of water quality constituents, and the need of further studies to identify suitable baseflow metrics in differentiating flow pathways. 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.

This study complements our preceding study on the impacts of other catchment characteristics - including land use, land cover,
390 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 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
395 in temporal coverage and sampling frequency. This is particularly relevant for Australia, as water quality monitoring is often undertaken under different local/regional programs focusing on specific management interests.

Data availability

Water quality and flow data used 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
400 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

405 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.

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425 **References**

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

430

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

435

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

440 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

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

445 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

450 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

Hydrology and
Earth System
Sciences
Discussions

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EGU

Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration–discharge relationships reflect chemostatic
455   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
460   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., 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

465   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.

Jensen, C. K., McGuire, K. J., McLaughlin, D. L., & Scott, D. T. (2019). Quantifying spatiotemporal variation in headwater
470   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

475   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

480   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

485 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 on water chemistry states and dynamics in rivers across Australia. Submitted to *Hydrological Processes*

Liu, S., Ryu, D., Webb, J. A., Lintern, A., Guo, D., Waters, D. & Western, A. W. (2021). A Bayesian approach to understanding 490 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 495 Engineers Australia National Conference.

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 500 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

505 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

510 Musolff A:, Q. Zhan, R. Dupas, C. Minaudo, J. H. Fleckenstein, M. Rode, et al. Spatio-temporal Variability in Concentration-Discharge Relationships at the Event Scale. Under review in Water Resources Research.

Hydrology and
Earth System
Sciences
Discussions

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.

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.

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

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

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

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