Controls on spatial variability in mean concentrations and export patterns of river chemistry across the Australian continent

Shuci Liu¹, Rémi Dupas², Danlu Guo³, Anna Lintern⁴, Camille Minaudo⁵, Ulrike Bende-Michl⁶, Kefeng Zhang⁷, and Clémence Duvert⁸

¹Nanjing University of Information Science and Technology
²INRAE, L’institut Agro, UMR 1069 SAS, 35000 Rennes, France
³University of Melbourne
⁴Monash University
⁵EPFLs
⁶Bureau of Meteorology (Australia)
⁷Department of Civil and Environmental Engineering, the University of New South Wales
⁸Charles Darwin University

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Abstract

The state and dynamics of river chemistry are influenced by both anthropogenic and natural catchment characteristics. However, understanding key controls on catchment mean concentrations and export patterns comprehensively across a wide range of climate zones is still lacking, as most of this research is focused on temperate regions. In this study, we investigate the catchment controls on mean concentrations and export patterns (concentration–discharge relationship, C–Q slope) of river chemistry, using a long-term data set of up to 507 sites spanning five climate zones (i.e., arid, Mediterranean, temperate, subtropical, tropical) across the Australian continent. We use Bayesian model averaging (BMA) and hierarchical modelling (BHM) approaches to predict the mean concentrations and export patterns and compare the relative importance of 26 catchment characteristics (e.g., topography, climate, land use, land cover, soil properties and hydrology). Our results demonstrate that mean concentrations result from the interaction of catchment intrinsic and anthropogenic factors (i.e., land use, topography and soil), while export patterns are more influenced by catchment intrinsic characteristics only (i.e., topography). We also found that incorporating the effects of climate zones in a BHM framework improved the predictability of both mean concentrations and C–Q slopes, suggesting the importance of climatic controls on hydrological and biogeochemical processes. Our study provides insights into the contrasting effects of catchment controls across different climate zones. Investigating those controls can inform sustainable water quality management strategies that consider the potential changes in river chemistry state and export behaviour.

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Shuci Liu¹, Rémi Dupas², Danlu Guo³, Anna Lintern⁴, Camille Minaudo⁵, Ulrike Bende-Michl⁶, Kefeng Zhang⁷, Clément Duvert⁸,⁹

¹ Institute for Disaster Risk Management, School of Geographical Sciences, Nanjing University of Information Science & Technology, Nanjing, Jiangsu, 211544, China

² INRAE, L’institut Agro, UMR 1069 SAS, Rennes, France

³ Department of Infrastructure Engineering, University of Melbourne, Victoria, 3010, Australia

⁴ Department of Civil Engineering, Monash University, Victoria, 3800, Australia

⁵ EPFL, Physics of Aquatic Systems Laboratory, Margaretha Kamprad Chair, Lausanne, Switzerland

⁶ Science and Innovation Group – Hydrology Research, Bureau of Meteorology, Canberra, 2601, Australia

⁷ Water Research Centre, School of Civil and Environmental Engineering, UNSW Sydney, NSW 2052, Australia

⁸ Research Institute for the Environment and Livelihoods, Charles Darwin University, Darwin, NT, 0810, Australia

⁹ National Centre for Groundwater Research and Training (NCGRT), Adelaide, SA, 5001, Australia

Corresponding author: Shuci Liu (shuci.liu@nuist.edu.cn)

Key Points:

• Consideration of climate zones in a hierarchical modelling structure improves the predictability of both mean concentrations and C–Q slopes

• Land use, topography and soil are the most influential factors for mean concentrations; while topographic controls show strong effects on export patterns

• The influence of catchment controls on mean concentrations/C–Q slopes varies across climates zones

Abstract

The state and dynamics of river chemistry are influenced by both anthropogenic and natural catchment characteristics. However, understanding key controls on catchment mean concentrations and export patterns comprehensively across a wide range of climate zones is still lacking, as most of this research is focused on temperate regions. In this study, we investigate the catchment controls on mean concentrations and export patterns (concentration–discharge relationship, C–Q slope) of river chemistry, using a long-term data set of up to 507 sites spanning five climate zones (i.e., arid, Mediterranean, temperate, subtropical, tropical) across the Australian continent. We use Bayesian model averaging (BMA) and
hierarchical modelling (BHM) approaches to predict the mean concentrations and export patterns and compare the relative importance of 26 catchment characteristics (e.g., topography, climate, land use, land cover, soil properties and hydrology). Our results demonstrate that mean concentrations result from the interaction of catchment intrinsic and anthropogenic factors (i.e., land use, topography and soil), while export patterns are more influenced by catchment intrinsic characteristics only (i.e., topography). We also found that incorporating the effects of climate zones in a BHM framework improved the predictability of both mean concentrations and C–Q slopes, suggesting the importance of climatic controls on hydrological and biogeochemical processes. Our study provides insights into the contrasting effects of catchment controls across different climate zones. Investigating those controls can inform sustainable water quality management strategies that consider the potential changes in river chemistry state and export behaviour.

1 Introduction

Freshwater ecosystems provide fundamental functions for human life and biodiversity (Carpenter et al., 2011; Pohle et al., 2021; Vanni, 2002). However, local anthropogenic activities such as land use change, land management (Das Kangabam et al., 2019; Mokaya et al., 2004) and global climate change (Cisneros et al., 2014; Yapiyev et al., 2021) have resulted in negative impacts on inland water quality across the world. Therefore, to mitigate the risks for and reduce impacts from impaired water quality, or to preserve good ecological riverine conditions and to sustainably manage water resources, we need appropriate assessments of water quality monitoring data and an improved understanding of river chemistry variability and its major controls.

The effectiveness of water quality mitigation measures is dependent on a thorough understanding of in-stream water quality processes in different physical settings (e.g., hydrology, climate, topography, land use and land cover) (Nainggolan et al., 2018; Schoumans et al., 2014). Previous studies have shown high spatial variability in river chemistry (solutes and particulates concentrations) at regional scales (Diamantini et al., 2018; Heathwaite et al., 2005; Liu, 2019). River chemistry varies considerably among different catchments, as a result of land use and land cover (Aronson et al., 2014; Calijuri et al., 2015; Hunter et al., 2008; Lintern et al., 2018a; Liu et al., 2018), climate (Huang et al., 2003; Lintern et al., 2018a; Sardans et al., 2008; Tockner et al., 1999), topography and geology (Grayson et al., 1997; Holloway et al., 1998; Ice et al., 2003). Furthermore, export dynamics of constituents may change at (sub)daily, seasonal and inter-annual time-scales (Marinos et al., 2020; Minaudo et al., 2019), due to a combination of hydrological and biogeochemical processes, and long-term changes in vegetation cover or land management practices (Basu et al., 2011; Paerl et al., 2018; Weyer et al., 2018).

Investigations of river chemistry concentration (C) and discharge (Q) relationships (referred to as C–Q hereafter) have been used to characterise and identify solute and particulate export dynamics, and the drivers of these dynamics at
the catchment scale (Bieroza et al., 2018; Moatar et al., 2020; Pohle et al., 2021). In particular, the $C$–$Q$ slope, defined as the exponent of a power-law function ($C = aQ^b$), which is derived from the slope of linear fit in $\log(C)$–$\log(Q)$ space, is used as an indication of the export pattern of a constituent (Basu et al., 2011; Godsey et al., 2009; Kim et al., 2017; Musolff et al., 2017). A $C$–$Q$ slope that is significantly positive indicates a flushing pattern, a $C$–$Q$ slope that is significantly negative indicates a dilution pattern and a $C$–$Q$ slope that is not significantly away from zero indicates a constant export pattern (Basu et al., 2011; Kim et al., 2017; Musolff et al., 2017). These export patterns are affected by the constituent type (particulates, geogenic solutes or biogenic solutes) (Lintern et al., 2021; Rose et al., 2018; Zhi et al., 2019), source type (point or diffuse) (Bieroza et al., 2018), dominant transport pathway (surface runoff or baseflow) (Zhi et al., 2019), and whether the constituent is a source- or transport-limited (Shogren et al., 2021).

Previous studies have shown that catchment characteristics such as land use, hydrological variability, topography and geology may control particulate and solute export (Fazekas et al., 2020; Marinos et al., 2020; Musolff et al., 2015; Seybold et al., 2019). For instance, Musolff et al. (2015) found that there was a strong relationship between $C$–$Q$ slopes for nitrate and the percentage of artificially drained arable land within a catchment, indicating that catchment land use has a significant effect (direct or indirect) on the export patterns of nitrate. Similarly, Godsey et al. (2019) identified a strong impact of soil and geological catchment characteristics and land cover on the spatial variability in $C$–$Q$ slopes between catchments in North America.

However, few studies have investigated the relative importance of multiple catchment characteristics and multiple constituents over large spatial scales (e.g., at the continental scale) and between different climate zones. Most of the previous studies are limited to local (e.g., nine sub-catchments in Bode River catchment in Germany with areas ranging from 16 to 593 km$^2$, Musolff et al. (2015)) or regional scales (e.g., 34 catchments within the Gulf of Alaska region with areas ranging from 16 to 63,187 km$^2$, Jenckes et al. (2022)). As such, previous studies have largely used a limited number of monitored catchments (Kim et al., 2017; Musolff et al., 2015), or have had a strong focus on temperate catchments in Europe (Dupas et al., 2018; Dupas et al., 2017; Ebeling et al., 2021; Minaudo et al., 2019; Moatar et al., 2017; Musolff et al., 2021) or North America (Marinos et al., 2020; Wen et al., 2020; Zhang, 2018). Furthermore, whilst there are a small number of continental-scale studies that investigated export patterns between event and interannual scales and identified the controls on mean concentrations (e.g., Godsey et al. (2019)), these are limited to catchments in the Northern Hemisphere, and are limited to few climate zones (e.g., focusing on the temperate zone). Findings from these Northern Hemisphere, mostly temperate catchments are not necessarily transferable to other parts of the world with different climates, as river chemistry may respond to ecosystems and climates differently in the Southern Hemisphere (Dallas, 2008; Hagen et al., 2014). In addition, there is a lack of comprehensive assessment of multiple types of
catchment controls. Therefore, our current understanding of key controls on spatial variability and export patterns across different climates and over large continental scales is still limited.

The potential interactions between different catchment characteristics and the impact of these interactions on river chemistry are not well understood, and even less so across multiple climate zones. Previous studies (e.g., Doody et al., 2016; Moatar et al., 2017; Ebeling et al., 2021) have suggested complex interactions between intrinsic characteristics (e.g., soil type and topography) and extrinsic characteristics (e.g., climate, hydrology, land use and land cover) drive river chemistry states and export patterns. Our recent study also showed that mean concentrations of river chemistry were more climate-dependent than export patterns in Australia (Lintern et al., 2021). Guo et al. (2022) found that the effect of baseflow contribution (baseflow index, BFI) in shaping the $C-Q$ slopes varies across climate zones in Australia, but using BFI as a predictor might not provide sufficient predictive power to simulate and characterise the $C-Q$ slopes. These findings raise the questions of (1) whether or not the controls on mean concentrations/export patterns of river chemistry; and (2) whether or not the effects of controls on export patterns vary across different climate zones.

As such, in this study, we test the hypothesis that climate zones significantly affect the relationship between mean solute and particulate concentrations/export patterns and landscape characteristics.

Thus, in this study, we explore the following research questions: (1) what are the key catchment characteristics that control mean concentrations and export patterns in river chemistry? (2) how do the key controls vary across each of the climate zones? and (3) considering the key catchment controls and their varying effects on mean concentrations/export patterns across climate zones, how well can we predict the spatial variability in these metrics using a statistical modelling framework? To address the research questions and the hypothesis, we used river chemistry and discharge data collected across the Australian continent (previously introduced in Lintern et al. (2021)). A cross-Australia data analysis is particularly interesting as the country covers a large number of contrasting climate zones: arid, Mediterranean, temperate, subtropical and tropical. This unique climatic gradient in a single database allows us to further our understanding of (1) the effect of climate types on river chemistry; (2) the relative importance of a wide range of catchment characteristics (e.g., land use, soil, topography, hydrology, land cover and climate) on mean concentrations/export patterns of river chemistry; and (3) the interactions between the wide range of catchment characteristics and climate zones. We use an integrated Bayesian statistical modelling framework to explore and understand the controls on spatial variability in mean constituent concentrations, and export patterns (i.e., $C-Q$ slope). We analyse six commonly monitored constituents (i.e., total suspended solid – TSS, total nitrogen – TN, the sum of nitrate and nitrite – NOx, total phosphorus – TP, soluble reactive phosphorus – SRP and electrical conductivity – EC) from 507 catchments across the Australian continent.
2 Materials and Methods

2.1 Water quality and discharge data acquisition

We used a national database of discharge and water quality (particulates and solutes, including nutrients) monitoring data from seven state/territory authorities (Table S1, Supporting Information and more details such as analytical methods can be found in Data Set S1 in Supporting Information). This database was collated based on all available water chemistry and discharge data from 507 monitoring sites from 1964 to late 2019. Both discharge and water quality data were checked for quality and cleaned through a quality control process (e.g., removal of high uncertainty measurements and water quality data not associated with discharge), by using quality codes and flags (Table S1) as recommended by individual state authorities (Guo et al., 2022; Lintern et al., 2021). We focused on six constituents, namely TSS, TN, NO\textsubscript{X}, TP, SRP and EC. The majority of the water quality data was collected manually using grab samples, with a few exceptions of high-frequency measurements of EC; while discharge data was recorded at a daily timestep.

To ensure the reliability and robustness of C–Q slope estimates, we selected the monitoring sites with (1) at least ten-year water quality and discharge monitoring records; and (2) at least 50 C–Q pairs (Lintern et al., 2021). This selection procedure led to a total number of 507 sites (Figure 1a) retained for further analysis, with the number of sites for individual constituents ranging from 143 sites for NO\textsubscript{X} to 479 sites for EC. The average length of the data series ranges from 17 (TN) to 27 (EC) years, and the average number of C–Q pairs varies from 246 (TN) to 1349 (EC). A detailed summary of water quality and discharge data for individual constituents can be found in Table S2.

2.2 Catchment characteristics

The 507 selected monitoring sites are located across the Australian continent. Catchment boundaries of the 507 monitoring sites were obtained using the Geofabric tool provided by the Australian Bureau of Meteorology (Bureau of Meteorology, 2012). According to the updated Köppen-Geiger Climate Classification (Peel et al., 2007), these catchments can be classified into five major climate zones (i.e., arid, Mediterranean, temperate, subtropical and tropical in Figure 1a) as per Lintern et al. (2021). The strong climatic gradient in these catchments results in drastic differences in catchment characteristics, such as catchment average annual rainfall (Figure 1b), catchment slope (Figure 1c) and land use (agriculture, Figure 1d). The distribution of these catchment characteristics within each climate zone can be found in the boxplots in Figures S1 to S3.
Figure 1. Location of monitoring sites and examples of catchment characteristics.
tics included in this study. (a) Location of 507 monitoring sites with different colours representing five climate zones (Ari – arid, Med – Mediterranean, Temp – temperate, Sub – subtropical and Tro – tropical). The total number of catchments is indicated next to the abbreviation of climate zones. (b) Catchment annual average precipitation. (c) Catchment average slope. (d) Catchment average percentage area as agricultural land use. States and territories shown on these maps are Northern Territory – NT, New South Wales – NSW, Queensland – QLD, South Australia – SA, Victoria – VIC, Western Australia – WA and Tasmania – TAS.

We obtained 26 catchment characteristics as explanatory variables (see Sect. 2.3.1) using publicly available datasets. These were categorised into topography, land cover, land use, soil, climate and hydrological characteristics (detailed description and temporal period in Table 1.; summary statistics in Table S3). These catchment characteristics were retrieved from a national Environmental Attributes Database (Geoscience Australia, 2011), other than soil characteristics which were extracted from the Soil and Landscape Grid of Australia’s National Soil Attribute Maps (Terrestrial Ecosystem Research Network, 2016). We selected catchment characteristics based on previous literature highlighting the characteristics that are most likely to influence the spatial variability and export patterns in riverine water quality (Chang, 2008; Guo et al., 2021; Kleinman et al., 2004; Lintern et al., 2018a; Lintern et al., 2018b; Liu et al., 2021b; Marinos et al., 2020; Musolff et al., 2015). There are a few pairs of catchment characteristics with strong cross-correlations (Figure S4, Supporting Information), e.g., a Pearson’s correlation coefficient $r = -0.84$ for slope and Topographic Wetness Index (TWI); $r = 0.91$ for catchment area and soil TN. We further discuss the influence of strong correlations between catchment characteristics on modelling performance as well as inference of modelling results in Sect. 4.

Table 1. Summary of 26 catchment characteristics investigated in this paper.

<table>
<thead>
<tr>
<th>Catchment characteristic</th>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Topography</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catchment area</td>
<td>Area</td>
<td>Upstream catchment area (km²)</td>
</tr>
<tr>
<td>Stream density</td>
<td>StreamDensity</td>
<td>The ratio of total length of all upstream stream segments to contributing area (km/km²)</td>
</tr>
<tr>
<td>Catchment average elevation</td>
<td>Elevation</td>
<td>The average elevation in the catchment (m)</td>
</tr>
<tr>
<td>Catchment storage</td>
<td>Storage</td>
<td>The proportion of upstream areas that are valley bottom (%)</td>
</tr>
<tr>
<td>Distance to source</td>
<td>UpstreamDist</td>
<td>Maximum flow path length upstream to the catchment outlet (km)</td>
</tr>
<tr>
<td>Catchment average slope</td>
<td>Slope</td>
<td>Average upstream catchment slope (°)</td>
</tr>
<tr>
<td>Topographic Wetness Index</td>
<td>TWI</td>
<td>The topographic wetness index is calculated as log (specific catchment area/slope)</td>
</tr>
<tr>
<td><strong>Climate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catchment solar radiation</td>
<td>Radiation</td>
<td>Catchment average annual mean solar radiation (MJ/m²/day)</td>
</tr>
<tr>
<td>Catchment temperature</td>
<td>Temperature</td>
<td>Catchment average annual mean temperature (°C)</td>
</tr>
<tr>
<td>Catchment rainfall</td>
<td>Rainfall</td>
<td>Catchment average annual mean rainfall (mm)</td>
</tr>
<tr>
<td>Rainfall erosivity</td>
<td>Erosivity</td>
<td>Catchment average rainfall erosivity R factor (MJ/ha/hr/yr)</td>
</tr>
<tr>
<td><strong>Land use</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catchment characteristic</td>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Agricultural land use</td>
<td>Agriculture</td>
<td>Sum of irrigated land, aquaculture, intensive animal production and intensive plant production (%)</td>
</tr>
<tr>
<td>Urban land use</td>
<td>Urban</td>
<td>The proportion of catchment that is urban (%)</td>
</tr>
<tr>
<td>Forestry land use</td>
<td>Forestry</td>
<td>The proportion of catchment that is used for forestry</td>
</tr>
<tr>
<td><strong>Soil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil TN</td>
<td>TN_soil</td>
<td>Mass fraction of total nitrogen in the 0-5cm soil by weight (%)</td>
</tr>
<tr>
<td>Soil TP</td>
<td>TP_soil</td>
<td>Mass fraction of total phosphorus in the 0-5cm soil by weight (%)</td>
</tr>
<tr>
<td>Soil sand</td>
<td>Sand_soil</td>
<td>0-5cm soil sand content (%)</td>
</tr>
<tr>
<td>Soil clay</td>
<td>Clay_soil</td>
<td>0-5cm soil clay content (%)</td>
</tr>
<tr>
<td>Soil carbonated</td>
<td>Carbonated</td>
<td>Mass fraction of carbon by weight in the 0-5cm soil</td>
</tr>
<tr>
<td><strong>Land cover</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Woodland and forest</td>
<td>Woodforest</td>
<td>Catchment percentage natural woodland cover and natural forests</td>
</tr>
<tr>
<td>Grass cover</td>
<td>Grass</td>
<td>Catchment percentage natural grasses cover</td>
</tr>
<tr>
<td>Shrubs cover</td>
<td>Shrubs</td>
<td>Catchment percentage extant/naturally shrub cover</td>
</tr>
<tr>
<td>Bare land</td>
<td>Bare</td>
<td>Catchment percentage extant/naturally bare</td>
</tr>
<tr>
<td><strong>Hydrology</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catchment average runoff</td>
<td>Runoff</td>
<td>Catchment average annual surface runoff (mm)</td>
</tr>
<tr>
<td>Coefficient of variation of annual runoff</td>
<td>CV_Runoff</td>
<td>Coefficient of variation of annual surface runoff</td>
</tr>
<tr>
<td>Perenniality</td>
<td>Perenni0lity</td>
<td>Contribution to mean annual discharge by the six driest months</td>
</tr>
</tbody>
</table>

2.3 Statistical analyses

2.3.1 Time-averaged mean concentration and $C$–$Q$ slope

We first calculated the time-averaged mean concentration, as well as computed the $\log(C) - \log(Q)$ slope for individual constituents at individual sites. Figures S5 to S10 show locations of sites, the spatial distribution of mean concentrations and $C$–$Q$ slopes of individual constituents. Summary statistics and boxplots of mean concentrations and $C$–$Q$ slopes across different climate zones are provided in Table S4, and Figures S11 and S12 (Supporting Information). We also tested the differences in mean concentrations and $C$–$Q$ slopes between different climate zones using a Kruskal-Wallis test ($\alpha=0.05$). These two metrics were used as response variables in a Bayesian modelling framework (see Sect. 2.3.2). Prior to the analyses, we transformed the data using power transformation, to improve the normality and symmetry of the response variables, i.e., Box-Cox for mean concentrations and Yeo-Johnson for $C$–$Q$ slopes (Atkinson et al., 2021; Yeo et al., 2000). The Yeo–Johnson transformation was selected as it can handle negative values in the $C$–$Q$ slopes. Histograms of mean concentration and $C$–$Q$ slopes before and after transformation, transformation parameters and normality test results can be found in Figures S13 and S14, Supporting Information.

2.3.2 Bayesian model averaging in a hierarchical structure

A Bayesian model averaging (BMA) approach was used to compare the relative importance of potential explanatory variables and identify the catchment characteristics that influence mean concentrations and export patterns (research
Unlike the traditional ‘single best’ model approach where prediction and inference are derived from one model, which may suffer from the over-confident inference issue resulting from ignoring the uncertainty in model selection, BMA accounts for the model selection uncertainty when determining the optimal model structure (Kaplan, 2021; Raftery et al., 1997; Yimer et al., 2021). This approach has been applied to investigate the spatial and temporal variability in-stream water quality in regional studies in Australia (Guo et al., 2021; Liu et al., 2021a) and elsewhere around the globe (Krueger, 2017; Wang et al., 2020). More details about Bayes’ theorem and the related mathematical background of BMA can be found in Raftery (1996) and Hoeting et al. (1999).

In Bayesian linear regression models, a binary latent variable - inclusion variable $I$ is introduced:

$$
(1)
$$

where $y$ is the response variable that is assumed to follow a normal distribution with the mean modelled by predictors and standard deviation $\sigma$, $X = [x_1, \ldots, x_p]$ is a matrix of $p$ potential predictors, $\beta$ is a $p \times 1$ vector of regression coefficients, and $I = (I_1, \ldots, I_p)'$ is a binary vector of inclusion variable that is defined as:

$$
(2)
$$

where $I_i = 1$ indicates that $i^{th}$ predictor $x_i$ is included in the model.

The inclusion variable $I$ for individual predictors is utilised to quantify the relative importance of model predictors, as well as identify the plausible model structures (i.e., different combinations of $I_n$) through assessment of posterior inclusion probabilities (PIP) and posterior model probabilities (PMP) (Höge et al., 2019; Kaplan, 2021). Additionally, the BMA can provide multi-model ensemble predictions using posterior model probabilities as weights, averaging over all visited models through Markov chain updating (i.e., the relative frequency at which each model is sampled) (Ley et al., 2007; Yimer et al., 2021). We considered variables with a PIP above 0.75 ($Pr(I = 1 | y) > 0.75$) as the cut-off to consider a predictor as important (Mutshinda et al., 2013; Thomson et al., 2010; Viallefont et al., 2001). A PIP of 0.75 indicates substantial evidence to support the importance of such a predictor given the prior distribution, as suggested by Jeffreys (1998).

To address the second and third research questions (i.e., how the key controls vary across climates and how well we can predict mean concentrations and export patterns, respectively), we further extended the classical BMA to account for differences in the effect of catchment characteristics across climate zones, in a Bayesian Hierarchical modelling (BHM) structure. We used this modelling framework to test our hypothesis that there is a significant difference in the
effect of key catchment characteristics across different climate zones. This modelling framework allows us to consider alternative model structures to reflect the complex interactions between water quality data and their key drivers across multiple catchments (Gladish et al., 2016; Wikle et al., 2001). BHM is a powerful tool to provide robust inference through ‘borrowing strength’ across different groups of observations as the model parameters are assumed to be sampled from a common distribution (Gelman et al., 2006; Gelman et al., 2013). This advantage enables the application of BHM to predict water quality that confounds issues such as a limited number of data or low sampling frequency (Guo et al., 2022; Liu et al., 2021a; Perera et al., 2021; Wan et al., 2014). The proposed modelling framework is as follows:

\[
(3) \quad (4)
\]

where, \( y_{i,j} \) – mean concentration or \( C-Q \) slope of the \( i^{th} \) catchment in the \( j^{th} \) climate zone, following a normal distribution with mean \( \mu_{i,j} \) and standard deviation \( \sigma_{i,j} \); \( I \) – inclusion variable (0 or 1); \( o_{j} \) – regression intercept of the \( j^{th} \) climate zone; \( n_{j} \) – regression coefficient of the \( n^{th} \) catchment characteristics in the \( j^{th} \) climate zone; \( X_{n,i} \) – the \( n^{th} \) catchment characteristics in the \( i^{th} \) catchment; and \( N \) – total number of catchment characteristics (i.e., 26).

Prior to the analyses, both response variables (i.e., mean concentration or \( C-Q \) slope) and explanatory variables (i.e., 26 catchment characteristics) were standardised (mean = 0 and standard deviation = 1), which ensured the regression coefficients were on the same scale and allowed us to compare the effect of catchment characteristics in a more direct way (Cade, 2015).

It is worth noting that in this modelling framework, we did not differentiate the relative importance of individual catchment characteristics (\( I \) in Eqn. (4)) across different climate zones, but the effect (i.e., magnitude of influence) of catchment characteristics (\( n_{j} \) in Eqn. (4)) were made climate-specific. This is because 1) a universal \( I \) term allows us to identify the same set of important catchment characteristics, which can be characterised as ‘overarching’ effect of individual catchment characteristics at the continental scale; 2) we aim to compare the climate-specific effect of key controls, which is captured by the coefficient \( n_{j} \); this cannot be achieved with a different \( I \) for each climate zone, which might otherwise lead to multiple sets of key controls for different climate zones.

2.3.3 Time-averaged mean concentration and \( C-Q \) slope

We used the \( R \) package \( rjags \) to implement our BHM framework, calibrate the model parameters and generate model predictions (Plummer, 2013; R Core Team, 2013). The prior distributions of individual model parameters were assigned and then updated through Markov chain Monte Carlo (MCMC) with the
Gibbs sampling method to derive the posterior distribution of model parameters (Gelman et al., 2013). The model parameters and predictions were obtained from three independent chains, each of which had 30,000 iterations. The prior distribution of (Eqn. (3)) is minimally-informative as an inverse gamma distribution with the same shape and scale parameters ( ~ IG (10^{-4}, 10^{-4})) (O’Hara et al., 2009). The prior distribution of \( I_n \) followed an independent Bernoulli distribution with a probability of 0.5 (\( I_n \sim Bern (0.5) \)) (Raftery et al., 1997), which assumed each model structure had equally prior likelihood as the ‘true’ model. The prior distribution of regression coefficient \( n,j \) was conditioned on \( I_n \):

\[
\text{(5)}
\]

where followed an uninformative uniform distribution between 0 and 10 ( ~ U (0, 10)) (Gelman, 2006; Gelman et al., 2013). We checked the convergence of Markov chains using the Gelman-Rubin statistic \( Rhat \), with \( Rhat < 1.1 \) indicating convergence (Gelman et al., 1992; Gelman et al., 2013).

The posterior distribution of \( I_n \) – posterior inclusion probability (PIP), quantified the relative importance of the individual catchment characteristics. In addition, the posterior distribution of \( I_n \) informed the likelihood of optimal models – posterior model probability (PMP), as different combinations of \( I_n \) formulate different model structures. The predictions of mean concentrations or \( C-Q \) slopes were derived from averaging of the multiple plausible models identified, based on the PMP of individual candidate models (Forte et al., 2018). The performances of multi-model predictions were evaluated using Nash-Sutcliffe efficiency (NSE) (Nash et al., 1970).

We first investigated the relative importance of individual categories of catchment characteristics (e.g., climate) on mean concentrations and \( C-Q \) slopes through a ‘leave-one-category-out’ analysis, in which we excluded one category of catchment characteristics and calibrated the model. This process is conducted on individual categories of catchment characteristics. We then compared the difference in the model performance (i.e., NSE) between the full model (using all the categories) and the ‘leave-one-category-out’ analyses across all categories.

We further assessed the consistency and reliability of the calibrated \( I_n \), as well as the robustness of the modelling framework based on uncertainty analysis. We first randomly selected 80% of the catchments, and subsamples of observations were used to calibrate the proposed Bayesian modelling framework. The remaining 20% of the catchments were used to validate the calibrated model. This process was repeated 1,000 times to obtain subsampling-based ensembles of \( I_n \) estimations (Iskandarani et al., 2016; Ramsey, 1997). Compared to the result derived from the full model (utilising the full set of catchment characteristics for calibration), the resulting posterior distribution of \( I_n \) from 1,000 subsampling ensembles for individual catchment characteristics were used to quantify the
uncertainty in PIP. We also compared the model performance between the calibration and validation catchments, which allowed us to evaluate the robustness of the modelling framework.

The magnitude and direction of effects of key controls were determined and evaluated for catchment characteristics with 1) a PIP > 0.75 from the full model calibration (i.e., over 75% likely models that contain such variables) which identifies an important predictor, see Sect. 2.3.2; and 2) the 95% credible interval (CI) of posterior distributions of $n_j$ not crossing zero (i.e., significant effect).

Finally, we compared the predictive performance of the proposed BHM (i.e., hierarchical BMA, H-BMA hereafter) framework to a classical BMA (C-BMA hereafter) without hierarchical structure, which was calibrated to the same data but with the effect of individual catchment characteristics kept identical across different climate zones (i.e., $n_j$ becomes $n$ in Eqn. (4)). We compared the performances (i.e., NSE) of the proposed H-BMA to the C-BMA structure to assess if improvement in modelling performances could be achieved using the BHM framework.

3 Results

3.1 Model performance

The proposed hierarchical Bayesian models perform well for explaining the variability in mean concentrations (Figure 2, average NSE of 0.70 across six constituents), with NSE ranging from 0.58 (SRP) to 0.86 (EC). In contrast, the modelling performances drop to an average NSE of 0.32 for predicting $C$-$Q$ slopes (NSE ranging from 0.25 for NO$\text{X}$ to 0.39 for both TP and TN, Figure 3). We also provide the modelling performance on the original (untransformed data) scale by back-transforming the predictions using corresponding transformation parameters (Figures S15 and S16). It is noted that the modelling performances for $C$-$Q$ slope on the original scale are comparable with those of transformed $C$-$Q$ slope, while there are large biases for predicting mean concentrations on the original scale for sites with large values, e.g., TN, TP and SRP (Figure S13b, d and e). This is because the Box-Cox transformation on mean concentrations normalises the data by minimising the influence of large values (e.g., outliers), focusing more on the lower values to ensure the validity of the assumption of normality. Thus, the model’s performance at sites showing high values is compromised. We provide a more detailed discussion on the implications of biases on back-transformed high-value sites in Sect. 4.3.
Figure 2. Scatter plots of observed and modelled mean concentrations for: (a) TSS; (b) TN; (c) NO\textsubscript{X}; (d) TP; (e) SRP; and (f) EC. Different colours indicate different climate zones. Grey bars represent 95\% CI from multi-model predictions. Note: variables are standardised with a mean of 0 and a standard deviation of 1.
Figure 3. Scatter plots of observed and modelled C–Q slopes for: (a) TSS; (b) TN; (c) NO\textsubscript{X}; (d) TP; (e) SRP; and (f) EC. Different colours indicate different climate zones. Grey bars represent 95% CI from multi-model predictions. Note: variables are standardised with a mean of 0 and a standard deviation of 1.

The comparison of the modelling performances between the C-BMA and H-BMA (Table 2) shows that there is an average NSE increase of 27% and 62% for the modelling of mean concentrations and C-Q slopes, respectively, suggesting that a significant improvement is achieved in predicting mean concentrations and export patterns when the effects of climate zones are incorporated explicitly using H-BMA. In addition, the median NSE between calibration and validation results from 1,000 replicates are comparable (difference in NSE < 0.2, Table S3, Supporting Information), indicating the robustness of the modelling framework.

Table 2. Comparison of model performances between classical and hierarchical Bayesian Model Averaging (C-BMA and H-BMA, respectively) for modelling mean concentrations and C–Q slopes for individual constituents.
### Constituent NSE - mean concentration NSE - C-Q slope

<table>
<thead>
<tr>
<th>Constituent</th>
<th>C-BMA</th>
<th>H-BMA</th>
<th>C-BMA</th>
<th>H-BMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>0.55</td>
<td>0.70</td>
<td>0.18</td>
<td>0.30</td>
</tr>
<tr>
<td>TN</td>
<td>0.58</td>
<td>0.73</td>
<td>0.21</td>
<td>0.39</td>
</tr>
<tr>
<td>NO\textsubscript{X}</td>
<td>0.41</td>
<td>0.69</td>
<td>0.18</td>
<td>0.25</td>
</tr>
<tr>
<td>TP</td>
<td>0.58</td>
<td>0.64</td>
<td>0.28</td>
<td>0.39</td>
</tr>
<tr>
<td>SRP</td>
<td>0.52</td>
<td>0.58</td>
<td>0.18</td>
<td>0.30</td>
</tr>
<tr>
<td>EC</td>
<td>0.72</td>
<td>0.86</td>
<td>0.16</td>
<td>0.28</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>0.56</strong></td>
<td><strong>0.70</strong></td>
<td><strong>0.20</strong></td>
<td><strong>0.32</strong></td>
</tr>
</tbody>
</table>

#### 3.2 Key catchment controls on mean concentrations and export patterns

The ‘leave-one-category-out’ analysis indicates that for mean concentrations (Figure 4a), land use has a large influence on NO\textsubscript{X} and SRP, while soil characteristics are important for TSS and TP. Catchment topography and climate have a high impact on TN and NO\textsubscript{X}, respectively. In addition, for C-Q slopes (Figure 4b), catchment topography is a strong driver for all constituents. In the following sections we provide more detailed results on the influence of individual characteristics within each category.
Figure 4. Changes in NSE between the full model and ‘leave-one-category-out’ analysis across individual constituents for (a) mean concentrations; and (b) C–Q slopes. Different colours indicate different categories of catchment characteristics. Each bar indicates the percent changes in NSE between performances of the full model and the model without the specific category of catchment characteristics.

3.2.1 Model concentration

Figure 5 presents the results of posterior inclusion probability (PIP) derived from the full model and subsample-based uncertainty analysis for the mean concentrations of individual constituents. These parameters represent the importance of each of the catchment characteristics in influencing spatial variability in mean concentrations of individual constituents. For example, for TSS, the variables with a PIP > 0.75 (above which we considered that effects are significant, as discussed in Sect 2.3.2) include catchment slope, catchment average radia-
tion, catchment average rainfall, soil TN, soil clay and coefficient of variation (CV) of runoff. When considering specific catchment characteristics, land use has a high impact on nutrient species, such as agriculture for NO\textsubscript{X} and TN, and urban for SRP. Catchment topographic characteristics also have consistently high relative importance, such as catchment slope for all constituents, except for EC; and catchment elevation for TN and EC. In addition, catchment soil characteristics contribute significantly to the spatial variability in TSS, TN and TP - % of clay in soil; NO\textsubscript{X} - % of TN in soil. In contrast, catchment hydrology and land cover only have a limited influence on mean concentrations, except for the coefficient of variation (CV) of runoff for TSS; woodland and forest for TN; and rainfall for EC. It is also worth noting that most of the PIP obtained from the full model are within the 95% confidence interval of distribution of 1,000 replicates (i.e., coloured error bar in Figure 5), indicating the reliability and robustness of the inference of our modelling framework.
Figure 5. Posterior inclusion probability (PIP) for each catchment characteristic and for the mean concentrations of: (a) TSS; (b) TN; (c) NOX; (d) NOX; (e) TP; (e) SRP; and (f) EC. Red triangles represent PIP from the full model. Error bars and dots indicate 95% confidence intervals and median, respectively, from 1,000 replicates of the subsampling uncertainty analysis. The abbreviations of individual catchment characteristics can be found in Table 1.

3.2.2 Export pattern

Similar to the PIP results for mean concentrations, we found that the key controls (i.e., PIP >0.75) of catchment characteristics on C·Q slopes vary among constituents (Figure 6). Catchment topography (e.g., upstream distance and elevation) is an important factor for sediment (TSS), sediment-bound constituents (TN and TP) and solutes (EC). In addition, land use and land cover characteristics have a relatively high impact on TSS and EC (forestry), and TP (shrubs), respectively. We also note that catchment hydrology and climate have a moderate effect on TN and TP (e.g., runoff CV for TN, and erosivity for TP). However, for NOX, we do not see any catchment characteristics standing out, as the PIPs for all variables are comparable, suggesting none of the predictors has high predictive power.
Figure 6. Posterior inclusion probability (PIP) for each catchment characteristic and for the $C-Q$ slopes of: (a) TSS; (b) TN; (c) NO$_X$; (d) TP; (e) SRP; and (f) EC. Red triangles represent PIP from the full model. Error bars and dots indicate 95% confidence intervals and median, respectively, from 1,000 replicates of the subsampling uncertainty analysis. The abbreviations of individual catchment characteristics can be found in Table 1.

3.3 Differences in key catchment controls across climate zones

Figures 7 and 8 show the magnitude and direction of significant effects of key controls on mean concentrations and export patterns across different climate zones. Overall, there are on average six variables identified as significant for each constituent’s mean concentration, compared to four variables for $C-Q$ slopes. Most of the significant effects have the same direction across different climate zones, but it is noted that certain key catchment characteristics either have different magnitudes of effects (e.g., rainfall has a strongly negative effect on the mean concentrations of EC in arid, temperate and subtropical zones but a much less negative effect in the tropical region), or different directions of effects (e.g., the CV of runoff has a positive effect on TSS in the arid zone but a negative effect in the temperate and tropical zones). We further discuss the underlying mechanisms responsible for these contrasting effects across climate zones in Sect. 4.
Figure 7. Effect of key catchment controls on mean concentrations across
different climate zones: (a) TSS; (b) TN; (c) NO\textsubscript{X}; (d) TP; (e) SRP; and (f) EC. Colours indicate the magnitude of the median coefficient, ranging from negative (blue) to positive (red). Significance is determined by both PIP and climate-specific effect ($n_j$). The abbreviations of individual catchment characteristics can be found in Table 1.
Figure 8. Effect of key catchment controls on $C/Q$ slopes across different
climate zones: (a) TSS; (b) TN; (c) NO\textsubscript{X}; (d) TP; (e) SRP; and (f) EC. Colours indicate the magnitude of the median coefficient, ranging from negative (blue) to positive (red). Significance is determined by both PIP and climate-specific effect (\( n_{ij} \)). The abbreviations of individual catchment characteristics can be found in Table 1.

4 Discussion

We first discuss the key catchment controls on mean concentrations and export patterns by jointly assessing the results of the ‘leave-one-category-out’ analysis (Figure 4) and PIP derived from the H-BMA (Figures 5 and 6). We then consider the differences (i.e., magnitude and direction of the effects) in the key catchment controls across climate zones (Figures 7 and 8). Lastly, we discuss how our results lead to an improved understanding of river chemistry processes and outline the limitations of the study.

4.1 Contrasting catchment controls of mean concentrations and export patterns

Our results indicate that key controls on mean concentrations vary across different constituents, while key controls are more consistent across different constituents for export patterns (Figure 4). This suggests the different constituents originate from different sources and are subject to different retention and reactive transport processes (Granger et al., 2010; Lintern et al., 2018a; Musolff et al., 2015), while the same topographic and flow path controls influence the export patterns of the constituents investigated in this study. The strong effect of topographic characteristics on both mean concentrations and export patterns highlights that the spatial and temporal variations in hydrological connectivity that links sources, flow pathways and streams control the solutes and particulates export (Ebeling et al., 2021; Musolff et al., 2017; Tunaley et al., 2017). Compared to mean concentrations, C–Q slopes are better explained by natural characteristics rather than anthropogenic factors (e.g., agricultural land use). This contrasts with earlier findings where spatial variability in export patterns of solutes (e.g., dissolved N) was associated with anthropogenic factors, both in Europe (e.g., Moatar et al., 2017; Minaudo et al., 2019; Musolff et al., 2021) and North America (e.g., Marinos et al., 2020; Seybold et al., 2019).

4.1.1 Land use controls on constituent sources

Land use controls were identified as the most important factors for mean concentrations of reactive nutrients (i.e., NO\textsubscript{X} and SRP), and moderately important factors for TN and TP. This indicates that certain activities (e.g., urbanisation, agriculture) act as sources of constituents in catchments, which is in line with previous studies across catchments in Europe and the United States (Hrachowitz et al., 2015; Li et al., 2008; Lintern et al., 2018a; Moatar et al., 2017). We found that agricultural activities were positively related to the mean concentrations of TN and NO\textsubscript{X}, suggesting that elevated levels of N species in rivers can be attributed to the increases in N inputs through the application of fertiliser (Azizian et al., 2015), as well as N-rich waste from livestock farming in Australia (Gourley et al., 2012; Scarsbrook et al., 2015). Inland arid catchments in Australia
are typically associated with long dry periods followed by intense rainfall events (Guo et al., 2020; Rouillard et al., 2015), resulting in ‘flash floods’ that tend to carry large amounts of eroded sediments (Dunkerley et al., 1999; Vanmaercke et al., 2010). This is also reflected by the highest TSS mean concentrations in the arid zone (Figure S11a). For TP and SRP, we found that urban land has a strong positive impact, indicating that cities and townships may be a large P source. Point sources of P discharged from wastewater treatment plants lead to an increase in P concentrations in rivers (Bunce et al., 2018; Whitehead et al., 2014). In addition to these point sources, Hobbie et al. (2017) who investigated seven urban catchments of the Mississippi River, found that large impermeable areas (e.g., streets and buildings) in urban areas increased the overland flow and enhanced the transport of P-rich materials from terrestrial ecosystems to stormwater.

In contrast to the studies in North America and Europe where land use patterns have been found to have a strong influence on the export of particulates and solutes (Basu et al., 2011; Bieroza et al., 2018; Dupas et al., 2019; Marinos et al., 2020; Musolf et al., 2015; Zhang, 2018), our Australia-wide study indicates that there is limited effect of land use on export patterns of the majority of constituents we examined. Our results also indicate that export patterns for most particulates and solutes in Australian catchments are flushing patterns (C–Q slopes > 0, Figure S12), leading to river chemistry that is largely transport-limited rather than source-limited (Lintern et al., 2021). This suggests that the interactions between source areas and catchment natural characteristics, e.g., topography and soil, rather than land use, might shape the export patterns of solutes and particulates (Ebeling et al., 2021).

4.1.2 Topography controls on connectivity between source to stream

For mean concentrations, catchment topographic characteristics have a high influence on TN and NO₃. Among the topographic characteristics we included in the models, catchment average slope is one of the most significant controls, with large negative effects on TN and NO₃. This can be explained by the fact that catchment retention and removal of dissolved N species tends to be greater in lowland catchments with subdued topography (r = 0.51 between slope and elevation, Figure S1), due to the longer transit time within these catchments (Dupas et al., 2020; Ehrhardt et al., 2021). For sediment-bound N in flat catchments, sediments tend to be trapped and settled out via buffers such as riparian vegetation (Pert et al., 2010; Poeppl et al., 2020). These processes can be further enhanced by a longer transit time in catchments with lower slopes and less developed stream networks (r = 0.55 between slope and stream network, Figure S1) (Boyer et al., 2006; Mulholland et al., 2008; Wakelin et al., 2011).

Our work identifies several topographic characteristics as the most important factors that control the export patterns for all constituents. These findings agree with previous studies (e.g., Zarnetske et al., 2018; Ebeling et al., 2021; Minaudo et al., 2019; Moatar et al., 2017) and can be explained by the key role of catchment topography on flow paths, transit times and the temporal variability in
hydrological connectivity (Detty et al., 2010). For instance, upstream distance (longest flow path) was one of the most important factors for TSS, TP and EC. TSS and TP exhibited a flushing export pattern ($C$–$Q$ slopes > 0, Figure S12a, d) across all climate zones, indicating that for most catchments, they were transport-limited. Catchments with longer flow paths are typically those with larger areas ($r = 0.86$ between upstream distance and catchment area, Figure S1), thus enhancing the flushing export pattern of sediments by increasing the potential supply of sediments. The lower turbulent energy in these large rivers would limit the sediment transport capacity which leads to a transport-limited behaviour. The flushing pattern is also a result of the increased mobilisation of sediment during high flow events (Croke et al., 1999; Prosser et al., 2001). Sediment erosion processes may also be enhanced with longer flow paths during high flow events (Voepel et al., 2013).

In contrast, EC showed a strong dilution export pattern ($C$–$Q$ slopes < 0, Figure S12f), suggesting that it was mostly source-limited within the study catchments, as found in previous studies (Basu et al., 2011; Cartwright, 2020; Meybeck et al., 2012). Maher (2011) and McGuire et al. (2010) highlighted that topographic controls (e.g., flow path length) determined the hydrological connection between hillslopes and streams, as well as the interaction between surface and subsurface flow paths. Many rivers in Australia have high solute concentrations at low flow, which can be attributed to large inflows of often highly mineralised (sometimes even brackish) groundwater (e.g., Cartwright et al., 2013). The strong dilution export pattern we observed for EC reflects the mixing of these solute-rich groundwater contributions with much fresher event water at high flow.

4.1.3 Soil controls on the mobilisation of solutes and particulates

We found that soil properties, in particular clay content, have large influences on mean concentrations of TSS, TN and TP, as well as the export patterns of TSS and TP. For instance, soil clay content has a positive effect on these constituents. This is potentially related to the mobilisation of solutes and particulates within catchments (Palansooriya et al., 2020; Rheinheimer et al., 2017). In Australia, catchments with high clay content are likely to have high soil erodibility (Teng et al., 2016), resulting in higher particulate concentrations from eroding sediments (Couper, 2003). Clay soils are also easily compacted under wet conditions, which often leads to saturation-excess runoff (Stewart et al., 2019). In these conditions, sediments tend to be mobilised and transported to the streams. High clay content is also likely to be associated with a high N mineralisation rate, leading to an increase in dissolved N in streams (Parfitt et al., 2001). In addition, we found that TSS and TP showed flushing export patterns ($C$–$Q$ slopes > 0, Figure S12a, d). The positive effect of clayey soils on export patterns of TSS and TP suggests that higher clay content would enhance the detachment, remobilisation, movement of sediment and sediment-associated P within catchments, due to the high susceptibility of clayey soils to erosion processes (Sun et al., 2021; Villa et al., 2012).

4.2 The influence of catchment characteristics on mean concentrations and ex-
port patterns differs across climate zones

In this study, we tested the hypothesis that climate zones significantly affect the relationship between mean solute and particulate concentrations/export patterns and catchment landscape characteristics, by explicitly considering the effect of climate zones in the proposed BHM modelling framework. We found that, when incorporating climate zones, the predictability of both mean concentrations and $C-Q$ slopes improved significantly (Table 2). This suggests that the magnitude of influence of catchment characteristics on mean concentrations and $C-Q$ slopes was dependent on climate zones, rather than universal across different climate zones.

Compared to previous studies (e.g., Godsey et al., 2019; Pohle et al., 2021; Ebeling et al., 2021) that encompassed a narrower range of climate zones and assumed the key catchment controls have similar effects on mean concentrations/export patterns, our results provide an improved understanding of how the interaction of climate and catchment landscapes affects the average levels of constituent concentrations and export patterns. In particular, we found that for most situations, the direction of effects of key controls on both mean concentrations and $C-Q$ slopes is consistent across climate zones (Figures 7 and 8). For example, soil clay shows a significantly positive effect on mean TP concentrations across arid, temperate and subtropical climates; catchment upstream distance exhibits a consistently positive influence on the export pattern of EC in the Mediterranean, temperate and subtropical climates. However, we also found that the magnitudes of the effects may vary across climate zones. For instance, the effect of upstream distance on the export pattern of EC is stronger in the Mediterranean and temperate zones compared to the subtropical zone (Figure 8f). The reasons for this are complex and may be related to the generally high EC levels in the groundwater of large Mediterranean and temperate catchments, which have been largely attributed to land clearing that causes the rise of regional water tables, resulting in the discharge of brackish to saline groundwater into streams and rivers (Metcalfe et al., 2016; Peck et al., 2003; Tweed et al., 2007).

In addition, it is worth noting that some key controls have opposite directions of influences across different climate zones. We found that for the export pattern of TSS, upstream distance showed a negative effect in arid and subtropical regions, but a positive influence in the temperate zone. This can be explained by the heterogeneities of landscape characteristics across climate zones. In arid and subtropical catchments, catchment flow pathways are longest compared to other catchments (Figure S1e). Catchments in arid and subtropical zones are also often located in large lowland areas (Figure S1a, c, and $r = 0.86$ upstream distance and catchment area and $r = -0.26$ upstream distance and slope, Figure S4) across the Australian continent, limiting the sediment transport capacity (Hesse et al., 2018; Jaeger et al., 2017), thus resulting in flatter $C-Q$ slopes of TSS in these climate zones. In contrast, catchments in the temperate zone have higher runoff and steeper slopes (Figure S1e, f), which enhances the erosive
capacity and flushing export pattern of TSS as discussed in Sect. 4.1.2.

Overall, there are a smaller number of key controls identified for $C-Q$ slopes, compared to mean concentrations. This is in line with the findings from Musolff et al. (2015) and can be attributed to the fact that the differences in $C-Q$ slopes across different climate zones are not as evident as those for mean concentrations (Kruskal-Wallis $p < 0.001$ for mean concentrations, compared to $p > 0.001$ for $C-Q$ slopes, except TSS, Figures S11 and S12). For example, Lintern et al. (2021) identified that export patterns of river chemistries in Australia have comparable ranges across climates (i.e., the same direction of $C-Q$ slope). In addition, compared to the influences on the mean concentrations, the influence of the majority of the catchment characteristics on the $C-Q$ slope was weaker (closer to 0, or non-significant, Figure 8) and more variable (positive or negative) across climates.

Our previous study found that whilst mean concentrations vary significantly between climate zones, export patterns of river chemistry in Australia are relatively consistent between climate zones, in that $C-Q$ slopes have the same direction regardless of climate zones (Lintern et al. 2021). In this current modelling study, we demonstrate that: (1) climate zone is a strong driver of mean concentration, confirming the findings of Lintern et al. (2021) and (2) even if the direction of the $C-Q$ slopes is not driven by climate zones (Figure S12), climate zones can influence the magnitude of the $C-Q$ slopes. As such, our study highlights the value in comprehensively assessing the underlying climate-specific mechanisms that drive both mean concentrations and export patterns over large spatial scales.

Thus, our results of the differences in the key controls across climate zones, either magnitude or direction, highlight that the responses of mean concentrations/export patterns of river chemistry to landscape characteristics vary across climate zones, indicating that water quality mitigation and control strategies should be implemented on the basis of these differences in climate-specific water quality responses. The contrasting impacts of landscape controls on the source, export and mobilisation of constituents across climates would be useful to identify risks to water quality in a multi-pollutant framework, particularly with respect to non-point source pollution. Disintegrating processes, landscape characteristics and key controls allow to ascertain those associated risks for water quality deterioration and finding appropriate mitigation measures that can inform the design of varying levels of specific interventions and therefore effectively targeted. Where spatial risks from similar source, mobilisation and delivery and key controls are shared, it also presents its opportunities in managing multiple pollutants at the same time and therefore creating multiple benefits.

4.3 Model performance and limitations

The H-BMA modelling framework was capable of predicting, as well as identifying the key controls on both mean concentrations and export patterns of river chemistry. Overall, the modelling framework can explain a large proportion of
variation in mean concentrations and a moderate level of variation in export patterns, indicating its effectiveness in providing understanding of how catchments function differently across climates. Compared to other statistical water quality models, our modelling framework was informed by a better conceptualisation that accounts for the spatial heterogeneity of catchment characteristics between climate zones. This enabled us to identify drivers of river chemistry that we were not able to identify using more conventional statistical methods in our previous work (Lintern et al., 2021). In the future, this modelling framework can allow identification of hotspots catchments that have relatively high concentrations or high potential in river chemistry export, thus informing future management activities. In addition, even though the models were developed on a transformed scale to ensure that key assumptions of the statistical modelling were met, and the model performance drops on the back-transformed scale (Figures S15 and S16), the inference of the modelling results still holds. This is because the data transformation did not change the relative importance of key controls of mean concentrations/export patterns.

Compared to our preceding investigation on the relationship between export patterns and catchment median base flow index (BFI) using the same continental-scale data set (Guo et al., 2022), we were able to improve the prediction of the export patterns for SRP and EC significantly (both constituents have a $R^2 < 0.01$ in Guo et al. (2022), compared to a NSE of 0.3 in this study). This indicates that using the extent of baseflow contribution (the only predictor used in Guo et al. (2022)) cannot accurately explain the spatial variability in export patterns of SRP and EC across the Australian continent. While other variables yielded similar performance with both models (e.g., for NOx, NSE = 0.25 in this study compared to $R^2$ of 0.22 in Guo et al., 2022), the generally better performances of the H-BMA lends support to our choice of considering further spatial drivers of export patterns based on a comprehensive set of catchment characteristics.

In addition, the proposed modelling framework can provide a better prediction of mean concentrations (NSE up to 0.86), compared to export patterns (NSE up to 0.39). The lower predictive ability for export patterns is not a surprising finding, and can be related to the following limitations: (1) most of the water quality monitoring data used in our study is low-frequency, which did not allow proper representation of event or seasonal changes in export patterns, or of the variability in export patterns under different flow regimes (e.g., baseflow vs. quick flow) (Guo et al., 2022; Minaudo et al., 2019; Moatar et al., 2017; Tunqui Neira et al., 2020); and (2) as discussed in Sect. 4.2, export patterns are more consistent than mean concentrations across different climates, such that relatively low spatial variability in export patterns is difficult to be predicted by using the catchment characteristics. This highlights the need for future research that investigates the temporal changes in export patterns, e.g., trend or seasonality, and their associated key catchment controls, focusing for instance on a subset of catchments that have long-term high-frequency water quality monitoring data.
5 Conclusions

We used a Bayesian approach to predict and simultaneously infer the key catchment controls on mean concentrations and export patterns of six constituents (solutes and particulates) over 507 catchments with a large climatic gradient across the Australian continent. We compared the relative importance of 26 catchment characteristics, identified the key controls that explain the spatial variability in mean concentrations and export patterns, as well as quantified the differences in the effect of key controls across five major climate zones. We can explain a larger part of the variability in mean concentrations than that of export patterns, due to a higher variation in mean concentrations between different climate zones, and its closer link with spatial variability in catchment characteristics.

We found that catchment land use, soil properties and topographic settings were the most influential factors that affect the mean concentrations across all climate zones. This indicates that the spatial heterogeneity in source, mobilisation and delivery jointly determine the average level of constituent concentrations. While, the strong impact of topographic controls on export patterns suggests that, the spatial and temporal variation in hydrological connectivity within catchments significantly influences constituent export and its expression in either dominant surface or subsurface flow. Also, the lower number of identified key controls on export patterns compared to mean concentrations indicates that the key controls on export patterns might change not only between climate zones, but also between upland and lowland catchments, leading to catchment characteristics indirectly determining the export patterns.

The hypothesis that the key controls vary across climate zones was supported by the fact that consideration for climate zones in a hierarchical modelling structure improves predictability of both mean concentrations and export patterns, as well as the differences in magnitude and/or direction of effects of key controls inferred from modelling results. This highlights a need for the catchment water resources managers to consider the climate-specific effects of key catchment controls. Such knowledge could aid the development of targeted and region-specific intervention measures using a ‘catchment function’ approach and thus could potentially create multiple benefits when managing multiple pollutants at the same time. The contrasting impacts of landscape controls on the source, export and mobilisation of constituents across climates would be useful to identify risks to water quality in a multi-pollutant framework, particularly with respect to non-point source pollution. Disintegrating processes, landscape characteristics and key controls allows to ascertain those associated risks for water quality deterioration and finding appropriate mitigation measures that can inform the design of varying levels of specific interventions and therefore effectively targeted. Where spatial risks from similar sources, mobilisation and delivery and key controls are shared, it also presents its opportunities in managing multiple pollutants at the same time and therefore creating multiple benefits.

Overall, the present approach and results enhance our understanding of dom-
inant controls on spatial variability in mean constituent concentrations and export patterns over a large spatial scale, considering the effect of climatic gradients. The methods used and insights in the understanding of climate-induced differences in pollutant export is likely to be transferable to other catchments, and can be tested against findings from other studies. With the investigation of high-frequency water quality monitoring data in the future, we could further improve our understanding of solutes and particulates export behaviours at different temporal scales (e.g., event or seasonal).

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