



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

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Response to Reviewer comments

Article title: Climate controls on water chemistry states and dynamics in rivers across Australia

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Dear Professor Tetzlaff,

Thank you for processing the reviews of the manuscript. We have revised the manuscript based on the reviewers' comments. We have submitted the revised manuscript (clean) along with a marked version (all changes highlighted in yellow). Our responses to each of the comments are listed in the table below.

We thank you again for considering this manuscript for publication in *Hydrological Processes*.

Yours Sincerely,
Anna Lintern

Reviewer comment		Author response
Editor		
1	In addition to the comments by the reviewers, can I please ask you to separate the result and discussion section? This usually increases the readability of a paper. It would also show that - currently - the critical discussion and wider contextualisation of the findings are quite limited and would need to be expanded.	<p>Whilst we have kept the Results and Discussion section combined, we have expanded the critical discussion and wider contextualisation of the findings. We have:</p> <ul style="list-style-type: none"> - embedded the wider discussion of the findings within individual paragraphs in the Results and Discussion section, where specific results are first presented (i.e., what these results mean, their implications) to streamline the discussion and ensure that we fit into the word limit - we have also added some paragraphs that synthesise the findings of Sections 3.1 and 3.2.1 and 3.2.2 and place them in the context of the literature. These are: the two paragraphs at the end of Section 3.1 (Lines 322-351), the paragraph at the end of Section 3.2.1 (Lines 390-401), the first paragraph in section 3.2.2 (Lines 443-456), the last two paragraphs of section 3.2.2 (lines 508-524) - In addition, in section 3.3 (Lines 535-582), we place the results in the wider context of managing and monitoring water quality management at a federal/national-scale
Reviewer #1		
2	<p>There are a number of places where the data being used need to be better defined. For example, please provide the units in the methods and graphs.</p> <p>Please also better define NO_x – what is nitrate-nitrite? Are these constituents being reported on a per compound or per element basis?</p>	<p>A check was completed to ensure that units are provided in the methods and graphs. These have been added to:</p> <ul style="list-style-type: none"> - the Figure 1 caption, and Figure 3 y axes - methods section - CQ slopes and CV ratios are dimensionless so they have not been added <p>NO_x is defined as the sum of 2 nitrogen species - nitrate (NO₃-N) and nitrite (NO₂-N) (i.e., NO₃-N +</p>

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21		<p>Mean and median concentrations are often mentioned but it's not clear in which case one is used over the other.</p> <p>Also, no information on discharge is given in the methods.</p>	<p>NO₂-N). NO_x is defined on a per element basis (NO_x-N mg/L). We have now defined this in line 142.</p> <p>We use mean concentration to describe the central tendency in constituent concentrations. We have changed all instances of 'median concentrations' to 'mean concentrations'.</p> <p>We have now included the following explanation on the provision of discharge data: "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." (Lines 153-154) We then discuss how the streamflow data was processed in lines 174-181.</p>
22 23 24 25 26 27 28 29 30 31 32 33 34 35 36	3	<p>Kruskal-Wallis tests are done to indicate that climate zone is a significant factor driving differences in mean concentrations and CQ slopes. However, this analysis doesn't indicate which climate zones differ from each other, although differences between individual zones comprise a large portion of the results and discussion. I recommend conducting means comparison in order to differentiate which climate zones are statistically different from each other for each constituent.</p>	<p>We have applied the Dunn post-hoc test for comparisons between climate zones. We chose to use the Kruskal-Wallis test for this study because the data do not satisfy the required assumptions for ANOVA (normality and homoscedasticity).</p> <p>This is detailed in the methods in line 218-227. "A non-parametric test was used 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 pair-wise comparisons between climate zones. "</p>
37 38 39 40 41 42 43 44	4	<p>The organization of section 3.1 is a bit confusing. It would be clearer to discuss each climate zone individually OR each constituent individually in the context of climate zones and land use rather than jump around between discussing groups of constituents and climate zones.</p>	<p>We have re-written Section 3.1 to be grouped in terms of constituents, starting with EC and Ca, then TSS and TP, then SRP, then TN and NO_x.</p>
45 46 47 48 49	5	<p>Table 1 is more helpful than Figure 5 in discerning patterns between climate zones.</p>	<p>We have moved Figure 5 to the supplementary materials.</p>
50 51 52 53 54 55	6	<p>Title: The title implies that climate controls water chemistry, but the main conclusion is that it controls state but not dynamics, so consider adjusting.</p>	<p>We have changed the title to not imply that climate controls water chemistry. The new title is: "The influence of climate on water chemistry states and dynamics in rivers across Australia"</p>
56 57 58 59 60	7	<p>Keywords: not sure what is meant by "data-driven" here and elsewhere. Isn't science data-driven? Perhaps chose a term more reflective of big data or data synthesis.</p>	<p>'Data-driven' has been changed to 'data synthesis'.</p>

8	<p>I.77. I disagree with the discussion of how CQ patterns relate to source proximity to the stream. In this case, you are discussing hydrologic connectivity as a driver of CQ patterns. In the case that a constituent is located close to the stream, concentrations would be high at low discharge and decrease as flow paths deliver more water from other parts of the catchment at higher discharge (dilution behavior). Conversely, flushing behavior would occur when distant sources of that constituent are accessed under high flow regimes.</p>	<p>We agree with the reviewer and as such have changed the discussion of CQ patterns in Line 77.</p> <p>Line 77 (now lines 76-82) now reads: “The C-Q slope is positive when concentration increases with increasing flows, and this indicates ‘flushing’ behaviour of the catchment. 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).”</p>
9	<p>I.250. This would indicate that the original hypothesis is rejected not because concentrations are high despite a lack of anthropogenic activity, but because there is meaningful anthropogenic influence.</p>	<p>The reviewer raises a good point. We have removed the discussion of the Darling River and agriculture from the Results and Discussion.</p>
10	<p>I. 257. Suggest “compared to other non-arid climate zones”</p>	<p>This has now been included.</p>
11	<p>I. 258. No information is available to assess whether these medians are meaningfully different from the other climate zones.</p>	<p>This information is provided in the Supplementary materials (Figure S8). This has now been specified.</p>
12	<p>I. 260. The soil P concentrations that are reported here are not correct. Perhaps the units are wrong? Soils have P concentrations ~600 mg/kg, so these values are orders of magnitude off.</p>	<p>Indeed, the units of the soil total P concentrations are incorrect. They should be %. This has been adjusted both in the text (lines 280) and in Figure S8.</p>
13	<p>I. 313. TP does not have a chemostatic export regime for the Mediterranean zone. I wasn’t sure if this was meant to indicate that all these constituents did in all these zones or just all these constituents did in some of these zones.</p>	<p>This sentence was meant to indicate that these constituents exhibited a chemostatic export regime in some of these zones. The wording has been adjusted accordingly to indicate that all the constituents did in some of these zones. Line 383-384 now reads: “Some nutrients (TP, TN, SRP) also have a chemostatic export regime in either temperate, Mediterranean or subtropical climate zones. ”</p>
14	<p>I. 372. This appears true and is interesting, but it is also interesting (but not discussed) that some patterns do trend with climate zone! For example, there’s a pretty clear trend of increasing CQ slope for SRP from arid to tropical zones.</p>	<p>We agree with the reviewer that there are apparent trends for some constituents (SRP, NO_x, TP and TSS) by climate zone.</p> <p>We state in Lines 443-446 the following: “There are statistically significant differences in C-Q slopes across climate zones for only four out of the seven constituents (NO_x, SRP, TP and TSS) (Figure 6). However, the signs of the C-Q slopes for all constituents do not appear to be climate-related (Figure 6).”</p>

		We discuss this in more detail in lines 446-456 drawing on the existing literature.
15	Section 3.3. Is more appropriate for conclusions than results.	<p>We agree with the reviewer that aspects of Section 3.3 may be more suited for the conclusions. However, there are some parts of this section - specifically where we discuss the management implications - that we believe should be kept in the Discussion section as we consider them to be too detailed for the conclusion. In addition, Section 3.3 directly builds on some of the findings from Sections 3.1 and 3.2.</p> <p>We have changed the title of this subsection to be: "Implications of the variability in water chemistry on future water quality management, monitoring and water policies"</p> <p>The last paragraph of this section has been moved to the conclusion, as we believe this is more suitable as a concluding paragraph.</p>
16	Table 1. I found this table helpful because it was really difficult to discern differences between climate zones from Figure 5.	We are glad to hear that table was helpful.
17	Figure 1. Unfortunately, this figure was not legible in the pdf. I could vaguely get a sense of color distribution, but the values could not be resolved.	This appears to be due to an issue with the resolution of the file and the submission system. We have attempted to upload a higher resolution file.
18	Figure 2. Overall, this is a nice conceptual figure, but I don't think it's appropriate to describe positive CQ slopes as biogenic/anthropogenic and negative slopes as geogenic unless it's in the context of this particular study. I recommend removing those descriptors from the figure. It's also not particularly true to differentiate the constituents as geogenic versus biogenic/anthropogenic as has been done. TSS, SRP, and TP are certainly geogenic although may be influenced by anthropogenic processes.	The descriptors of concern (biogenic/anthropogenic and geogenic) have been removed from Figure 2 and replaced with 'deep' and 'shallow' sources.
19	Figure 3. The Kruskal-Wallis results indicate that climate zone is a significant variable for each constituent, but there's no information on how means for each climate zone differ from each other. I suggest doing a means comparison to indicate the differences that are driving the KW significance. Also, include more detail on the plot. What values do the boxes and whiskers represent? Are the symbols outliers? Are these means or medians? Also need to include units for the constituents.	<p>We are unable to do a means comparison because the data do not meet the assumptions of ANOVA (normality and homoscedasticity). We have conducted a Dunn's post-hoc test to compare between climate zones. We have included the results in Table 1 for average constituent concentrations. This has enabled us to determine some finer-scale patterns - such as the fact that there are statistically significant differences in mean SRP concentrations only between the temperate regions and other climate regions. This has been detailed in lines 287-292.</p> <p>"For SRP, Dunn's pair-wise comparisons showed that there were statistically significant differences in mean SRP concentrations between Temperate climate zones and the others (Table 1). This is likely due to the</p>

		<p>similar mechanisms affecting the low TSS and TP concentrations in temperate streams - the low agricultural level of agricultural activities and lower levels of soil TP (Figure S8, Supplementary Materials).“</p> <p>We have also included more details in the plots including the units and descriptions of the boxplots. The caption now reads: “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.”</p>
20	Figure 4. Median is used here but mean is discussed elsewhere. Not clear where each is being used or why.	We have revised the manuscript so that we only refer to ‘mean’ concentrations rather than median. Figure 4 has been updated accordingly.
21	Figure 5. Poor resolution in the proof, and difficult to discern the different colors from each other regardless. Dotted lines indicate 1:1 lines and distinctions between solute behaviors indicated in Figure 2 (not x and y axes).	<p>This figure has been moved to the supplementary materials. The captions of the figure in the supplementary materials have been updated to state that the dotted lines indicate 1:1 lines and distinctions between solute behaviours indicated in Figure 2.</p> <p>We will ensure that we check the resolution in the proof prior to the submission.</p>
22	Figure 6. Same comment here as for Figure 3 regarding means comparison. Also, it doesn’t seem necessary to include an asterisk to indicate when a p-values is less than 0.05 next to the actual p-value.	<p>This post-hoc pair-wise comparison test has been performed. However, since we do not see large-scale shifts in CQ slopes between climate zones (i.e., we don’t see shifts from dilution to flushing patterns), we do not discuss these finer scale differences between the pairs in detail in the text. As such, these post-hoc results have been included in the supplementary materials (Table S3).</p> <p>The asterisks have been removed from Figure 6.</p>
23	Figure S1.1. Indicate here and elsewhere that C = concentration (not carbon!).	In Figure S1.1 we have changed C to concentration. We have changed all instances of C to concentration in the text.
24	Figure S9. What is the y-axis here?	Each row on the graph represents a single site where monitoring data were collected. This is now specified in the caption of the figure.
25	Figure S11. What do the asterisks indicate?	The red asterisk represents statistical significance ($p < 0.05$). This is now specified in the figure caption.
Reviewer #2		
1	The authors assemble river chemistry data from seven sub-national state and territory agencies in Australia. They present data on flow:concentration relationships for calcium, conductivity, total P, SRP, total N, NO _x and total suspended solids. However, I am concerned about the quality control measures used. For example, Figure S10 appears to show NO _x :TN ratios greater than one. I am at a loss	<p>We have checked the data used to create Figure S10 (and the other analyses in the manuscript), and have found a mistake, which we have corrected. This has led to a new Figure S10, which shows NO_x:TN ratios below 1.</p> <p>However, we have found that this correction has not led to a change in our results.</p>

1		to understand this as it seems to imply there is more reactive than total nitrogen.	
2	3	I am surprised that no information is provided about whether the different agencies collecting and curating the data presented in this study use the same analytic methods or sampling protocols. I am also surprised that while the authors highlight the importance of a national scale data set to support management decision making (lines 462-463), as far as I can tell, they have chosen not to make the national scale data used in this paper publicly available. From my perspective, this is a major shortcoming as it seems to negate the overall purpose of the work presented here.	<p>We have obtained a summary of the sampling protocols and analytical methods from each of the state agencies. The description of each of these protocols is provided in the Supplementary Materials S2. Whilst the level of detail recorded by each state agency differs, we can verify that all state agencies have water quality samples analysed by NATA (National Association of Testing Authorities) accredited laboratories using standard methods. This is now stated in Lines 135-138:</p> <p>“Details on monitoring and analytical methods for each state are available in the Supplementary Materials (File S2). In summary, for all states, water chemistry is analysed by National Association of Testing Authorities (NATA) accredited laboratories following standard methods.”</p> <p>The reviewer makes an excellent point about the availability of this dataset. Unfortunately as authors, we do not hold the right to re-distribute this dataset. Each state-based dataset is available online through the relevant state agencies. We have included the links to the online data portals via the citations to these sources in the text in the Methodology (Section 2.1).</p> <p>Through this study, it is our hope that this study demonstrates the need and the value in developing a national dataset. As the state datasets are being continuously updated, we are of the opinion that this should probably be initiated and maintained by a federal agency.</p>
3	4	For me, Figure 4 was one of the most interesting results presented. The relative importance of spatial (regional) versus temporal (variability within a single time series) is a relatively underexplored topic that is worthy of further investigation. Lines 409-417 highlight an important point about the potential shortcomings of using simple metrics to evaluate solute behaviour. This section is worthy of further expansion.	<p>We have followed the reviewers’ suggestion and have added the following;</p> <p>In Line 357-359, we address the importance of spatial vs temporal variability:</p> <p>“The greater spatial variability could be indicating that the driving forces of stream chemistry vary more across space than across time.”</p> <p>In addition, we state the following in Line 361-363:</p> <p>“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”.</p> <p>We also further expand on the potential shortcomings of using simple metrics to evaluate solute behaviour by stating in lines 518-525</p>

1			“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 calculate metrics based on the hydrological observations (Minaudo et al., 2019; Tunqui Neira et al., 2020).”
2	6	Lines 98-104 seem to overlook the large body of work conducted in, e.g., Europe, the USA and China	<p>We have clarified this statement by stating in Lines 93-98:</p> <p>“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.”</p> <p>We have added a citation of an American study in addition to the already cited European and Australian studies: Godsey, S. E., Hartmann, J. and Kirchner, J. W.: Catchment chemostasis revisited: Water quality responds differently to variations in weather and climate, Hydrol. Process., 33(24), 3056–3069, doi:10.1002/hyp.13554, 2019.</p>
3	7	Line 122 – I suspect the USA, China, Europe and perhaps Canada contain as many or more climate zones	This sentence has been changed to: “Australia contains most of the Earth’s climate zones”.
4	8	Line 166-167 – I would like some indication of how many observations were below detection limits as this will influence estimates of the concentration coefficient of variance and possibly the C:Q relationship	We have identified the percentage of observations below the detection limit and have noted them down in Lines 197-181.
5	9	Line 203 – the authors use the Kruskal Wallis test throughout. This test can give unreliable results when applied to groups with different shape distributions, as appears to be the case in Figures 3 and 6.	<p>We agree that often parametric tests can provide more reliable results in terms of identifying differences between groups. However, the dataset in this study does not meet the assumptions of normality and homoscedasticity for parametric tests .</p> <p>We also qualify in the Methods that as we are using a non-parametric test, we are assessing statistically significant differences between the distributions of the water quality metrics from different climate zones.</p>

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17		<p>Lines 220-225 now read:</p> <p>“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”</p> <p>We also note that previous studies (Purnell et al. 2016; Ekklesia et al. 2015; Pieper et al. 2018) have used the Kruskal-Wallis test to compare WQ between different groups with skewed distributions.</p>
18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36	10	<p>Lines 212-220 – a quick look at Figure S11 suggests that many of the relationships identified by the authors are driven by a small number of extreme values. In some circumstances, this might be justified but is very weak evidence for management decision making. Please consider a multivariate analysis (e.g., PCA or NMDS) to support the statement made here.</p> <p>We agree that in some correlation relationships (especially Pearson correlations), extreme values can affect the strength of relationships.</p> <p>In this particular study however, we used a rank correlation method (Spearman Correlation), which is less sensitive to extreme values (de Winter et al. 2016).</p> <p>In addition, this paragraph is not intended to provide guidance into management decision-making, but rather, justify our choice of climate zones as a key catchment characteristic of interest to be investigated in this study. The high cross-correlation between climate variables and others (both linear and non-linear, as summarized by the Spearman correlations) provides solid evidence for this justification.</p>
37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55	11	<p>Lines 222-233 – I am intrigued by the apparently contradictory statements on lines 224 and 230-231. How can higher rainfall lead both to a dilution of particulates and an increase in total P, which is often particulate (line 246) ?</p> <p>We have revised this paragraph to remove the contradictory statement in line 230-231.</p> <p>Lines 252-260 now read:</p> <p>“For EC and Ca, the tropical zones of northern Australia tend to have lower concentrations compared to the other climate zones (Figure 3). This is likely related to the high rainfall rates in the tropics that may result in significant dilution of solutes in rivers (S Liu et al., 2018; Shuci Liu et al., 2021a). Median rainfall across tropical catchments is higher than the other climate zones at approximately 1,334 mm (2.5th percentile of 857 mm and 97.5th percentile of 2,674 mm). Intensely weathered and soils are typical of the tropics and particularly of tropical savannas (Pellegrini, 2016; Reich & Oleksyn, 2004; Wright et al., 2011).”</p>
56 57 58 59 60	12	<p>Lines 275-278 and 388-391 both state the same thing</p> <p>The sentence from lines 275-278 has been removed.</p>

13	Line 393 – I am surprised that the authors treat TSS as a non-geogenic parameter. After reading the paper, I also wonder if some significant fraction of P, especially in arid catchments, might also be geogenic in origin.	Due to feedback from Reviewer 1, we have removed all classifications of ‘biogenic’ and ‘geogenic’ from the results and discussion.
14	Lines 427-442 – This was one of the weakest paragraphs of the paper. It is not clear if there is any federal oversight of water monitoring in Australia, or if all work is done at a sub-national level. This paper does present some preliminary arguments for national-level water quality assessments but the authors do not make a convincing case that this should replace or supersede existing regional monitoring programs in areas of impaired water quality.	<p>We have revised the first few lines of this paragraph to make clear that the current framework of monitoring occurs at the sub-national level and there is no federal oversight of water quality monitoring or management. Lines 570-573 now read: “In Australia, water quality monitoring and management is administered and legislated at a sub-national (state and territory) level rather than at the federal level.”</p> <p>The paragraph has also been restructured and moved to the end of Section 3.3 (Lines 570-583).</p> <p>It was not the intention of this paper to make an argument for a national-level water quality monitoring program to supercede existing regional monitoring programs. Rather, it was intended to make a case for assessments of national-level water quality data (as we have done here). We have removed phrases throughout the text (especially in the Abstract, Introduction and Conclusion) which could be misinterpreted to suggest otherwise.</p>
15	Lines 453-455 – these seem to contradict much of lines 438-442.	<p>We believe lines 453-455 to be in line with the statement in lines 438-442, as lines 438-442 states that the monitoring program should expand to include more monitoring sites in climate zones that are currently less monitored (e.g., Arid zones).</p> <p>However, we do see the confusion that could be caused by the wording so we have rephrased lines 438-442 and 453-455 (now Lines 564-568) to read: “A systematic approach that distributes resources more evenly across multiple climate zones within the framework of state-wide or national-scale monitoring programs may be needed for enhancing our understanding of river chemistry and for monitoring risks and vulnerabilities faced by human communities and ecosystems.”</p> <p>“The findings from this study demonstrate that the current practice of state and territory-based water quality monitoring should be expanded”</p>
16	Lines 453-460 – the authors need to give greater consideration of the challenges of implementing nationally standardised data collection methods. Harmonising the results of multiple sampling and analysis methods is useful but can be exorbitantly expensive.	<p>We agree with the reviewer that managing a national monitoring framework across such a large (and heterogeneous) continent would be a highly challenging endeavour.</p> <p>It was not our intention to suggest that the current system of state/territory-based water quality</p>

1		monitoring be replaced by a national-monitoring
2		framework. Instead, it was our intention to make the
3		case for national-scale water quality assessments
4		(synthesis of state/territory data). We have therefore
5		moved this paragraph to the conclusions (based on a
6		comment from Reviewer 1) and have changed the
7		wording to: (Lines 611-617):
8		“Systematic national-scale assessments of water
9		quality conditions are crucial for the development and
10		implementation of successful water management
11		policies and strategies. The findings from this study
12		demonstrate the value in synthesising the data
13		collected by state and territory-based agencies. These
14		syntheses would enable future use in regular national-
15		scale water quality assessments (e.g., UN
16		Sustainability Reporting 3.6.2 reporting), water quality
17		trend analyses and can target further development of
18		evidence-based federal water quality policies, such as
19		Australia's National Water Quality Management
20		Strategy (NWQMS) as well as tracing its successes”
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22		
23		
24		

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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 with climate zones
- Spatial variability in water chemistry generally exceeds temporal variability

Keywords

Concentration-discharge, export regime, export pattern, water quality, variability, climate zones, dynamics, data synthesis

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 ratio of 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;

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 $\mu\text{S}/\text{cm}$ (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.

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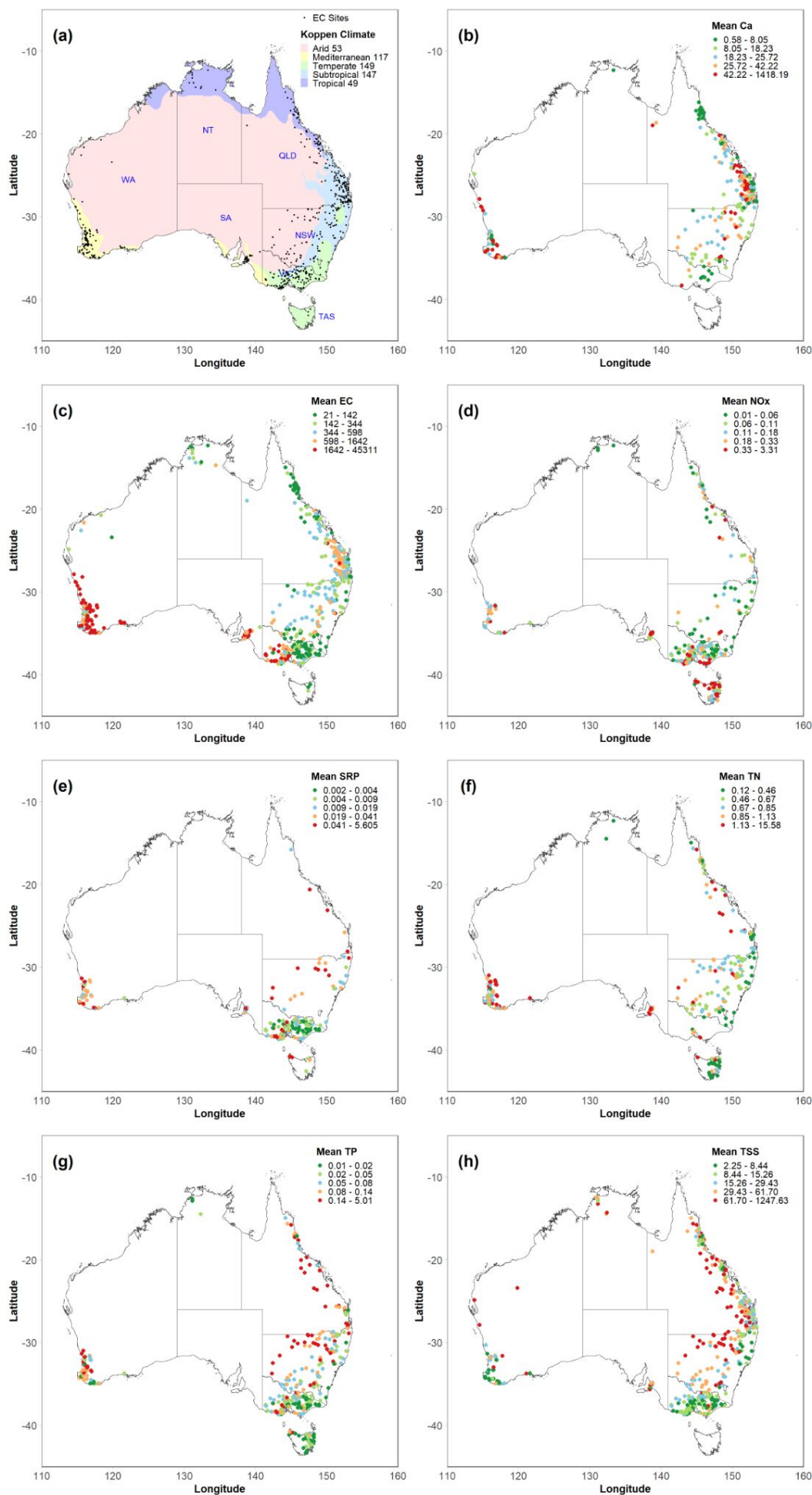


Figure 1: Map showing the location of sampling sites for EC in Australia included in data analysis on a map of the Köppen-Geiger Climate Classification (a). Map showing mean constituent concentrations for each site for Ca mg/L (b), EC $\mu\text{S/cm}$ (c), NO_x-N mg/L (d), SRP mg/L (e), TN mg/L (f), 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 km² to 888,682 km². 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).

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

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).

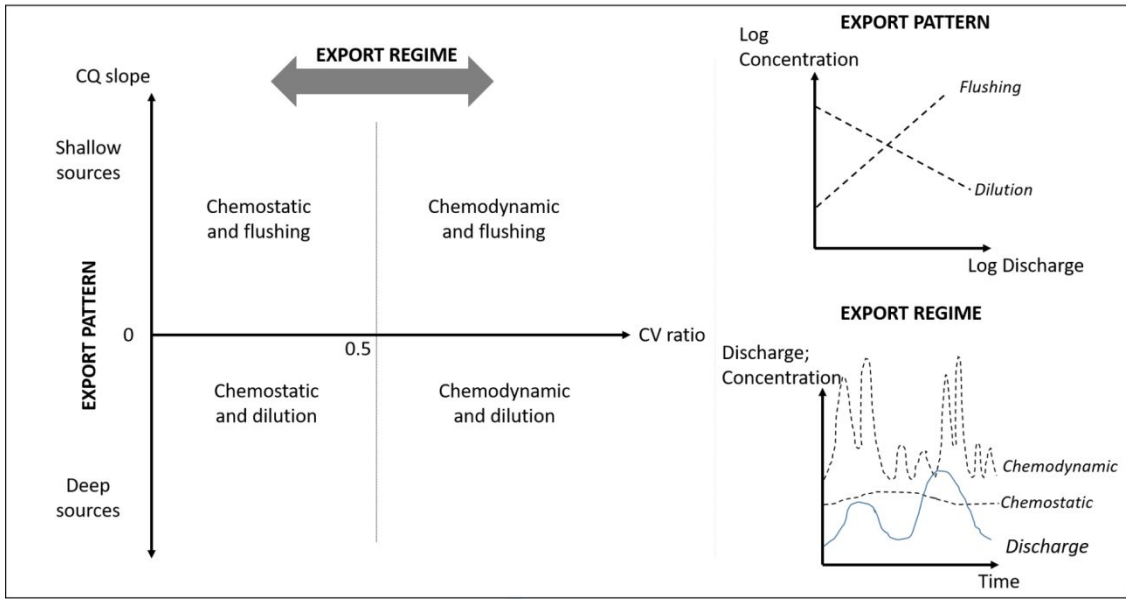


Figure 2: Relationship between CV ratios (export regimes) and CQ slopes (export patterns). Adapted from Musolff et al. (2015).

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 $\mu\text{S}/\text{cm}$) (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; Nihwatiwa 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).

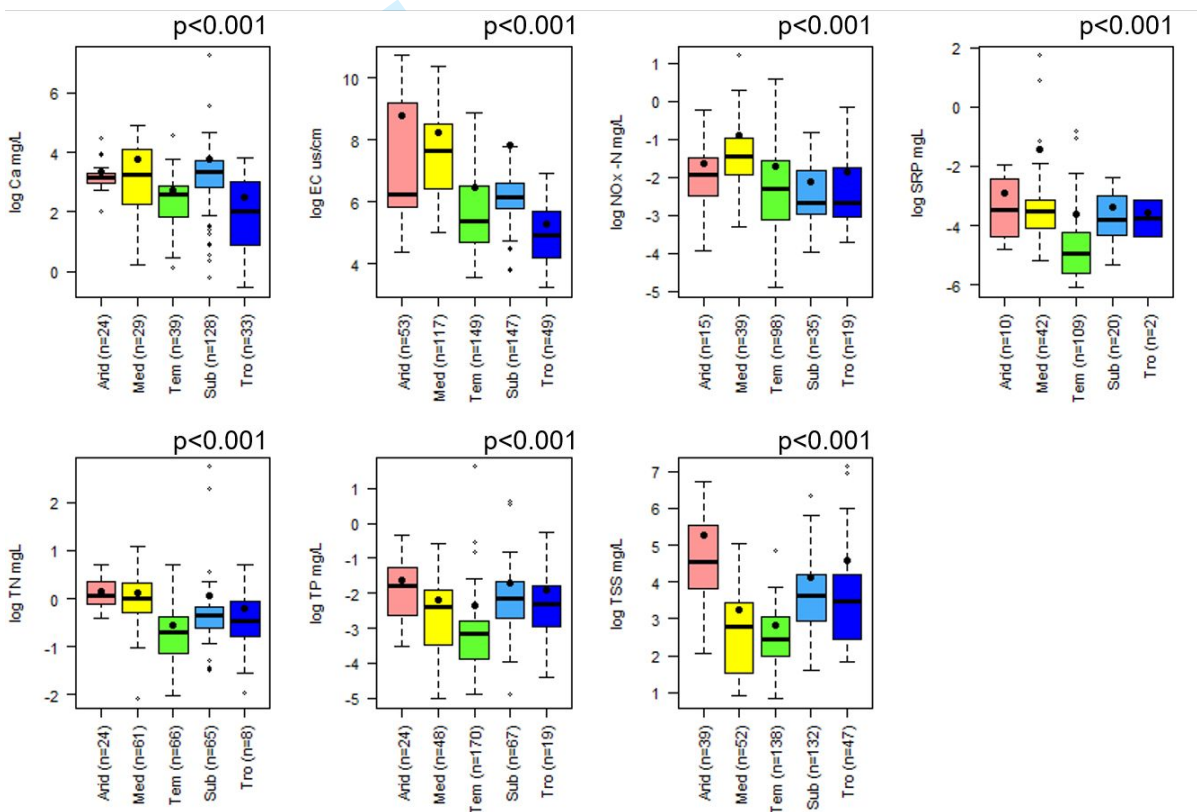


Figure 3: Variability in mean constituent concentrations for each climate zone. Results of Kruskal-Wallis test (p-values) to identify statistically significant variability in mean constituent concentrations across climate zones shown above each boxplot. n in x axis denotes the number of monitoring sites 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	NOx	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, NOx 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 NOx 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, NOx 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

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339 be key areas of risk of high constituent concentrations. In fact, it appears that two of the climate zones
340 with the least number of monitoring sites (arid and Mediterranean catchments) have the highest mean
341 constituent concentrations, indicating that resources may need to be shifted to focus future monitoring
342 efforts on these catchments.

343
344 These findings are in line with previous studies of national-scale spatial variability in water quality.
345 These studies have found that in general, land use and lithology most strongly correlate to long-term
346 means in water chemistry (Ebeling et al., 2021; Godsey et al., 2019; Guillemot et al., 2020). In
347 addition, a study of 787 catchments in Germany, Ebeling et al., (2021) found correlations between
348 climate and long-term means in NOx concentrations. As such, it appears that previous studies have
349 identified both land use and climate as key drivers of spatial variability in water quality. In our study,
350 we find that there appear to be systematic differences in long-term mean water chemistry across
351 climate zones, which is likely driven by land use and land cover differences.

352
353 **3.2 Spatial variability in export regimes and patterns across the Australian continent**

354 **3.2.1: Export regimes**

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

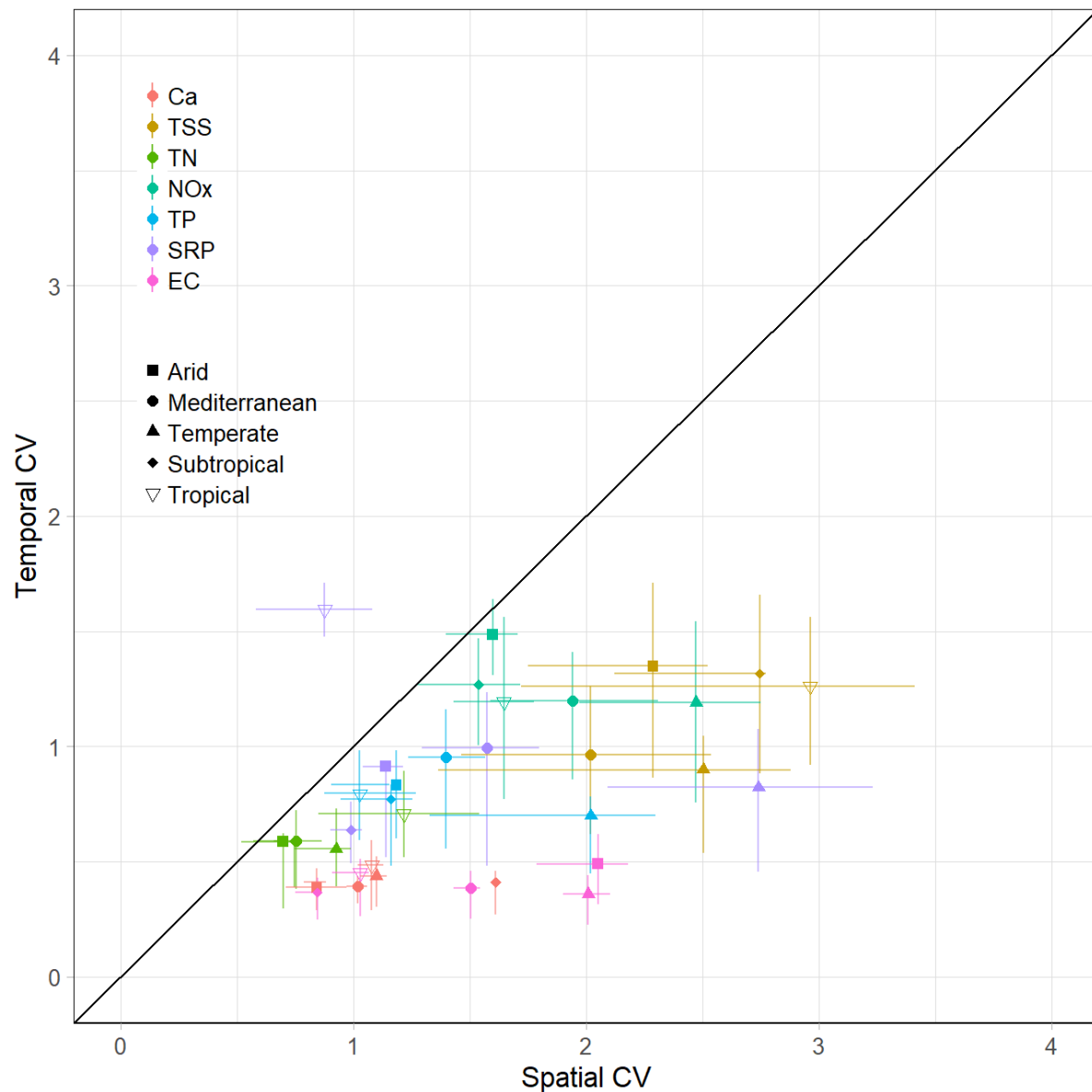


Figure 4: Comparison between variability in constituent concentrations over time and space. 'Spatial CV' indicates the spatial coefficient of variation determined monthly across all sites located in a given climate zone, and 'Temporal CV' represents the coefficient of variations determined for each site.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

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

389
390 Previous studies have found that chemodynamic behaviour occurs in catchments when the hydrologic
391 connection between constituent stores and rivers vary over time (Hoagland et al., 2017). TSS and
392 NOx show chemodynamic export regimes across all climate zones (Table 2, Figure S12). This is a
393 export regime for TSS identified in previous European studies (Mellander et al., 2015; Musolff et al.,
394 2015; Ockenden et al., 2016). Previous studies have found that NOx can demonstrate chemostatic
395 properties (e.g., Long et al., 2014), however our study found that NOx has chemodynamic export
396 regimes in Australia. The chemodynamic behaviour of NOx may be indicating that the agricultural
397 land uses in Australia are not as intensely managed as in other countries. In addition, Australia has a
398 shorter history of agricultural intensification and this may be resulting in less legacy stores of NOx in
399 the soils and groundwater. With less consistent NOx stores throughout the catchments, NOx export
400 can vary from storm to storm, depending on spatial rainfall patterns of a particular storm and the flow
401 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)

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3.2.2: Export patterns

There are statistically significant differences in C-Q slopes across climate zones for only 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).

There are significant differences in CQ slopes across climate zones for NO_x, SRP, TP and TSS (Figure 5, Table S3, Supplementary materials). In particular, we see steeper CQ slopes for tropical catchments compared to arid catchments for TP and SRP. In a study of over 2000 catchments, Godsey et al. (2019) also found that CQ slopes 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 solute 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 ones for NO_x and TSS.

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).

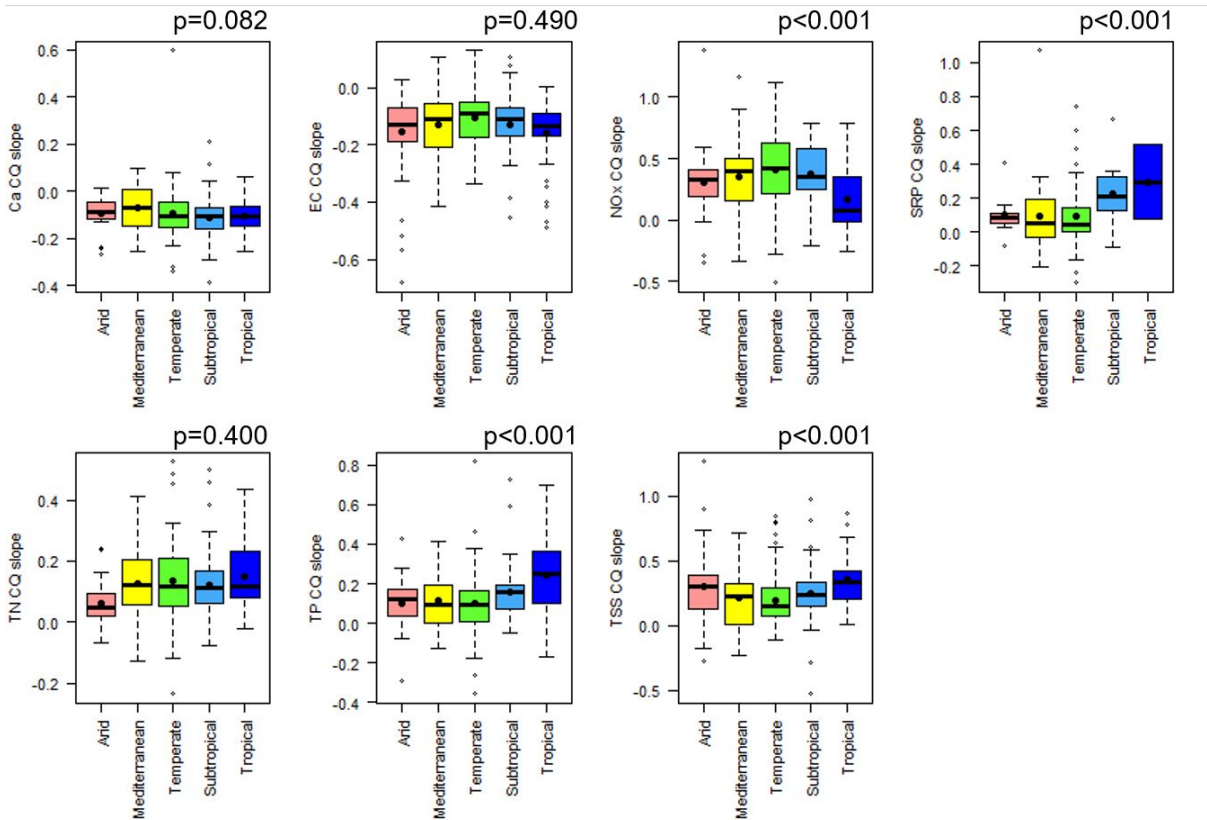


Figure 5: Variations in C-Q slope for each climate zone. Results of Kruskal-Wallis test (p-values) to identify statistically significant variability in C-Q slopes across climate zones shown above each boxplot. Boxes represent the interquartile range, whiskers represent 1.5 times the interquartile range, 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 NOx) 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 (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 understand the behaviour of water chemistry across the Australian continent. Ongoing assessments and understanding if the status of the Nation's 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 water policy development. Through this work we have gathered all 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 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 Sustainability Reporting 3.6.2 reporting), water quality trend analyses and 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.

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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>)

- 640 - Surface Water Data (<https://www.waterconnect.sa.gov.au/Systems/SWD/Pages/Default.aspx>)
- 641 - Water Data Portal ([https://nt.gov.au/environment/water/water-information-systems/water-data-](https://nt.gov.au/environment/water/water-information-systems/water-data-portal)
- 642 [portal](https://nt.gov.au/environment/water/water-information-systems/water-data-portal))
- 643 - DPIPWE Water Data Portal (<https://portal.wrt.tas.gov.au/>)

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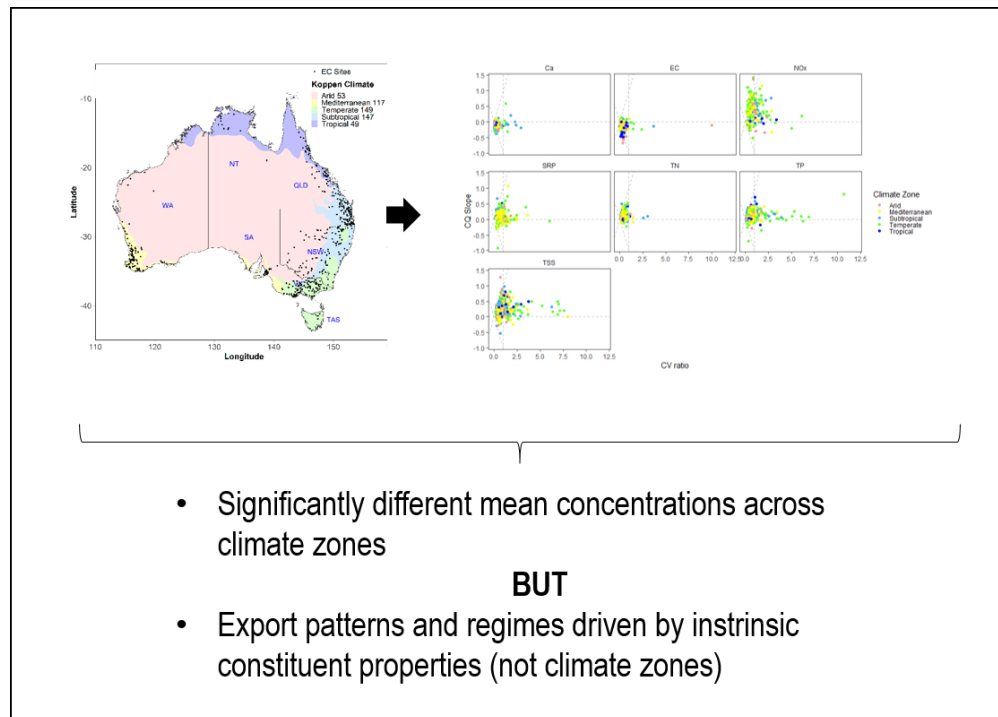
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Graphical Abstract

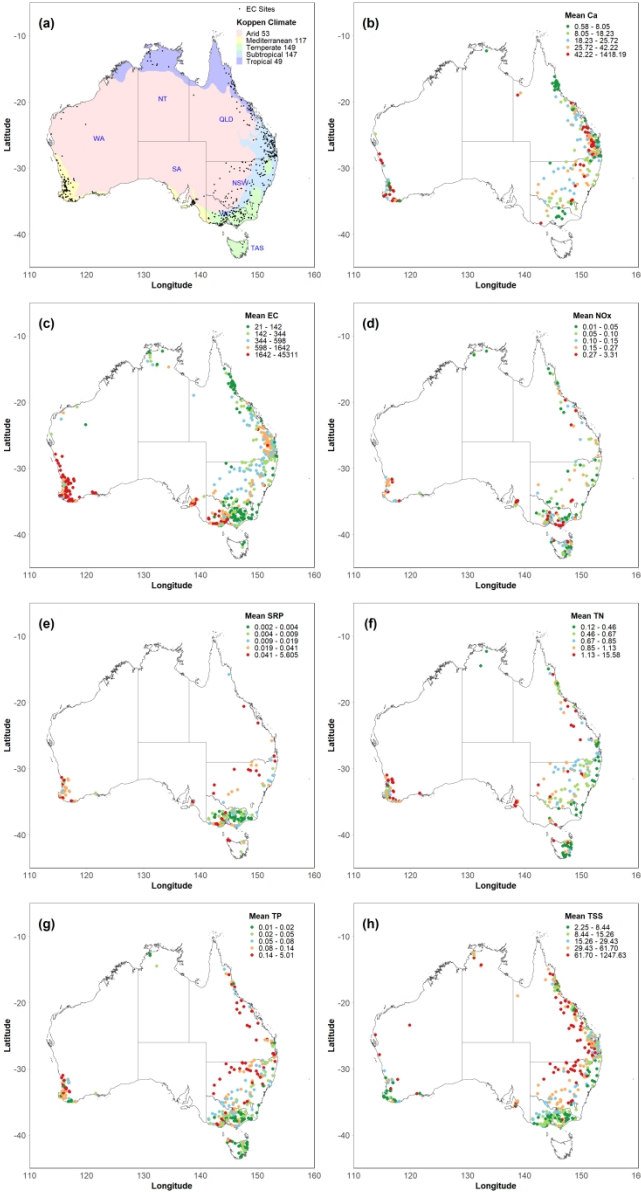


Figure 1: Map showing the location of sampling sites for EC in Australia included in data analysis on a map of the Köppen-Geiger Climate Classification (a). Map showing mean constituent concentrations for each site for Ca mg/L (b), EC μ S/cm (c), NOx -N mg/L (d), SRP mg/L (e), TN mg/L (f), TP mg/L (g), 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.

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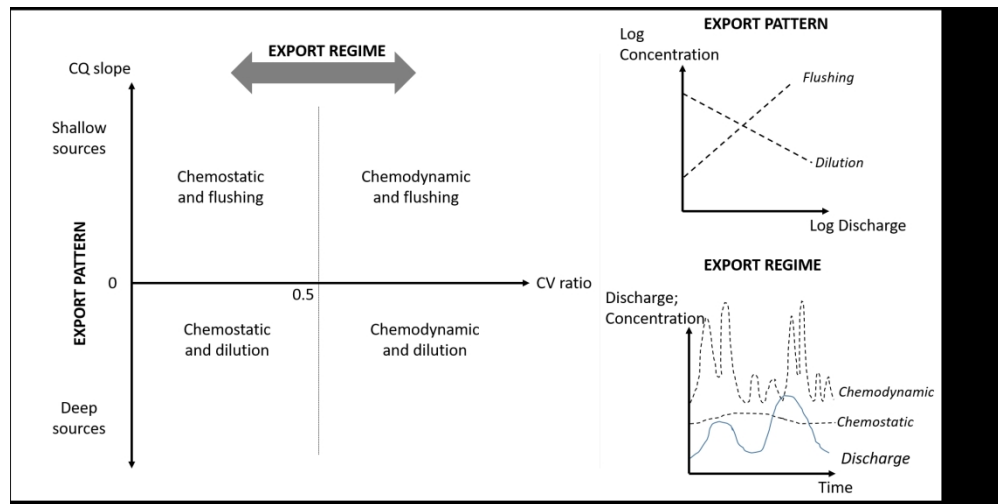


Figure 2: Relationship between CV ratios (export regimes) and CQ slopes (export patterns). Adapted from Musolff et al. (2015).

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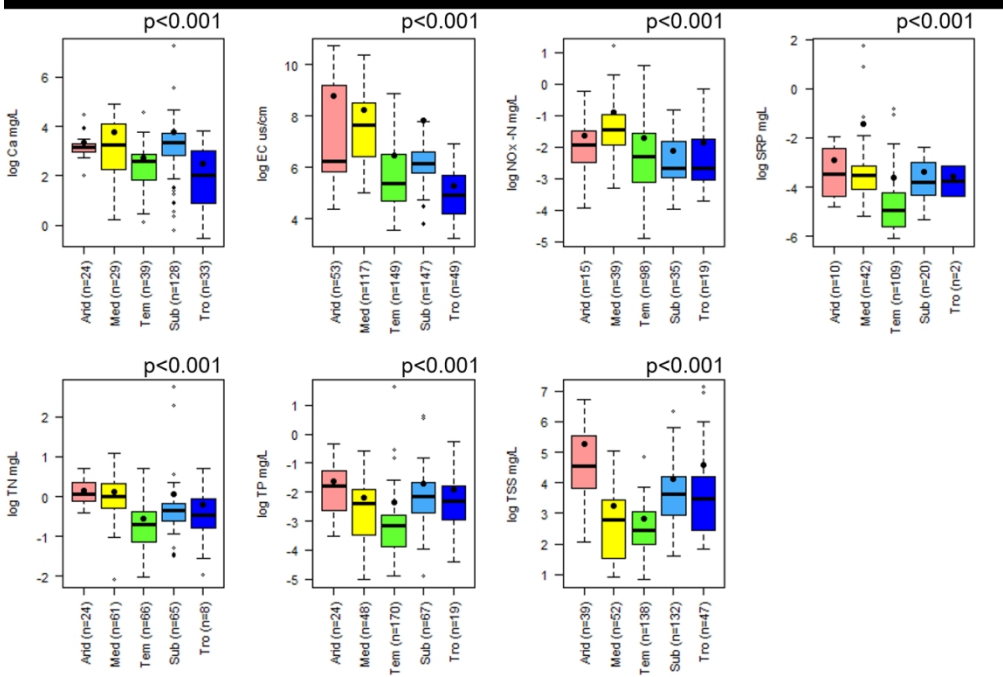


Figure 3: Variability in mean constituent concentrations for each climate zone. Results of Kruskal-Wallis test (p-values) to identify statistically significant variability in mean constituent concentrations across climate zones shown above each boxplot. n in x axis denotes the number of monitoring sites 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.

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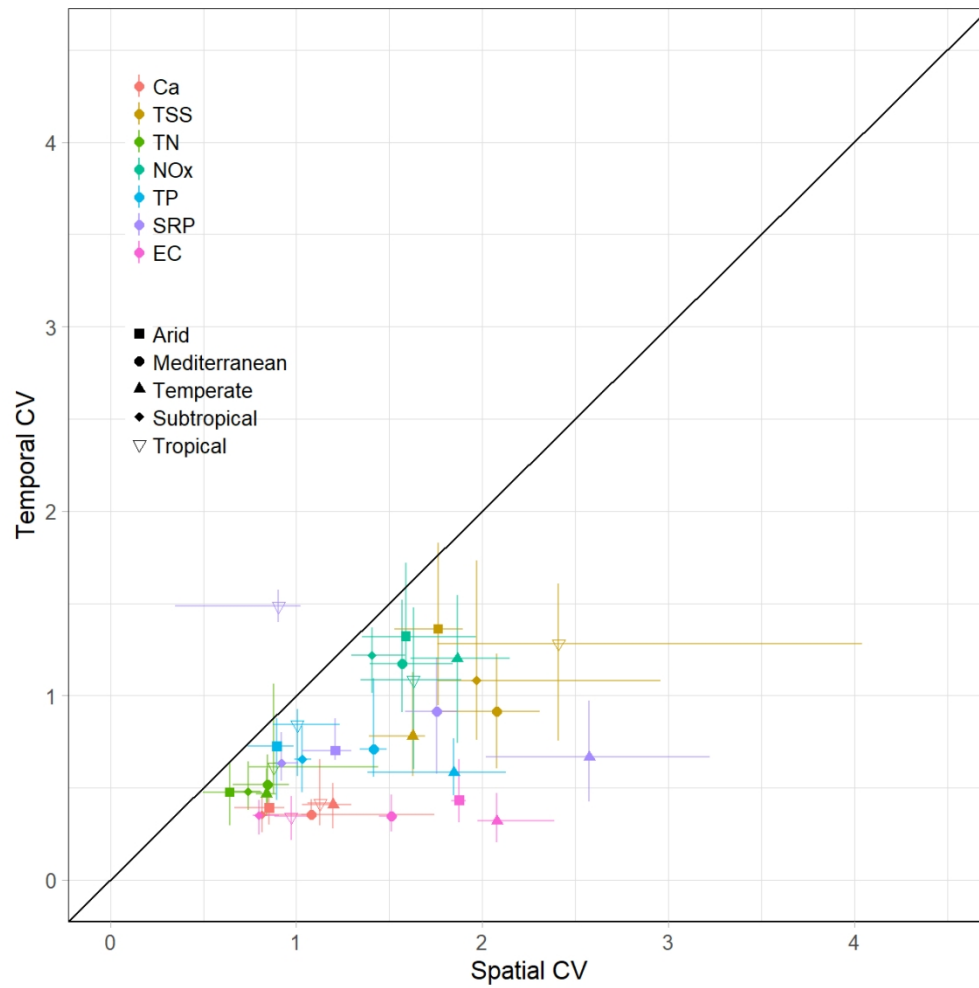


Figure 4: Comparison between variability in constituent concentrations over time and space. 'Spatial CV' indicates the spatial coefficient of variation determined monthly across all sites located in a given climate zone, and 'Temporal CV' represents the coefficient of variations determined for each site.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

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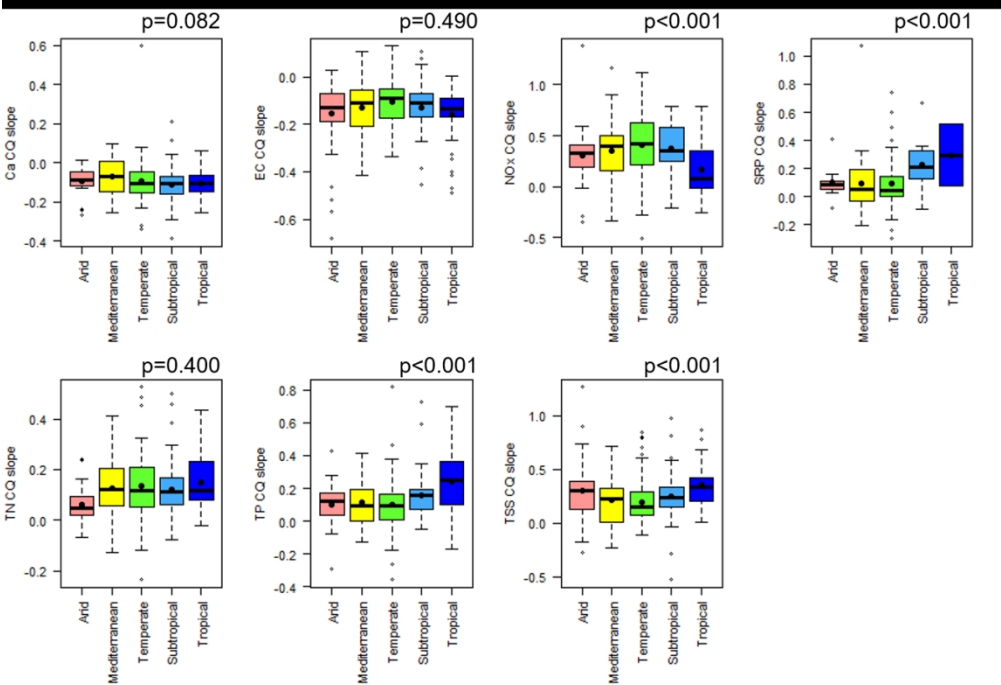


Figure 5: Variations in C-Q slope for each climate zone. Results of Kruskal-Wallis test (p-values) to identify statistically significant variability in C-Q slopes across climate zones shown above each boxplot. Boxes represent the interquartile range, whiskers represent 1.5 times the interquartile range,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

576x398mm (59 x 59 DPI)

This sheet provides an outline of the methods used for water quality analysis in each department. The level of detail provided by each state department differs, and each state department have been provided should the reader want to investigate further.

Key contacts:

NT: waterresources@nt.gov.au

TAS: WRT.Portal@wrt.tas.gov.au

WA: wir@water.wa.gov.au

QLD: wqi@qld.gov.au

SA: DEW.CustomerServiceCentre@sa.gov.au

VIC: water.data@delwp.vic.gov.au

NSW: waterdataservices@waterNSW.com.au

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Laboratory Analysis Methods*

Parameter	Method	Description	Sampling method
NO ₂	APHA 4500 NO ₂ I	Nitrate/Nitrite by Ca	Field filtered, frozen
NO ₃	APHA 4500 NO ₃ I	Nitrate/Nitrite by Ca	Field filtered, frozen NTEL
NH ₃	APHA 4500 NH ₃ H I	Ammonia by automa	Field filtered, frozen
FRP	APHA 4500 P G	Orthophosphate by ε	Field filtered, frozen
TN	APHA 4500 N C	Nitrogen by persulfat	Frozen
TP	APHA 4500 P B3 G	Phosphorus by perch	Frozen
Cations (Ca ⁺ , Mg ²⁺ , I	APHA 3120 B	Calcium by ICP	Refrigerated
TSS	APHA-2540 D	Total Suspended solli	Refrigerated

***These are for all samples collected after 1994. For samples collected prior to 1994, TN may have been done**

Field Sampling Methods

Field sampling is done by trained department staff, using standard sampling protocols, which include clean collection

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as a calculation of TKN (organic nitrogen and NH3) (APHA 4500-Norg D) plus NOx at times. Note that all sam

1 methods and holding times for samples (30 days for frozen nutrients)

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Laboratory Analysis Methods

Samples requiring laboratory analysis (ex situ analysis) are processed by Analytical Services Tasmania, a NATA accredited labor
The following analysis methods are used.

Pesticides method is 1515-Water, 1501-Water, 1508-Water,

Nutrients are 1205-Water, 1206-Water

Back in 2001, nutrients were 1203-Water, 1204-Water

Physico-chemical measurements methods by AST back in 2001 were 1001-water, 1002-water, 1004-water, 1005-water, 1007-v

For microbiological examination of water (back in 1999), method is AS4276.1995

Heavy metals methods are: 1301-water

Two published standardised methods and protocols for AWQM include:

United States Geological Surveys, 2000. Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Site Sele
White, E.T., comp., 1999. Automated water quality monitoring field manual: Version 1.0. Ministry of the Environment Lands an

The DPIWE protocols for continuous water quality monitoring outlined in this chapter have therefore been developed with ref

Field Sampling Methods

In situ analysis is carried out in accordance with the instrument manufacturers instructions using instruments calibrated to trac

Hand-held meters are checked for drifts in calibration every 3 months. Calibration of meters is to be completed by a NATA app

Two published standardised methods and protocols for AWQM include:

United States Geological Surveys, 2000. Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Site Sele
White, E.T., comp., 1999. Automated water quality monitoring field manual: Version 1.0. Ministry of the Environment Lands an

The DPIWE protocols for continuous water quality monitoring outlined in this chapter have therefore been developed with ref

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18 id Parks, Water Management Branch for the Aquatic Inventory Task Force Resources Inventory Committee, British Columbia, Ca
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26 roved agency every three (3) years.
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31 id Parks, Water Management Branch for the Aquatic Inventory Task Force Resources Inventory Committee, British Columbia, Ca
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33 erence to the above US and Canadian publications, and should be applied in conjunction with relevant manufacturer’s specifica
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Laboratory analysis methods

Constituent	Method Description
Ca	Major cations determined by an inductively coupled plasma atomic emission spectrometer. Based on APHA 21st ed., 3120; USEPA SW846 - 6010. Hardness calculated from Calcium and Magnesium as per APHA 21st ED 2340B. Compliant with NEMP (2013) Schedule B(3).
NOx	Nitrite and nitrate as nitrogen in natural waters by copper cadmium reduction, determined by a flow injection analyser.
EC	Electrical conductivity (uncompensated) calculated from compensated conductivity at 25 deg C.
SRP	Soluble reactive phosphorus as phosphorus by direct colourmetric analysis, determined by a discrete analyser.
TN	Nitrogen (inorganic, organic, total filtered, total) determined by calculation
TP	Total phosphorus as P. Sample is digested with sulfuric acid. The orthophosphate produced reacts with ammonium molybdate and antimony potassium tartrate. Concentration determined on the reduced complex by a discrete analyser (APHA 21st ed. 4500-P B&F).
TSS	Total suspended solids by filter residue drying at 105 deg C, and/or loss on ignition dried at 550 deg C. Determined by gravimetric analysis.

Laboratory Analysis Methods

Constitute	Method Description
NOx	Colorimetric (automated cadmium reduction) method (sum of nitrate and nitrite)
EC	Conductivity probes, compensated conductivity at 25 deg C
SRP	Flow Injection Analysis method
TN	Persulphate digestion method
TP	Persulphate digestion method
TSS	Gravimetric method

For Peer Review

Laboratory Analysis Methods

All samples were analysed at NATA accredited laboratories using standard methods.

Field Sampling Methods

Flow Proportional Composite Sampling methodology.

The method requires a continuous measurement of water flow, through either direct measurement (flow meter) or us

The monitoring system is required to continuously totalise the cumulative flow passing the sampling location.

Programmed into the system is a predetermined volume increment (eg. 0.2 ML), based on the expected flow regime

Each time the volume increment is reached, the auto sampler is triggered to pump a sample.

The sampler process includes:

- A purge of the sample line
- Pump initiation to pump fresh water through the sample lines and flush the system.
- After flushing, a 500ml aliquot of water is extracted and delivered into a 60 litre composite sample tub.

The flow volume increment for triggering the collection of each sample is a site specific volume based on the expecte

The increment is reviewed and adjusted as necessary based on the current and expected flow conditions to attempt

At each site visit for sample collection, the composite tub is stirred vigorously and one representative sample set rem

The tub is then emptied and cleaned.

The determined sample result represents the mean flow-weighted concentration of the flow during the sample period

Multiplying the mean concentration value by the total flow volume for the sampling period produces a reliable estimat

using a predetermined calibration of the river flow versus height relationship if available.

of the location, to initiate the sample.

and flow regime to ensure that a maximum number of samples are taken without overtopping the composite sample tube

to achieve the maximum number of samples.

removed for analysis.

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Laboratory and Field Sampling Methods

Constituent	Method
Ca	The current analytical method for the determination of Calcium is Standard Method No. 3120B (A
NO _x	The current analytical method for the determination of Nitrate and Nitrite is Standard Method No. 4
EC	The current analytical method for the determination of Electrical Conductivity is Standard Method
SRP	The current analytical method for the determination of filterable (0.45 micron pore size) reactive p
TN	Total Nitrogen is determined by persulfate digestion within an autoclave followed by the analysis
TP	The current analytical method for the determination of total phosphorus is Standard Method No. 4
TSS	The current analytical method for the determination of suspended solids is Standard Method No.

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(APHA, 2012). The analysis is performed using an inductively coupled plasma optical emission technique (ICP-OES).
4500-NO₃ (APHA, 2012). The conversion of nitrate to nitrite prior to colorimetric determination is achieved using an i
No. 2510B (APHA, 2012). The analysis is performed on an autosampler combined with an Electrical Conductivity m
phosphorus is Standard Method No. 4500-P (APHA, 2012). The analysis is performed using a segmented flow analys
for nitrate
4500-P (APHA, 2012) which follows off-line digestion to convert all forms of phosphorus into orthophosphate using an
2540 D&E (APHA, 2012). The analysis is performed by filtering a measured volume of sample through a pre-washed

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in-line copper coated cadmium reduction column. The colorimetric reaction involves diazotising the nitrite with sulphur
meter. The meter is calibrated daily with 0.001M, 0.01M and 0.1M potassium chloride solutions to ensure adequate line
arity. The phosphate reacts with ammonium molybdate and antimony potassium tartrate, in acid medium, to form phospho
molybdate. The analysis is performed using a segmented flow analyser. The phosphate reacts with ascorbic acid
in acidic persulfate digestion. The analysis is performed using a segmented flow analyser. The phosphate reacts with ascorbic
acid, dried and weighed Whatman GFC filter. After adequate rinsing with distilled water to ensure removal of dissolved solids.

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nilamide and coupling the N-(1-naphthyl)ethylenediamine dihydrochloride. The absorbency is measured at 543 nm. The temperature compensation is also checked daily. The results are reported to the nearest integer from 2 μ S. This is reduced by ascorbic acid. The absorbency of the resultant blue complex is then measured. Ammonium molybdate and antimony potassium tartrate, in acid medium, to form phosphomolybdic acid. This is reduced by ascorbic acid. The absorbency of the resultant blue complex is then measured. The filter is dried (103–105 C) desiccated and reweighed.

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µS/cm at 25°C to 100 µS/cm at 25°C. Above this the results are reported to 2 significant figures.
at 710 nm.

reduced by ascorbic acid. The absorbance of the resultant blue complex is then measured at 710 nm

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Laboratory analysis and field sampling methods

All water quality constituents are measured at NATA (National Association of Testing Authorities) accredited laborati

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es using standard methods

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Supporting Materials for

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

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³ EPFL, Physics of Aquatic Systems Laboratory, Margaretha Kamprad Chair, Lausanne, Switzerland

⁴ INRAE, L'institut Agro, UMR 1069 SAS, 35000 Rennes, France

⁵ Water Research Centre, School of Civil and Environmental Engineering, UNSW Sydney, High St, Kensington, NSW 2052, Australia

⁶ Canberra, ACT, 2614 Australia

⁷ Research Institute for the Environment and Livelihoods, Charles Darwin University, Darwin, NT, Australia

⁸ National Centre for Groundwater Research and Training (NCGRT), Australia

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Contents of this file

Text S1
Figures S1 to S11
Tables S1 to S2

Text S1. Justification of Data Choice

Methods:

Four water quality monitoring sites were randomly selected for each of the seven states and territories (Table S1.1). For these sites we randomly sampled 10, 20, 30, 40, 50, 100 and 200 pairs of flow and constituent concentration data. This was done for all seven constituents. We calculated the mean constituent

concentration, the C-Q slope and the CV ratio for each of the seven randomly sampled sub-samples. We repeated this 1000 times. We then compared the parameters of interest calculated for each of the seven random sub-samples to identify how sensitive our calculated parameters are to the number of datapoints used to calculate the parameters.

Table S1.1: The water quality monitoring sites used for the analysis.

State	Site 1	Site 2	Site 3	Site 4
NSW	416032	418054	421025	425005
NT	G8140152	G8140159	G8260001	G8260054
QLD	422321B	912101A	915016A	923001A
SA	A4260533	A4261007	A5031006	A5031007
TAS	2209	2219	18309	18313
VIC	22202	227231	401226	405214
WA	612009	612044	709009	802156

Results:

We compared the mean constituent concentrations, C-Q slopes and CV ratios calculated for each of the seven randomly sub-sampled datasets. We present results for EC and TSS at one site (VIC405214) in Figures S1.1, S1.2 and S1.3. These results indicate that using 50 points (i.e., constituent concentration-discharge pairs) are sufficient to represent the mean constituent concentration, C-Q slope and CV ratio.

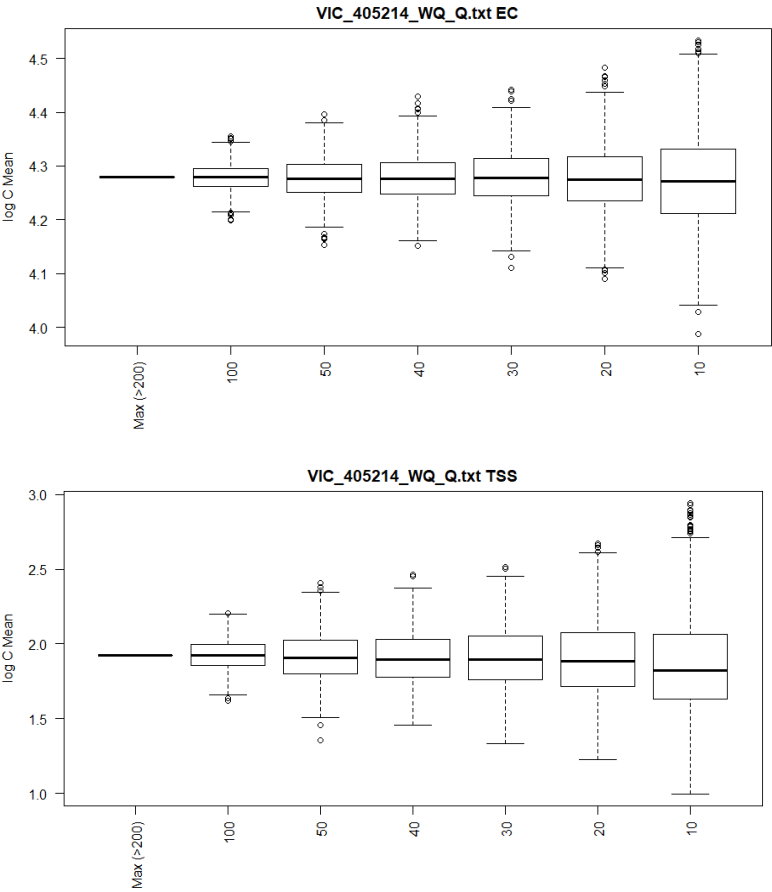


Figure S1.1: Mean C (concentration) calculated using sub-sampled datasets consisting of 10, 20, 30, 40, 50, 100 and the maximum number (>200) of data points for EC and TSS at VIC405214.

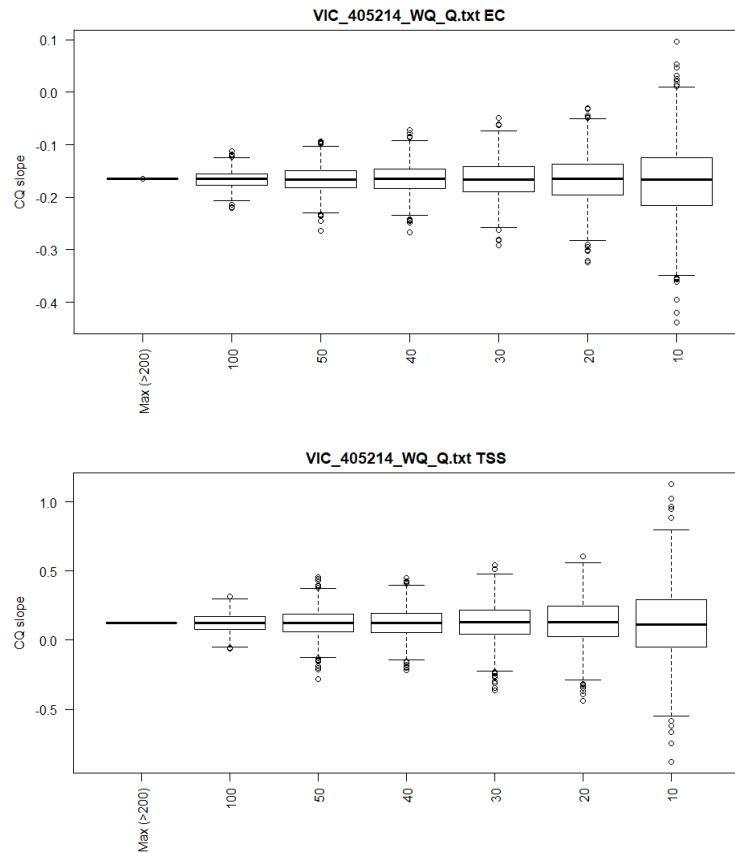


Figure S1.2: C-Q slope calculated using sub-sampled datasets consisting of 10, 20, 30, 40, 50, 100 and the maximum number (>200) of data points for EC and TSS at VIC405214.

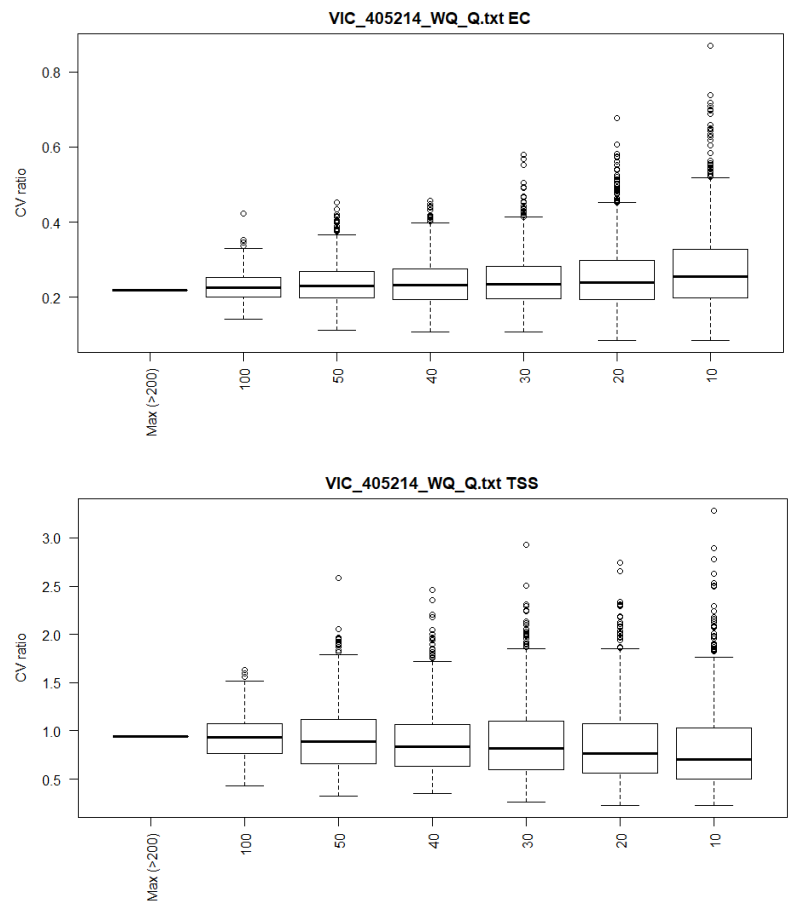


Figure S1.3: CV ratio calculated using sub-sampled datasets consisting of 10, 20, 30, 40, 50, 100 and the maximum number (>200) of data points for EC and TSS at VIC405214.

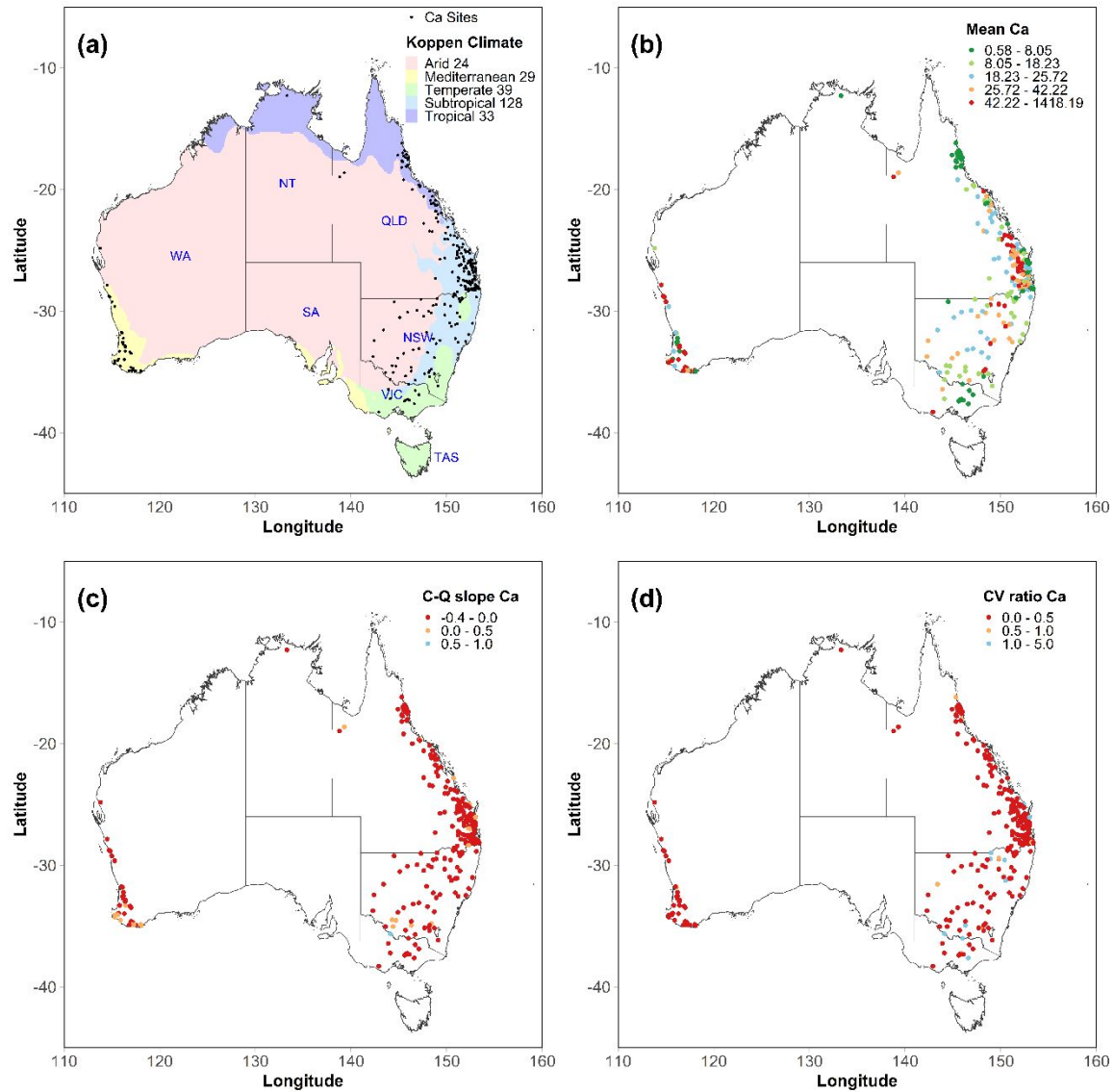


Figure S1. Maps showing site locations (a), mean concentrations (b), concentration-discharge (C-Q) slopes (c), and CV ratio (d) at each site for Ca.

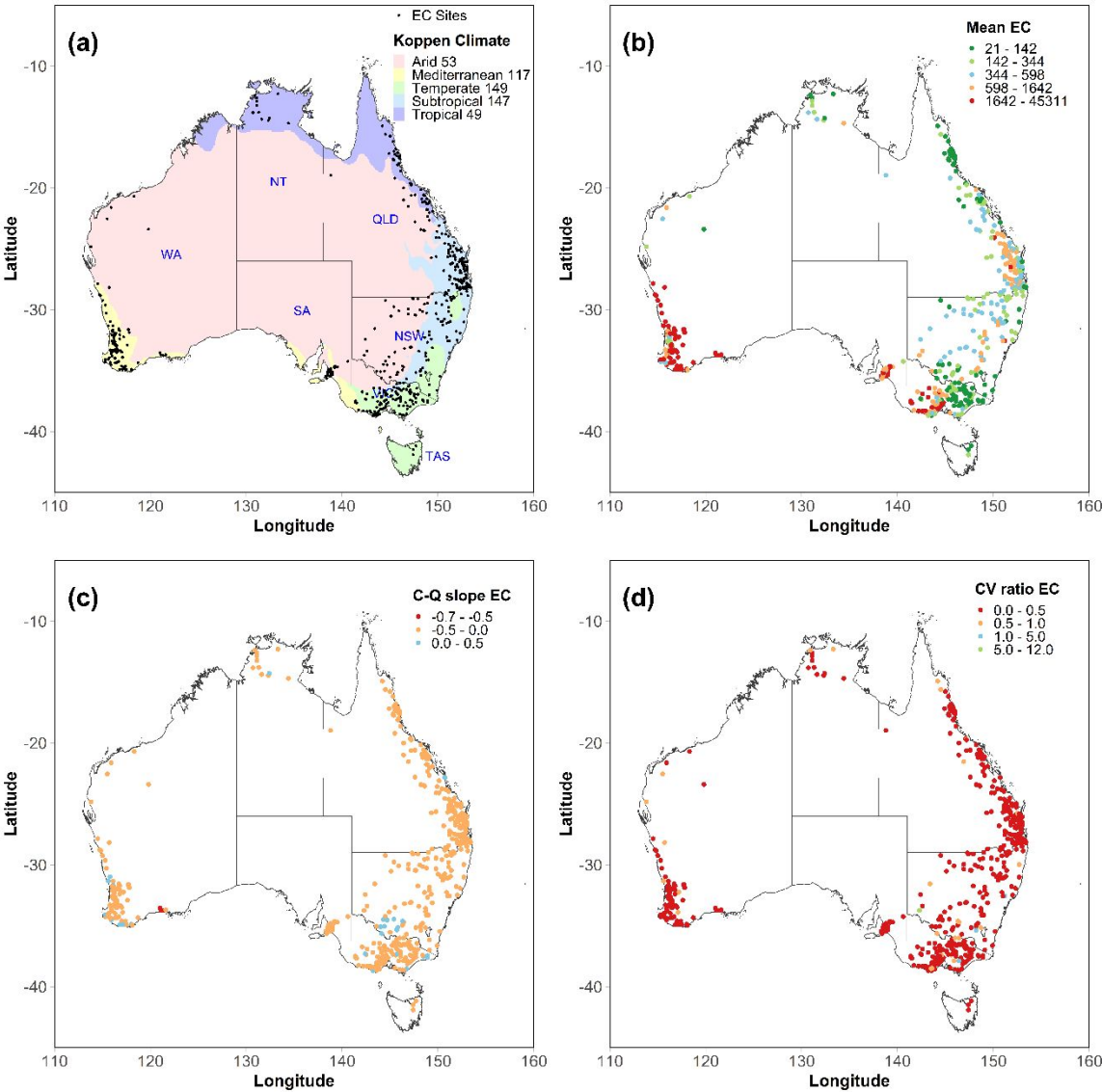


Figure S2: Maps showing site locations (a), mean concentrations (b), concentration-discharge (C-Q) slopes (c), and CV ratio (d) at each site for EC.

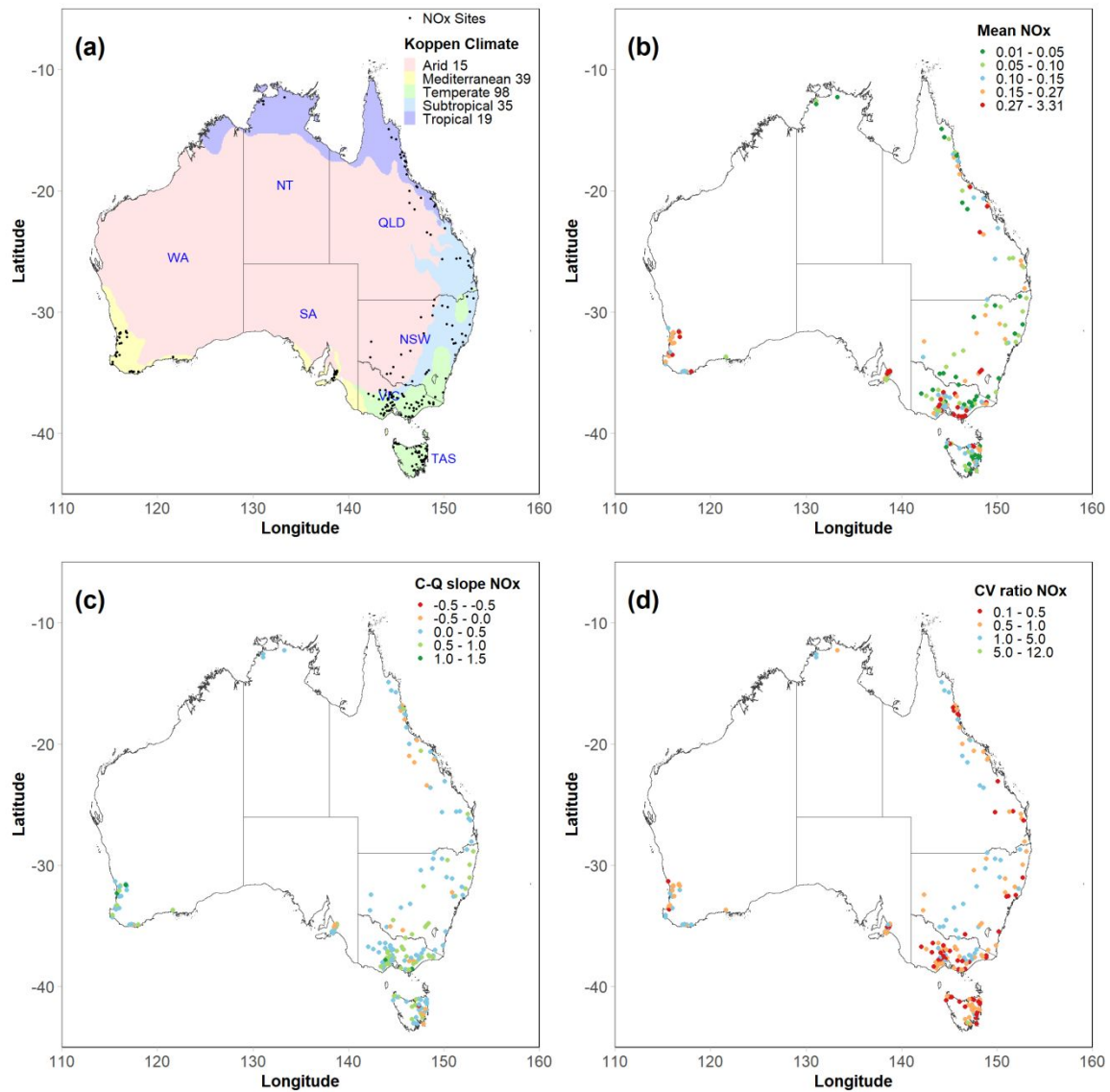


Figure S3: Maps showing site locations (a), mean concentrations (b), concentration-discharge (C-Q) slopes (c), and CV ratio (d) at each site for NOx.

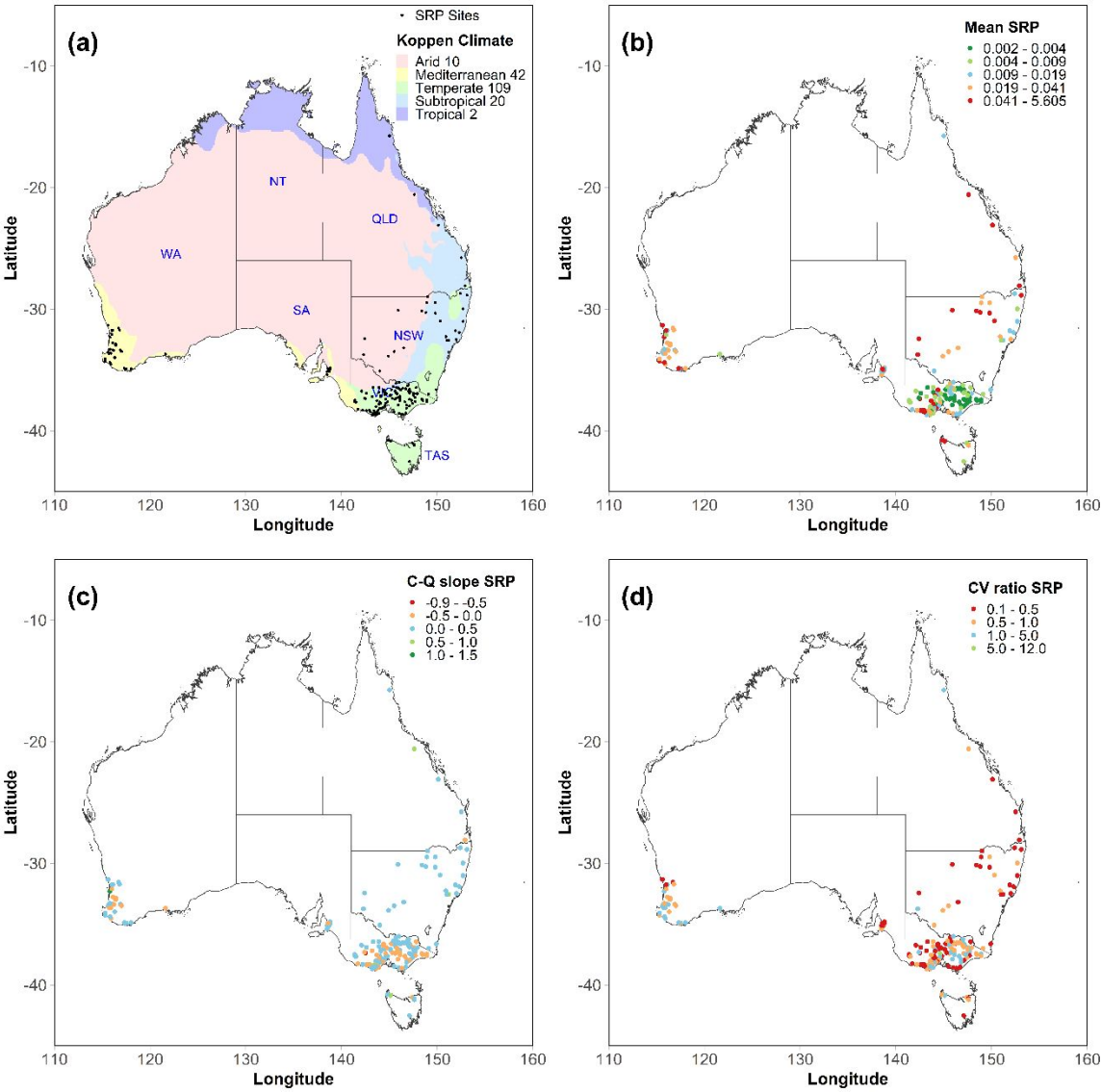


Figure S4: Maps showing site locations (a), mean concentrations (b), concentration-discharge (C-Q) slopes (c), and CV ratio (d) at each site for SRP.

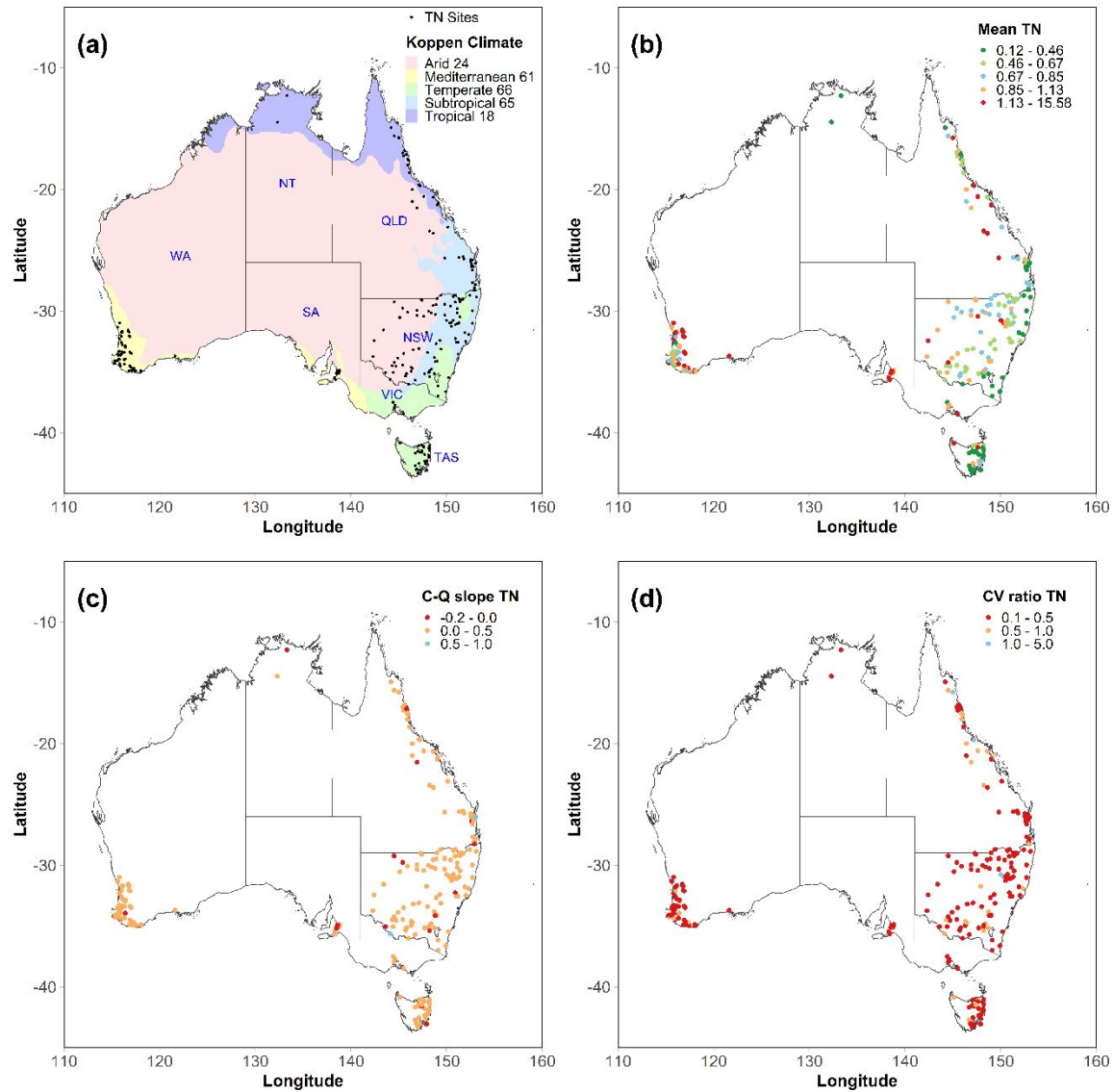


Figure S5: Maps showing site locations (a), mean concentrations (b), concentration-discharge (C-Q) slopes (c), and CV ratio (d) at each site for TN.

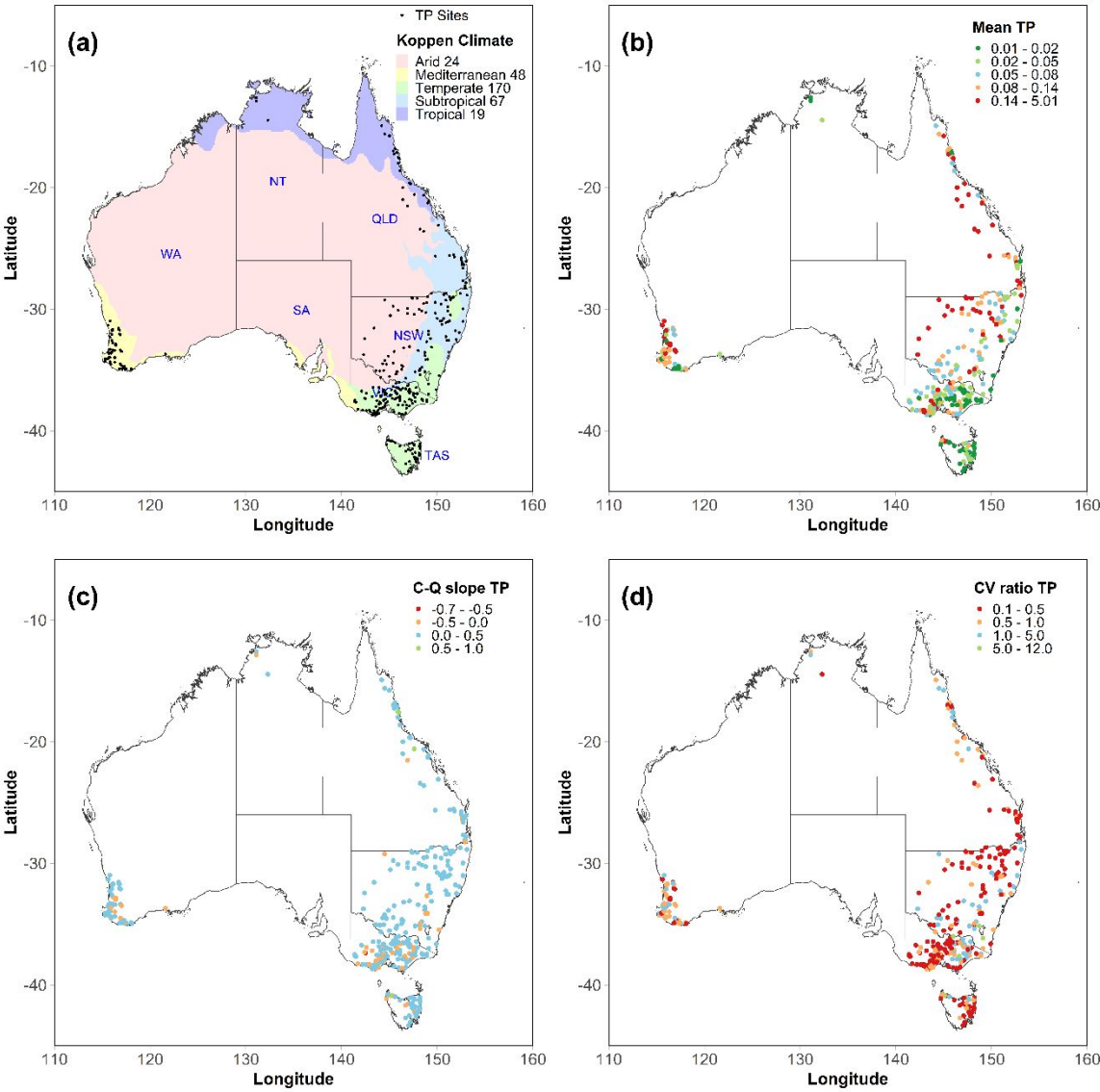


Figure S6: Maps showing site locations (a), mean concentrations (b), concentration-discharge (C-Q) slopes (c), and CV ratio (d) at each site for TP.

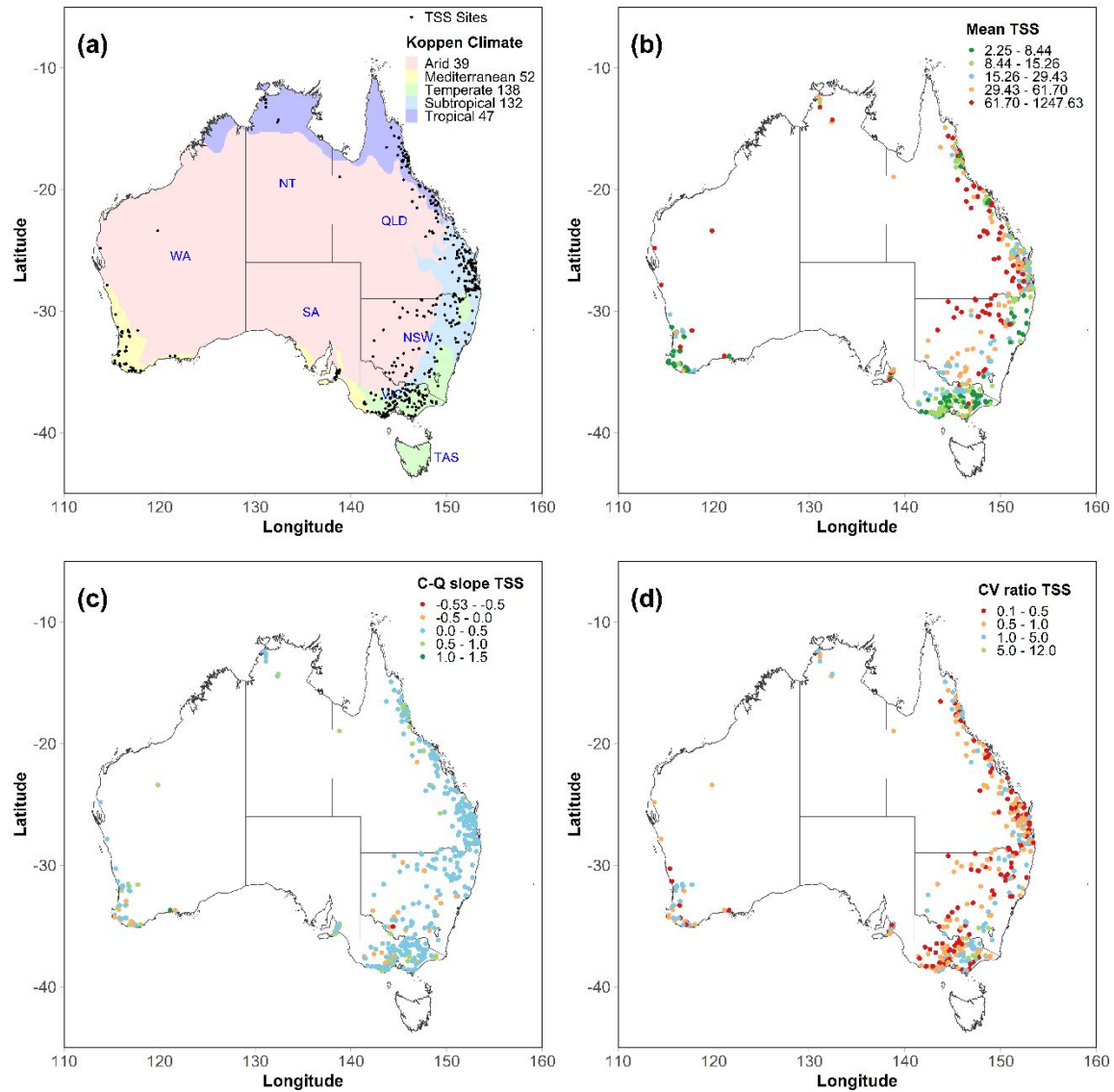


Figure S7: Maps showing site locations (a), mean concentrations (b), concentration-discharge (C-Q) slopes (c), and CV ratio (d) at each site for TSS.

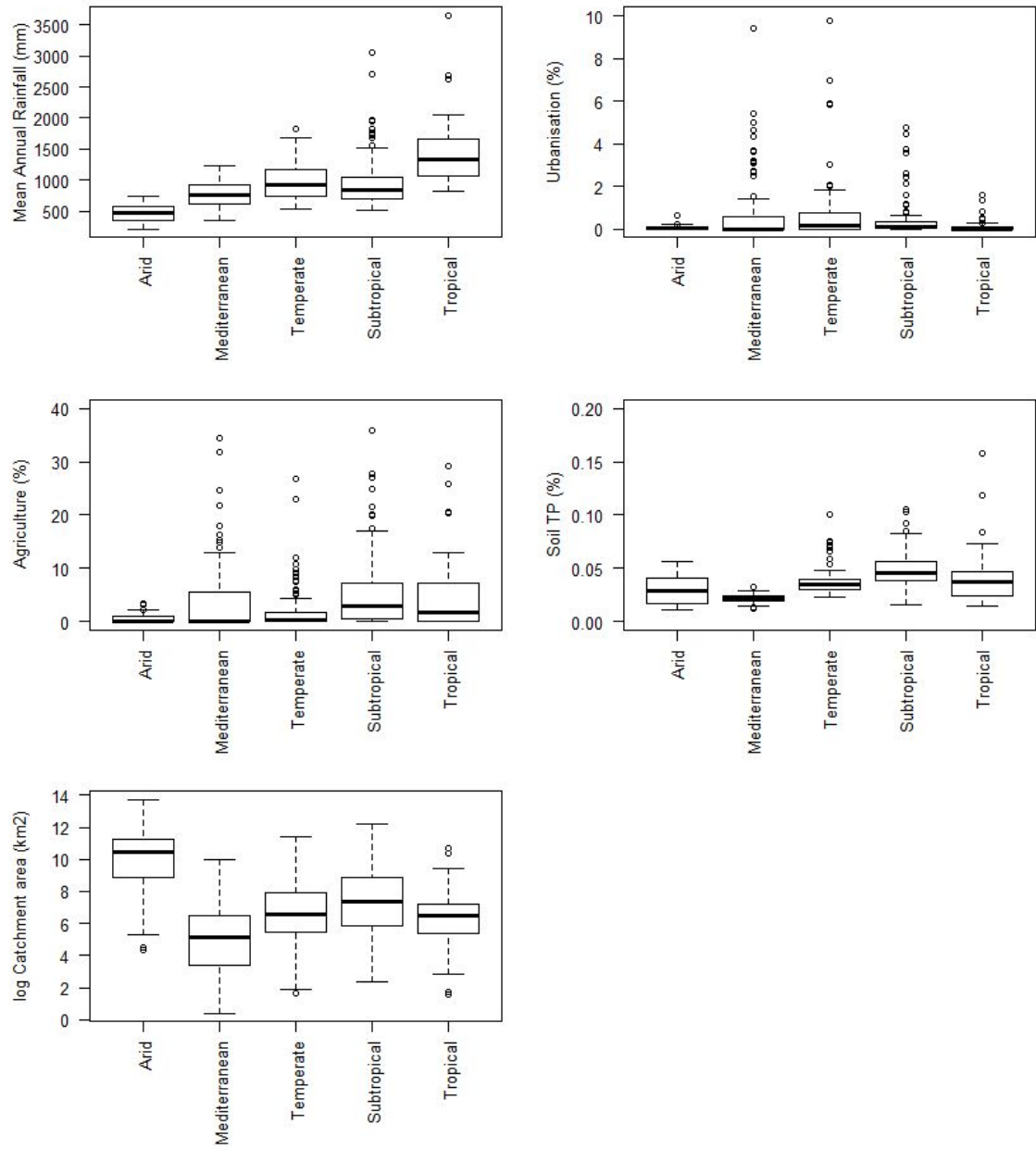


Figure S8: Climate, land use and soil type in catchments in each climate zone. a) Mean annual rainfall (mm), b) % urbanisation, c) % agricultural land use, d) Soil TP content, e) catchment area.

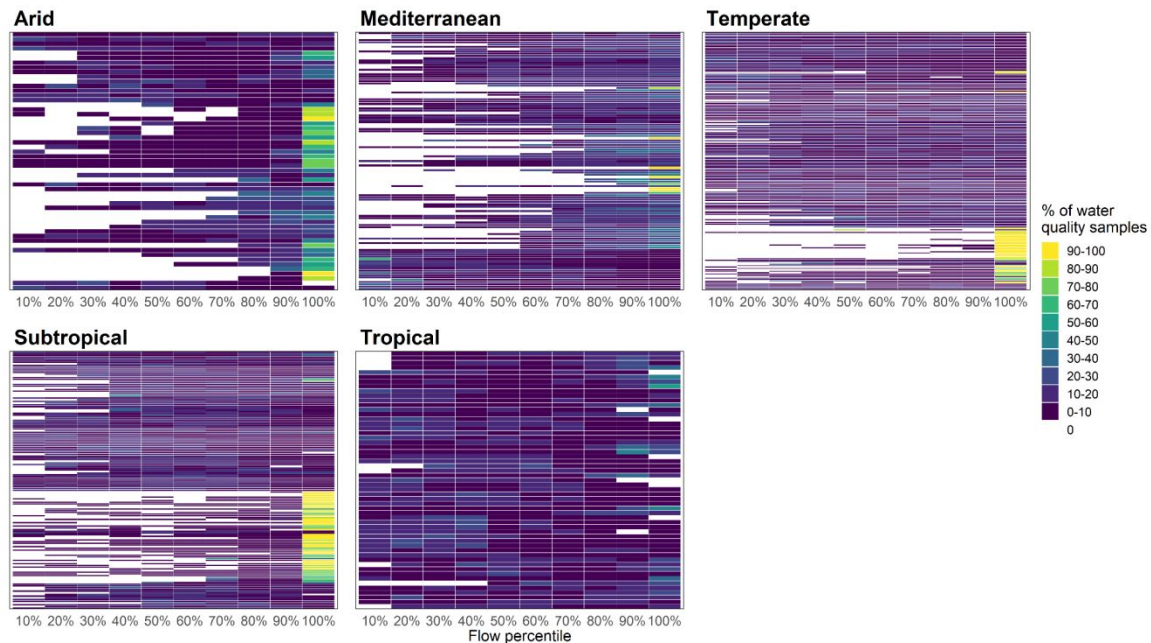


Figure S9: Distribution of water quality sampling for specific flow percentiles in the five climate zones. Each row on the graph represents a single site where monitoring data were collected.

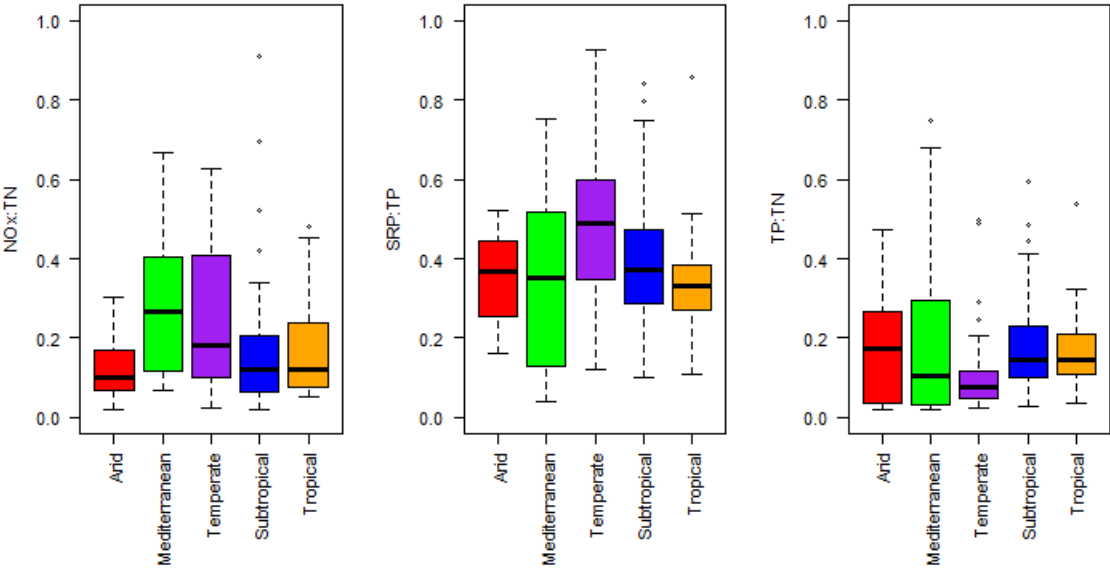


Figure S10: Nutrient ratios by climate zone

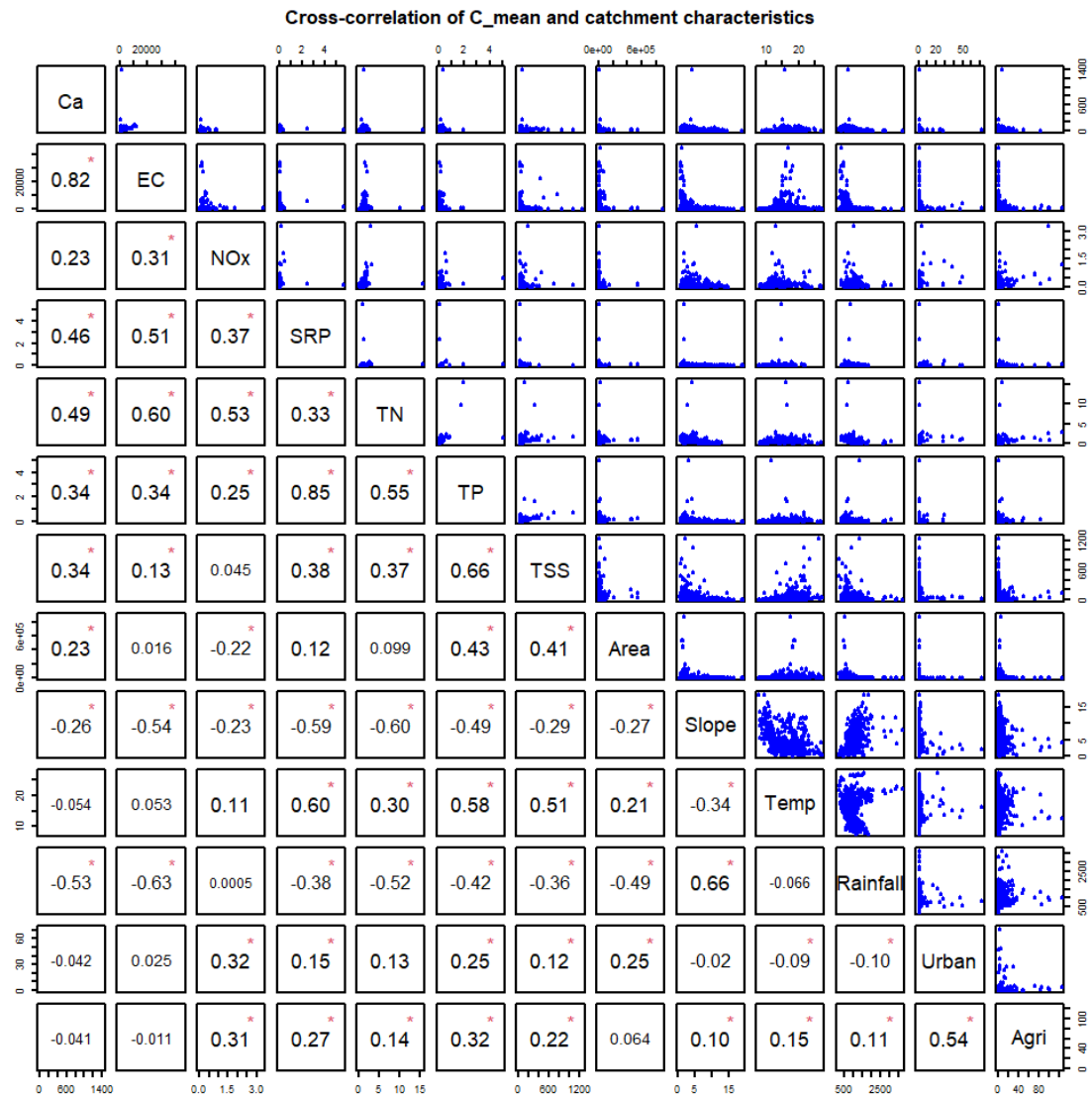


Figure S11: Spearman correlation coefficients between constituent mean concentrations (C_{mean}) and key catchment characteristics. Red asterisk represents statistical significance ($p < 0.05$).

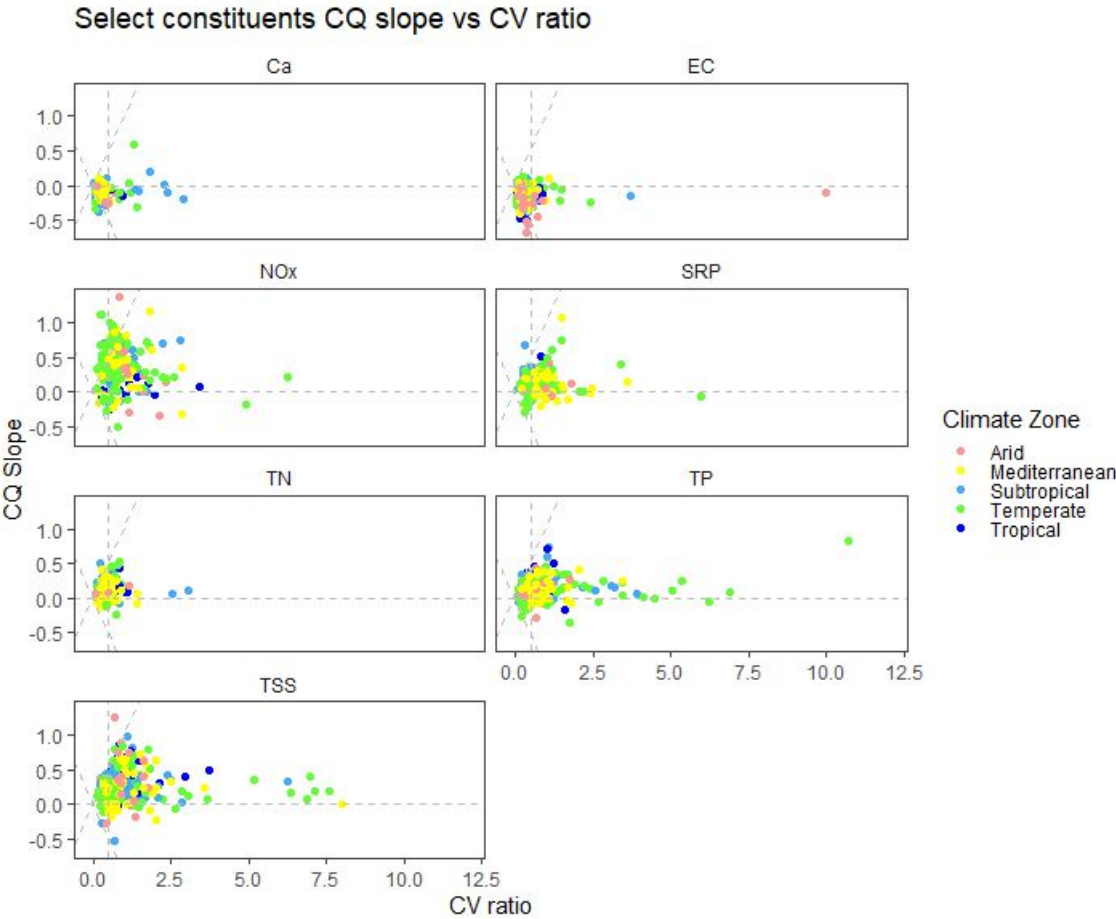


Figure S12: Relationship between CV ratio and C-Q slope for Ca, EC, NOx, SRP, TN, TP and TSS. Dotted lines indicate 1:1 lines, $x=0.5$ and $y=0x$ and y axes. Chemostatic behaviour is indicated by $CV\ ratio < 0.5$ and chemodynamic behaviour by $CV\ ratio > 0.5$.

Table S1: Criteria used to remove data from water quality and discharge database. Green text indicates quality codes representing 'good quality' data that were used in analysis. Orange and red text represent data quality codes that were removed from the data prior to analysis.

State	NSW	SA	TAS	VIC	NT	QLD	WA
State agency contacted	WaterNSW	SA DEW	TAS DPIPWE	VIC DELWP	NT DENR	QLD DNRME	WA Department of Water and Environmental Regulation
Quality Code (QC) recommendation for discharge	QC<152 identifies suitable data for analysis	QC<=30 identifies suitable data for analysis	QC>=51 good data 12<=QC<=41 are uncertain data that are either estimated or from another data source outside of DPIPWE QC=11 represents erroneous data	QC<=150 good to use QC>150 should not be used	QC<100 Fine to use 101<=QC<=149 High level of uncertainty QC>=150 Should not be used	QC<=26 Good/Fair record QC>= 30 Poor or estimated values In addition, for WQ: QC=125 Fair historic data	QC<=3 Uncertainty <+-10% 4<=QC<=6 +-10%<=Uncertainty <+-20% QC= 100, 104 discrete data - recorded value represents the true value QC =150, provisional data from another data source outside of DWER
QC recommendation for concentration	No QC	QC for WQ not generally used, unsure how to apply					

Table S2: Mean number of concentration-discharge (C-Q) pairs and mean length of water quality time series (in years) used for analysis for each constituent. The 2.5th and 97.5th percentiles are provided in parentheses.

Constituent	C-Q Pairs	Time series length (years)
Ca	106 (51-284)	24 (7-40)
EC	1968 (55-7623)	26 (6-47)
NOx	213 (53-751)	15 (4-27)
SRP	229 (58-514)	18 (5-27)
TN	203 (52-880)	14 (4-28)
TP	265 (54-909)	20 (5-38)
TSS	239 (52-869)	21 (6-31)

Table S3: Pairwise comparison of CQ slopes between climate zones using Dunn's post-hoc test. Statistically significantly different catchment mean concentrations between specific climate zone pairs 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							