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Key Points:

- Human-influenced (land use) and natural catchment characteristics (e.g., topography) affect spatial variability in stream water quality
- Spatial variability in electrical conductivity can be most easily explained by catchment characteristics
- There was minimal change in model performance when different hydrological periods were modeled

Supporting Information:

- Supporting Information S1
- Data Set S1
- Data Set S2

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What Are the Key Catchment Characteristics Affecting Spatial Differences in Riverine Water Quality?

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Abstract This study uses water-quality data collected over 20 years, from 102 predominantly rural sites across Victoria, Australia, to further our understanding of spatial variability in riverine water quality. We focus on concentrations of total suspended solids, total phosphorus, filterable reactive phosphorus, total Kjeldahl nitrogen, nitrate/nitrite (NO_x), and electrical conductivity. We used an exhaustive search approach to identify the linear models that best link catchment characteristics to time-averaged constituent concentrations. We ran additional analyses to (1) assess the performance of these models under drought conditions, and (2) understand the key drivers of site-level variability (standard deviations) of constituent concentrations. Natural catchment characteristics appear to have a greater effect on spatial differences in average constituent concentrations. Performance of the statistical models of time-averaged constituent concentrations varied, and spatial variability in mean electrical conductivity levels could be more readily explained by catchment characteristics compared to more reactive nutrients. Notwithstanding, the models performed relatively well under varying hydrologic conditions for most constituents. As such, these models provide an insight into the key factors affecting spatial variability in average stream water-quality conditions. We also identified that hydrologic, climatic, and topographic characteristics of the catchment helped explain the spatial variability in temporal changes in constituents. After calibration and validation, these models of both average water quality and variability in water quality could be used to forecast stream water-quality responses to future land use, climate, or soil and land management changes.

1. Introduction

Worldwide, rivers are experiencing declining water quality (Loucks et al., 2005; Schwarzenbach et al., 2010). This contributes to the impairment of aquatic ecosystems (Smith et al., 1999; Vorosmarty et al., 2010) and threatens their use as a source of water for humans (Jiang, 2009). There is significant spatial and temporal variability in water quality (Aubert et al., 2013; Chang, 2008). For example, time-averaged total suspended solid (TSS) concentrations can be as low as 10 mg/L in some parts of the globe and as high as 1,700 mg/L in other locations (Meybeck & Helmer, 1989). Even within individual river basins, there can be significant sub-basin-scale variations in water quality. For example, in the 730-km² Jinshui River basin in China, time-averaged total nitrogen (TN) concentrations in 2006–2008 ranged from 0.01 to 4.38 mg/L (Bu et al., 2010). In addition, water quality at one site can vary significantly over time, often as a result of changes in streamflow, hydrological processes, and source availability in the catchment (Ahearn et al., 2004; Arheimer & Lidén, 2000; Lecce et al., 2006; Robson, 2014; Stutter et al., 2008). TN concentrations measured between 1994 and 2008 at the Fitzroy River basin outlet (north-east Australia) had a minimum of 0.36 mg/L and a maximum of 4.1 mg/L (Packett et al., 2009). To develop effective and site-specific management strategies for polluted aquatic systems, it is critical to understand the drivers of spatial variability in water quality. While both temporal and spatial variability are important, this study concentrates on the spatial aspect, by identifying the factors affecting spatial differences in riverine water quality across a region of approximately 200,000 km² and analyzing their relative importance. While the results from a study of this scale will not be sufficient to clearly identify the key management practices that should be implemented to improve stream water quality, they may be able to guide further investigation of potential water-quality management strategies.

Studies have previously identified significant positive correlations between the extent of human activities such as grazing, agriculture and urbanization in a catchment, and concentrations of total suspended sediments (TSS), nutrients (e.g., phosphorus and nitrogen), and electrical conductivity (EC, Allan, 2004; Drewry et al., 2006; Giri & Qiu, 2016; Lintern et al., 2018; Suárez & Puertas, 2005). For example, there can be higher concentrations of TSS, nutrients, and salts in areas affected by human activities, in particular urban areas (Paul & Meyer, 2001). There is also a clear link between the removal of vegetation from the landscape and reduced water quality (Meybeck et al., 1989). A smaller number of studies have also acknowledged the role of natural catchment characteristics such as topography, hydrological processes, geology, and climate on water-quality responses (Tramblay et al., 2010; Young et al., 2005). All of these characteristics can potentially impact stream water quality because they can affect (i) the source (i.e., the amount of material that is present in the catchment), (ii) the mobilization (i.e., the release of constituents from being stored or bound in the catchment), and (iii) the delivery (i.e., the conveyance of the constituents from its source to the receiving stream or river) of constituents (Granger et al., 2010). While the effect of landscape characteristics such as climate, topography, land use on the source, mobilization, and delivery processes is understood (Lintern et al., 2018), the relative importance of these natural characteristics compared to human-derived catchment impacts is not well known.

Several studies have developed statistical models linking spatial variability in water-quality responses to catchment characteristics (e.g., Chang, 2008; Onderka et al., 2012; Tramblay et al., 2010). However, these studies have used limited numbers of study sites, limited numbers of potential catchment characteristics, and/or limited variability in environments. This study extends these scales. Moreover, previous studies have been conducted in North America, Europe, and Asia, which have different agricultural practices (e.g., higher fertilizer usage) compared to Australia (Lu & Tian, 2017). As such, we currently have a limited understanding on the key factors affecting spatial variability in water quality in a region with relatively lower fertilizer inputs. Furthermore, from previous studies it is not clear whether anthropogenic factors or natural catchment characteristics are more important in affecting spatial variability. We explore spatial variability in water quality and develop statistical models linking spatial variability in time-averaged water-quality responses to catchment characteristics for TSS, total phosphorus (TP), filterable reactive phosphorus (FRP), total Kjeldahl nitrogen (TKN), nitrate/nitrite (NO_x), and EC. We acknowledge that water quality varies both across space and time. This particular study is part of a larger project that aims to model water quality both over space and time. As this is the first step in this larger undertaking, we address only average catchment characteristics in this particular study, to develop simple models that can be made more complex as necessary. This is done using a spatially extensive data set of monthly water quality and flow data collected over a 20-year period from 102 riverine sites in south-east Australia and data obtained for 50 different characteristics of these catchments.

2. Methods and Materials

2.1. Data Collection and Preparation

Water-quality data used here are from the Victorian Water Quality Monitoring Network, which monitors monthly ambient water quality at approximately 400 sites across the state, with monitoring having commenced in 1990. Sites with a 20-year record (1994–2014) of monthly water quality and flow data were selected to provide a subset of long-term records with consistent climatic conditions to enable robust spatial comparison of sites. This resulted in a subset of 102 water-quality monitoring sites for analysis. The locations of these water-quality monitoring sites in the state of Victoria, south east Australia, are shown in Figure 1. The state of Victoria has varying climatic, vegetation and topographic conditions, with wet, forested mountainous regions in the east, central west, and south west of the state (Figure 1b). Most of these sites are dominated by nonpoint discharges; 98% of sites have point discharges equivalent to less than 10% of the average annual discharge.

Data were obtained from the Water Measurement Information System (Department of Environment, Land, Water and Planning Victoria, 2016a). These data were analyzed in National Association of Testing Authorities accredited laboratories. As the water quality and flow data were not normally distributed, data were log transformed prior to analysis. The site-level means were calculated for each constituent and for instantaneous flow using the log-transformed data, which were used for further analyses in this study. Site-level mean constituent concentrations were utilized for most of this study because we are mainly

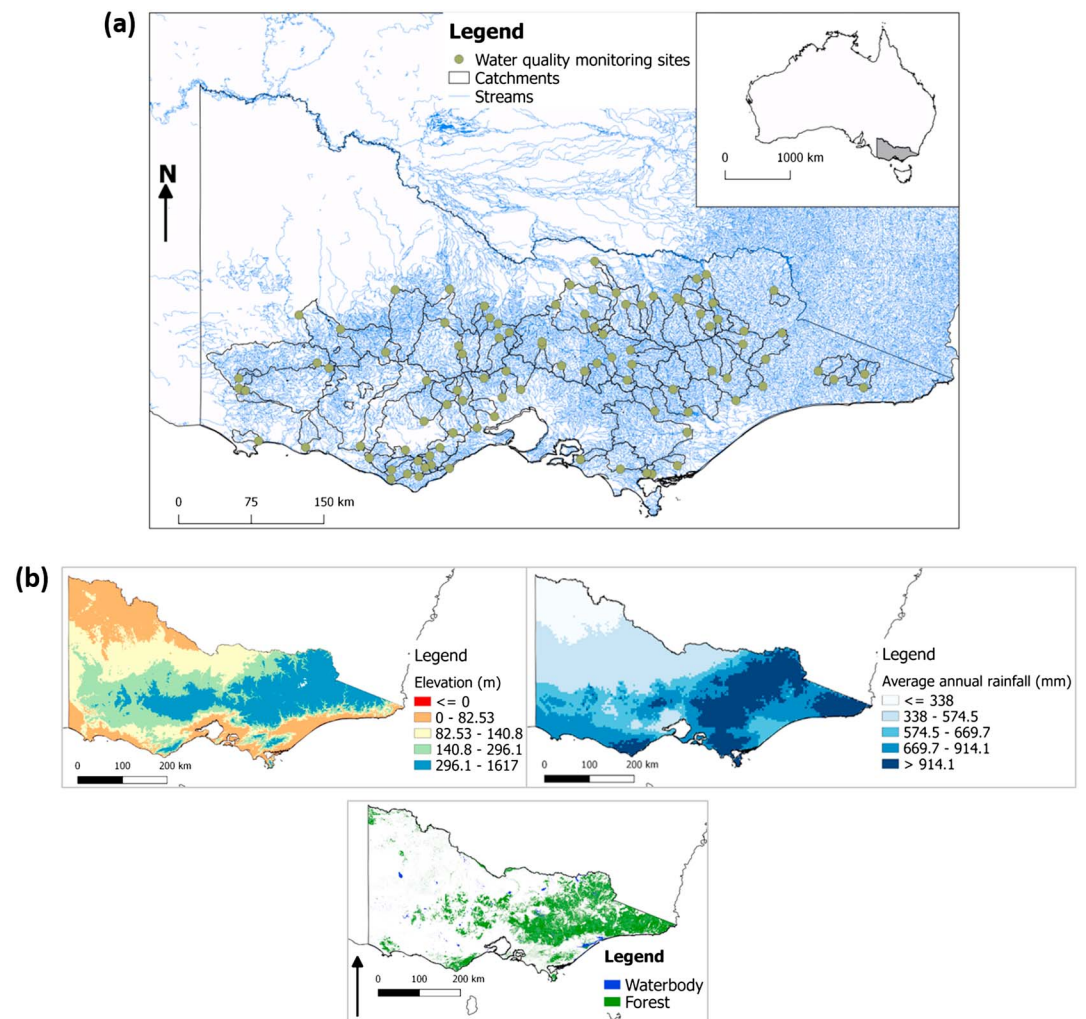


Figure 1. Maps of study sites. (a) 102 water-quality monitoring sites and their catchment boundaries. Insert shows location of the state of Victoria in Australia. (b) Topographic, climatic and vegetation characteristics across the state of Victoria.

interested in the spatial, landscape characteristics that influence water quality. In addition, due to the fact that sampling is evenly distributed throughout the year (i.e., occurs once a month), we expect there to be minimal bias introduced as a result of taking the average constituent concentrations.

Catchment boundaries of the 102 water-quality monitoring sites were derived using the Geofabric tool provided by the Australian Bureau of Meteorology (2012). The catchments ranged in area from 5 to 16,000 km². Land use, land cover, topographic, climatic, geological, lithological, and hydrological catchment characteristics were derived using publicly available data sets from the Geoscience Australia (2004, 2011), the Bureau of Meteorology Australia (2012), the Bureau of Rural Sciences (2010), the Victorian Department for Environment Land Water and Planning (2014), the Victorian Department for Environment Land Water and Planning (2016a, 2016b), and the Terrestrial Ecosystem Research Network (2016). Fifty different catchment characteristics were obtained from these data sets (Table S1 in the supporting information). All data provided by Geoscience Australia (2011) were provided as catchment averaged climate, land use, land cover, topographic, and geographic data. For the remaining data sources, catchment averages were calculated using areal averages (dam storage, land use, and saline aquifer area data) and gridded data (soil nutrient and clay content data). These characteristics (including climate, land use, land cover, soil and geology, topography, and hydrology) were selected based on a literature review previously conducted to identify the key factors affecting spatial variability in in-stream water-quality constituent concentrations (Lintern et al., 2018). It should be noted that half

Table 1

Summary Statistics of Selected Catchment Characteristics (Summary Statistics and Histograms of All 50 Characteristics Provided in Supporting Information Table S2 and Figure S1)

Characteristic	Min	Percentile					Max
		5th	25th	50th	75th	95th	
Annual average temperature (degrees Celsius)	7.6	9.0	10.8	11.8	12.6	13.2	13.8
Average annual rainfall (mm)	532	591	744	970	1,175	1,533	1,822
Urbanized area (%)	0.0	0.0	0.0	0.1	0.7	2.7	29.1
Area used for agriculture (%)	0.0	0.0	6.5	44.5	73.3	88.6	98.6
Area used for pasture (%)	0.0	0.0	3.2	37.7	59.9	81.7	90.8
Area used for cropping (%)	0.0	0.0	0.0	0.4	5.4	18.5	29.9
Forested area (%)	0.0	3.7	15.4	38.9	66.7	96.5	99.9
Area covered by shrubs (%)	0.0	0.0	0.0	0.0	0.4	2.2	6.7
Mean soil TP (mg/kg)	0.00	0.01	0.01	0.01	0.02	0.03	0.04
Mean elevation (m)	69.4	136.4	257.4	434.1	663.5	1,054.7	1,313.3

of the 102 catchments are nested within each other. For the internal catchments, the areas are on average, less than 20% of the larger catchment. This implies that there will be some small interdependence introduced; however, since we always relate the water quality to the average catchment characteristics upstream of the corresponding sampling point, we believe that this is unlikely to affect the analysis results. All data are provided in Data Set S2 in the supporting information.

The characteristics of the 102 catchments vary widely (Tables 1 and S2 and Figure S1). The majority of catchments experience a temperate climate (Peel et al., 2007). Average annual rainfall ranges from 523 to 1822 mm, agricultural area ranges from 0% to 99%, the area used for pasture ranges from 0% to 91%, and forested area ranges from 0 to 100%. There are some catchment characteristics with less variability, such as shrub cover (0–7%), urban area (0–29%), and cropping area (0–30%). Agricultural areas include both irrigated and dryland cropping areas, pastures, horticulture, and forest plantations. The distinction between vegetation types (forest, shrub, and woodland) is based on the height and density of vegetation. Forests have the tallest vegetation and greatest vegetation density, and shrubs have the shortest vegetation and smallest vegetation density. These definitions have been provided in more detailed in the supporting information (Table S1). As is apparent from Figure 1b, there are strong cross correlations between landscape characteristics throughout the state. For example, higher-elevation regions have higher rainfall and higher forest cover (Figure 1b). These visual observations are supported by the high Spearman rank correlation coefficients between annual average rainfall and forest cover ($\rho = 0.66, p < 0.05$) and between annual average rainfall and catchment mean elevation ($\rho = 0.58, p < 0.05$). The full cross-correlation matrix is provided in Data Set S1 in the supporting information.

2.2. Data Analysis

2.2.1. Initial Exploration of Spatial Variability and Cross Correlations

Time-averaged mean constituent concentrations at each site in the state of Victoria were mapped to explore overall trends in spatial variability in average constituent concentrations. In addition, the Spearman correlation coefficients (Spearman, 2010) between constituent means were calculated to identify similarities in the spatial variability in the central tendency of the constituent.

2.2.2. Statistical Models of Spatial Variability in Constituent Concentrations

Identifying statistical models. Statistical models of spatial variability in mean constituent concentrations were developed using an exhaustive search approach, assuming a linear additive model structure (Saft et al., 2016). The dependent data (averages of the log-transformed constituent concentrations) were not normally distributed, and so were Box-Cox transformed. In addition, independent (catchment characteristics) data were Log-Sinh transformed (Wang et al., 2012) to maximize symmetry of the distributions using the GA package in R. The Log-Sinh transform was used for the catchment characteristics data because the transformation can manage 0 values and it was effective in improving symmetry. The transformed data were also standardized to have a mean of 0 and a variance of 1. The exhaustive search process had two steps, and ordinary least squares regression was utilized in both steps.

In the first step, we randomly selected a sample of 80% of the catchments (i.e., 86 of 102 catchments). For this sample, we conducted an exhaustive search of all possible models of average constituent concentrations as a linear function of up to six catchment characteristics (Saft et al., 2016). We repeated this step 20 times for each constituent. A maximum of six catchment characteristics was included in each model to reduce the computational demand of the exhaustive search. For each model, we calculated the adjusted coefficient of determination (R^2_{adj}), the corrected Akaike Information Criterion (AIC_c) (Hurvich & Tsai, 1989, equation (1)), and the corresponding weights for each model (equation (2), Burnham & Anderson, 2002). In equation (1), m is the dimensionality of the model, and n is the number of observations. The corrected AIC was used because it penalizes overfitted models. In equation (2), W_i represents the weight for model i , and Δ_i represents the AIC difference (i.e., difference in AIC_c between model i and the minimum AIC_c). The model weights were used to calculate the proportion of evidence for each predictor (i.e., catchment characteristic), as the sum of the weights of the models containing that catchment characteristic (Burnham & Anderson, 2002; Saft et al., 2016).

$$AIC_c = AIC + \frac{2(m+1)(m+2)}{n-m-2} \quad (1)$$

$$W_i = \exp(-0.5 \times \Delta_i) / \sum \exp(-0.5 \times \Delta_i) \quad (2)$$

We calculated the sum of the weights of evidence of each catchment characteristic (i.e., sum of the weights of evidence across the 20 samples). All catchment characteristics with the sum of the weights of evidence below 2 were deemed to be unimportant catchment characteristics and were excluded from the data set for the second step of the exhaustive search. This resulted in the following numbers of catchment characteristics for each constituent included in the second step of the exhaustive search: 11 for TSS, 20 for TP, 18 for FRP, 12 for TKN, 12 for NO_x , and 20 for EC.

In the second step, we ran another exhaustive search of possible linear models of average constituent concentrations. However, this time, the potential predictor set (i.e., set of catchment characteristics) for these models was the truncated set identified in the first step of the search. The reduced number of potential catchment characteristics allowed a greater number of catchment characteristics in any linear model without significantly increasing computational demand. As such, we set the maximum number of catchment characteristics to be included in the model to 10. This is approximately 10% of the size of the data set (as recommended by Elliott & Woodward, 2007). We assessed each of the models produced in this step using the Complete Akaike Information Criterion ($CAIC$, Bozdogan, 1987; equation (3)), which provides an even heavier penalty for overfitted models than the AIC_c . In equation (3), llf is the log-likelihood function. AIC differences and model weights were calculated for each possible linear model. All models where the difference in $CAIC$ was less than 2 were selected as the *likely* models (Symonds & Moussalli, 2011).

$$CAIC = -2 \times llf + m(\ln(n) + 1) \quad (3)$$

Fitting regression coefficients of statistical models. Using a Bayesian regression approach, we fitted the regression coefficients of the likely models found in the exhaustive search. The structure of the model is presented below in equations (4) and (5). In these equations, the average constituent (TSS, TP, FRP, TKN, NO_x , or EC) concentration at site i (y_i) is drawn from a normal distribution with mean μ_i and standard deviation σ . The mean (μ_i) is modeled as a function of the global intercept (int), and the sum of the effect of catchment characteristic n ($eff.x_n$) multiplied by the value of catchment characteristic n (x_n), where n takes a value between 1 and the maximum number of predictors (catchment characteristics) included in the model. The global intercept and the parameter coefficients ($eff.x_n$) were assumed to be drawn from a minimally informative prior normal distribution (mean of 0 and standard deviation of 1; recalling that all x are standardized). The standard deviation (σ) is assumed to be drawn from a minimally informative prior uniform distribution with boundaries of 0 and 10.

$$y_i \sim N(\mu_i, \sigma) \quad (4)$$

$$\mu_i = int + eff.x_1 \times x_1 + eff.x_2 \times x_2 + \dots + eff.x_n \times x_n \quad (5)$$

The models were run in OpenBUGS version 3.2.1 (Lunn et al., 2009) using R and the R2OpenBUGS package (Sturtz et al., 2005). Model runs included three independent Markov chains, with a burn-in of 5,000 iterations, and a total number of iterations of 10,000 per chain. Convergence was verified by checking that the *Rhat* statistic was approximately 1 (Sturtz et al., 2005). The complete OpenBUGS code is provided in the supporting information (Text S1).

Model fit and performance were assessed using the Nash-Sutcliffe Coefficient of Efficiency (Nash & Sutcliffe, 1970; Obenour et al., 2014). In addition, the probability that the coefficients were different from 0 was calculated using the *Step* function in OpenBUGS. Probability values near 0 and 1 indicate strong evidence in favor of negative and positive coefficient values, respectively.

Model residuals were plotted against the predictors to assess our assumption of linearity. The randomness of the plots indicated that we could continue to assume linearity.

Assessing spatial correlation of residuals. The mean regression coefficients and intercept terms obtained using Bayesian fitting were used to calculate model residuals. These residuals were assessed for spatial correlation using semivariograms created using the *gstat* package in R (Pebesma, 2004). The semivariograms show distances up to 250 km, which is one third of the maximum distance between sites.

Assessing model performance under drought conditions. We also explored the performance of the statistical models under varying hydrologic conditions. We partitioned the water-quality data into three groups: data collected from 1994 to 1996 (predrought years), data collected from 1997 to 2009 (drought years), and data collected from 2010 to 2014 (postdrought years, Saft et al., 2015). We calculated the mean constituent concentration at each site for the predrought period, the drought period, and the postdrought period. We then refitted the statistical models of spatial variability in mean water quality for each of these three periods using the same Bayesian regression approach described above. Where the constituent had more than one *best performing* model, the model with the lowest difference in *CAIC* was used for this model refitting. Model performances were assessed using the Nash-Sutcliffe coefficient (Nash & Sutcliffe, 1970).

Statistical models of spatial variability in standard deviation. We also explored the key catchment characteristics affecting spatial variability in site-level standard deviation of each of the six constituents. This was done by calculating the standard deviation of the log-transformed constituent concentrations at each site. We then repeated the exhaustive search using the 50 catchment characteristics (with the same transformations as above), but this time using the site-level standard deviation as the dependent variable. The 102 standard deviations (of the log-transformed constituent concentrations) were Box-Cox transformed for this analysis. We fitted the *best performing* models using the Bayesian regression approach outlined above.

3. Results

3.1. Spatial Variability in Constituent Concentrations

The time-averaged constituent concentrations differ greatly across the state of Victoria (Figure 2). Most constituents exhibit low concentrations in the eastern parts of the state and higher concentrations in the northern and western regions. There are some similarities in these spatial trends among different constituents. First, sites with high time-averaged concentrations of TSS also tend to have high concentrations of TP and TKN. In addition, sites with high average concentrations of TP also tend to have high concentrations of FRP and EC; and sites with high average TKN concentrations tend to have high average EC concentrations (all relationships $\rho > 0.5$, $p < 0.05$; Table 2).

3.2. Statistical Models of Spatial Variability in Constituent Concentrations

The weights of evidence for each catchment characteristic vary across the six water-quality constituents (Figure 3). Although none of the catchment characteristics play a consistently important role in all models, some are consistently poor predictors. These include annual runoff depth (millimeter), the proportion of the catchment that is bare (i.e., with no vegetation cover), and the total catchment length. There were 1 to 12 models identified as *likely* models of average TSS, TP, FRP, TKN, NO_x , and EC concentrations. These likely models include between five and nine predictor variables (Figure 4).

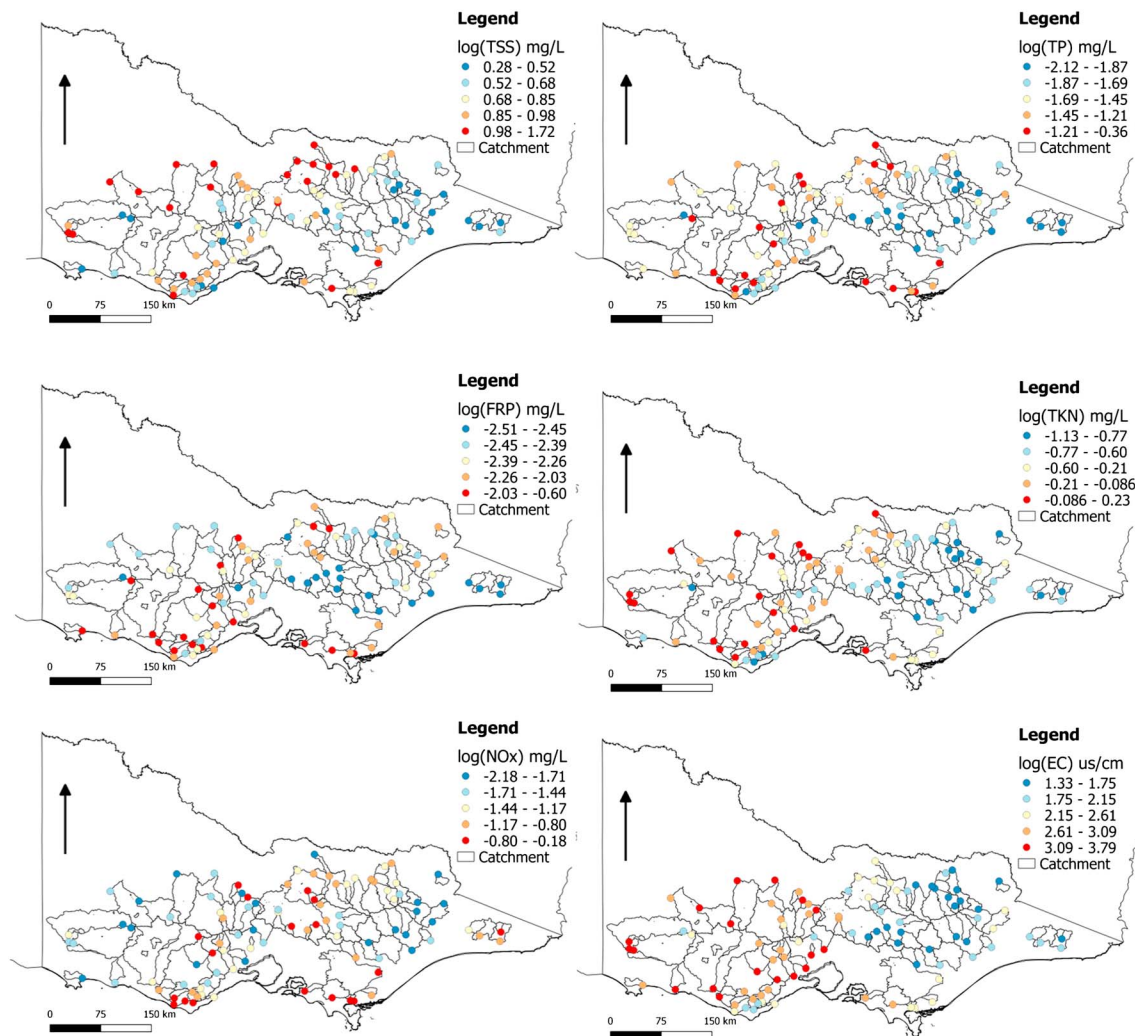


Figure 2. Map showing the mean time-averaged (1994–2014) TSS, nutrient, and EC concentrations. TSS = total suspended solid; TP = total phosphorus; FRP = filterable reactive phosphorus; TKN = total Kjeldahl nitrogen; NO_x = nitrate/nitrite; EC = electrical conductivity.

4. Discussion

4.1. The Effect of the Landscape on Average Constituent Concentrations

The weights of evidence obtained from the exhaustive search of linear regression models (Figure 3) and fitting of the regression coefficients of the most likely linear regression models (Figure 4) provide an indication of the relationships between landscape characteristics and average constituent concentrations in streams. We will discuss the relationship between landscape characteristics and water quality in terms of larger groups of catchment characteristics (i.e., climate, land use, land cover, hydrology, geology, and soil properties, and topography).

Climate. Measures of climate in the catchment had high weights of evidence for all constituents (Figure 3), which suggests the importance of spatial differences in climate for explaining the spatial variability in stream water quality. As 20 different subsamples of each constituent were assessed, the high weights of evidence of these predictors indicate the importance of these climate characteristics in explaining the spatial differences in constituent

Table 2
Cross Correlations Between Time-Averaged Constituent Concentrations Across 102 Water-Quality Gauges (Represented as Spearman Correlation Coefficients)

	TSS	TP	FRP	TKN	NO _x	EC
TSS	1					
TP	0.64*	1				
FRP	0.30*	0.87*	1			
TKN	0.68*	0.79*	0.55*	1		
NO _x	0.19*	0.24*	0.15	0.12	1	
EC	0.49*	0.65*	0.50*	0.86*	-0.096	1

Note. TSS = total suspended solid; TP = total phosphorus; FRP = filterable reactive phosphorus; TKN = total Kjeldahl nitrogen; NO_x = nitrate/nitrite; EC = electrical conductivity.

* $p < 0.05$.

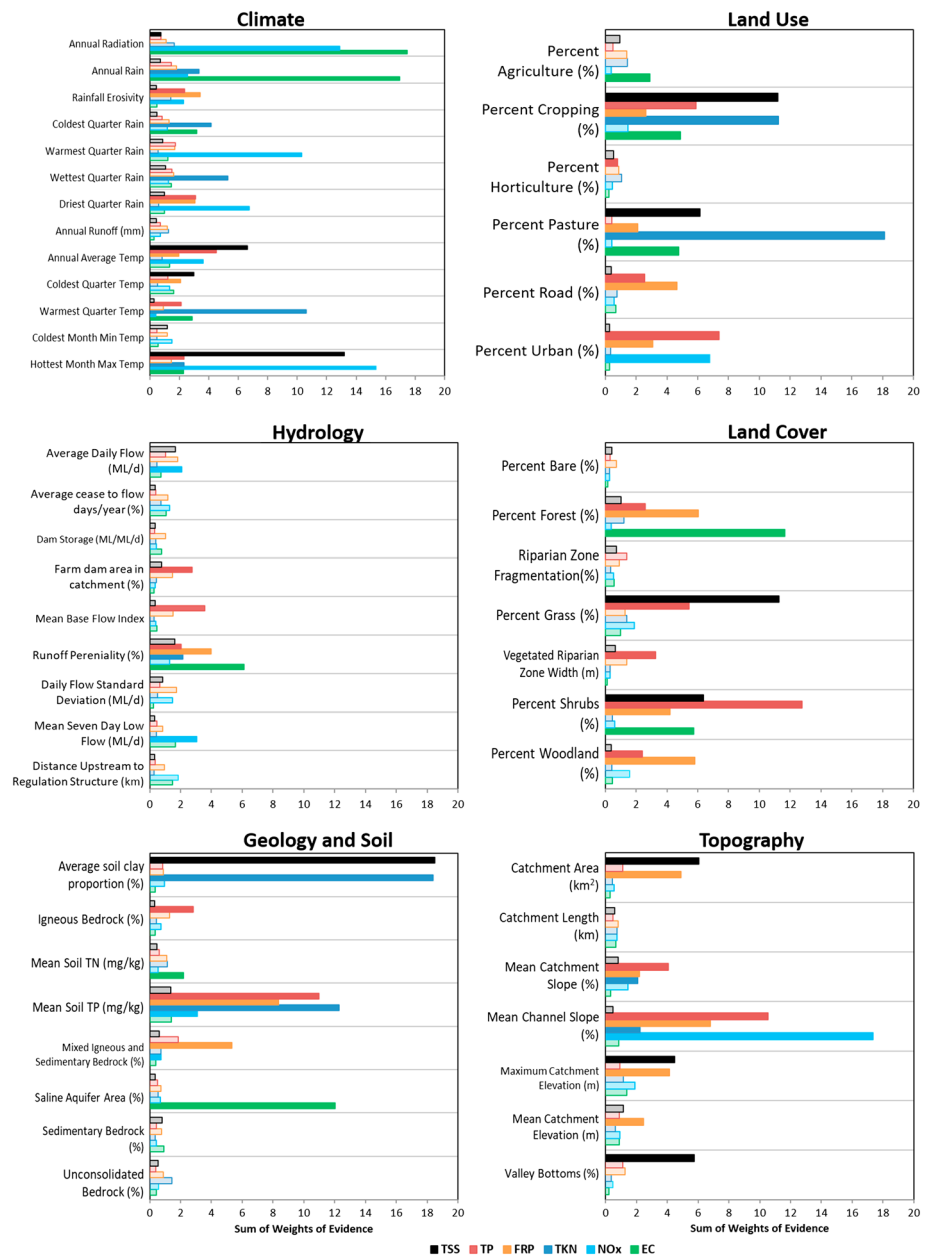


Figure 3. Weights of evidence for each catchment characteristic (predictor) used to model spatial variability in time-averaged constituent concentrations. Transparent bars represent those where the sum of the proportions of evidence is below 2. See Table S1 in the supporting information for more details of these characteristics. TSS = total suspended solid; TP = total phosphorus; FRP = filterable reactive phosphorus; TKN = total Kjeldahl nitrogen; NO_x = nitrate/nitrite; EC = electrical conductivity.

concentrations. Climate characteristics also appeared in the likely models of all constituents except FRP (Figure 4).

For TSS and TKN, measures of temperature (maximum temperature of the hottest month and average temperature of the warmest quarter) had a positive effect on constituent concentrations (Figure 4). These relationships could be influenced by interrelationships between temperature (or climate in general) and land use and land cover characteristics. In the state of Victoria, there are cross correlations between forest cover and climate (Figure 1b), with greater forest cover in the regions with higher rainfall ($\rho = 0.66$, $p < 0.05$).

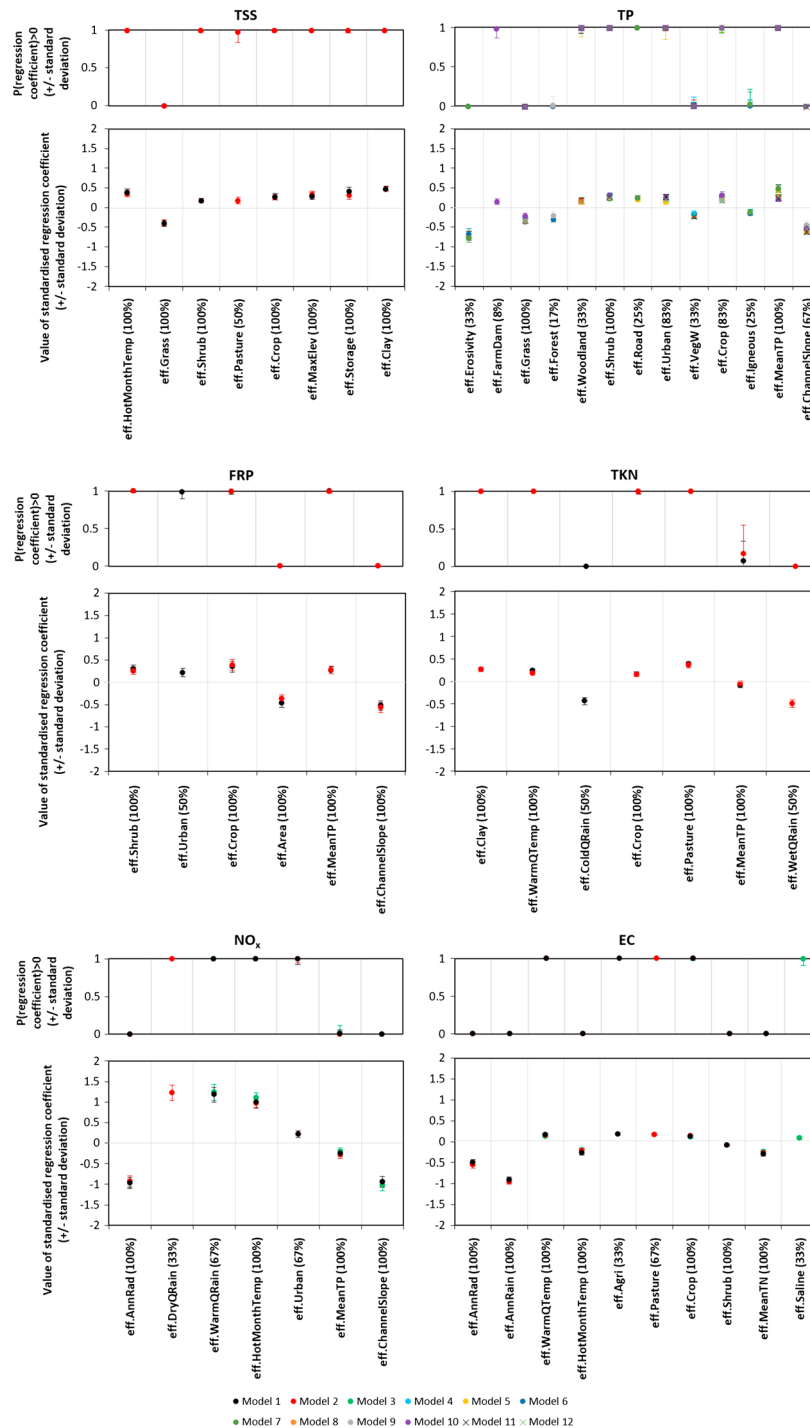


Figure 4. Regression coefficients of predictors (catchment characteristics) for likely models of mean concentration ($\Delta CAIC < 2$) solved by Bayesian regression. All regression coefficients along x axes have the prefix *eff*. The frequency at which the variable appears in the most likely models provided in parentheses as X%. (The regression coefficient abbreviations mean: *HotMonthTemp*, hottest month maximum temperature; *Grass*, area covered by grass; *Shrubs*, area covered by shrubs; *Pasture*, area used for pasture; *Crop*, area used for cropping; *MaxElev*, maximum catchment elevation; *Storage*, area valley bottoms; *Clay*, mean clay content; *Erosivity*, mean catchment rainfall erosivity; *FarmDam*, area covered by farm dams; *Forest*, area covered by forest; *Woodland*, area covered by woodland; *Road*, area covered by road; *Urban*, area urbanized; *MeanVegW*, mean riparian vegetated area width; *Igneous*, area underlain by igneous bedrock; *MeanTP*, mean soil TP content; *ChannelSlope*, mean channel slope; *Area*, catchment area; *WarmQTemp*, warmest quarter temperature; *WarmQRain*, warmest quarter rainfall; *ColdQRain*, coldest quarter rainfall; *WetQRain*, wettest quarter rainfall; *Rad*, annual average radiation; *DryQRain*, driest quarter rainfall; *AnnRain*, annual average rainfall; *Agri*, area used for agriculture; *MeanTN*, mean soil TN content; *Sal*, saline aquifer area.) See Table S1 in the supporting information for more details of these characteristics. TSS = total suspended solid; TP = total phosphorus; FRP = filterable reactive phosphorus; TKN = total Kjeldahl nitrogen; NO_x = nitrate/nitrite; EC = electrical conductivity; CAIC = Complete Akaike Information Criterion.

There are also correlations between spatial patterns of rainfall and temperature, which also likely lead to variations in land cover, with higher temperature and lower rainfall likely to lead to lower cover and more potential for sediment movement. Indeed, modeling suggests that the majority of sediment erosion in the region of Victoria is due to riverbank and gully erosion (Prosser et al., 2001), and those processes may be more active due to a combination of climate and the modified land use impacts on vegetation cover.

In addition, there were negative effects of measures of rainfall (rainfall erosivity and average rainfall in coldest quarter) on TP and TKN concentrations. It would have been expected that TP and TKN would have higher concentrations in catchments with higher rainfall levels, because rainfall can mobilize sediments and the nutrients associated with these sediments (Granger et al., 2010). The negative effects that we observed in Figure 4 of rainfall measures on in-stream constituent concentrations may be due to the negative cross correlation between rainfall and the percentage of the catchment used for cropping and grazing, and the positive cross correlation between rainfall and forest cover in the catchment (Data Set S1). It is important to note the negative cross correlation between cropping and pasture areas and forest cover in the catchment ($\rho < -0.65, p < 0.05$; Data Set S1). Greater vegetation cover and lower land cropping and grazing rates in the catchment have previously been identified as linked to lower nutrient concentrations in streams (Jones et al., 2001).

The NO_x models contain at least two measures of climate. This suggests the importance of climatic parameters on NO_x source availability and mobilization. The negative effect of radiation could be due to the fact that NO_x that is accumulated in soils during dry months is likely transported via subsurface runoff to receiving waters during wet periods (Ahearn et al., 2004; Edwards & Withers, 2008). In addition, the positive effect of temperature (maximum temperature of the hottest month) could be a result of the cross correlation between temperature and agricultural activities in the catchment. It is likely that areas with greater agricultural activity would experience higher fertilizer application and NO_x source availability in the catchment (Drewry et al., 2006). It is also possible that this is a result of organic nitrogen mineralization, which tends to occur at high temperatures (Bingham & Cotrufo, 2016).

Four climatic measures appeared in all EC models. The negative effect of rainfall on EC is likely due to the fact that greater evapotranspiration rates and lower rainfall can lead to the accumulation of salts within the soil strata (Boyd, 2015; Poulsen et al., 2006; Sivapalan et al., 1996). However, it is important to note that there are also negative effects of radiation and the maximum temperature of the hottest month on EC levels.

Land use. Land use measures had high weights of evidence in the exhaustive search of statistical models (Figure 3) and appeared in more than 80% of the likely TSS, TP, FRP, TKN, and EC models (Figure 4). The regression coefficients suggest that increases in human activities (e.g., urbanization, cropping, and pasture) in the catchment contributes to greater concentrations of constituents in streams. These findings are not unexpected, as previous studies have noted the positive correlation between catchment cropping and pasture area on soil erosion rates due to (1) the presence of certain types of livestock that can trample or consume vegetation faster than it can recover, (2) tillage practices, and (3) land clearing and plowing (Agouridis et al., 2005; Mouri et al., 2011; Skaggs et al., 1994). Additionally, a larger proportion of cropping and pasture in the catchment can lead to greater nutrient concentrations within the catchment due to fertilizer application and the deposition of animal fecal matter and urine. Similarly, increasing urbanization in the catchment can also result in higher nutrient concentrations due to the use of fertilizer on urban lawns and the presence of nutrients in wastewater and stormwater discharges (Arheimer & Lidén, 2000; Drewry et al., 2006; Edwards & Withers, 2008; Law et al., 2004; McKergow et al., 2003; Perry & Vanderklein, 1996; Polsky et al., 2014).

The land use measures appearing in the TKN models (the area covered with pasture) explain most of the spatial variability in mean TKN concentrations. This is indicated by the fact that the standardized regression parameter for *eff.Pasture* is the highest of all regression parameters (Figure 4). For TSS, TP, FRP, and EC, the land use measures appearing in the models account for a smaller proportion of the spatial variability in mean concentrations. As such, while these land use measures are important, they are not the most significant variable affecting spatial variability in mean concentrations.

It should be noted that the proportion of the catchment covered by urban areas appeared in the likely TP models. The catchments used for the analyses mostly have low levels of urbanization, with the mean level of urbanization being 0.1% (Table 1). The fact that the exhaustive search approach picked urban areas as

an important factor affecting in-stream constituent concentrations emphasizes the findings of previous studies that even small amounts of urbanization can have effects on TP concentrations in streams (e.g., Duan et al., 2012; Mouri et al., 2011; Petrone, 2010).

The NO_x models did not include any land use parameters. Previous American studies (Allan, 2004; Johnson et al., 1997) have found strong relationships between NO_x concentrations in streams and agricultural activities in the catchment. The difference between these previous studies and this current study could be due to the different agricultural practices in Australia and North America, with greater nitrogen application in the United States per square meter of cropland compared to Australia (Lu & Tian, 2017).

Land cover. The exhaustive search suggests the importance of land cover metrics on in-stream water quality, with land cover metrics having high weights of evidence (greater than 2) for all constituents except TKN and NO_x (Figure 3). Land cover measures are also prominent in the statistical models for TSS, TP, FRP, and EC (Figure 4).

The results of the statistical modeling provide two observations. First, it is interesting to note that while land cover metrics correlate strongly with TKN according to the Spearman correlation coefficients (Figure S2), land cover measures do not appear in the likely models for TKN. Thus, land cover and vegetation characteristics do not play an important role for TKN when other catchment characteristics are considered. This is likely due to cross correlations between land cover characteristics and climatic and topographic catchment characteristics (supporting information Data Set S1).

Second, it is important to note that the specific land cover measures included in the TSS, TP, FRP, and EC models differ from the land cover measures identified as important in Spearman correlation coefficient analysis (Figure S2). Specifically, the statistical modeling identified shrub cover as an important variable for explaining spatial variability in TSS, TP, FRP, and EC concentrations, rather than forest cover. Shrub cover appeared in 100% of models for these four constituents. In this study, shrublands have vegetation lower in height and sparser than forests. In addition, grass cover appeared in 100% of TSS and TP models. The presence of these land cover measures (shrubs and grass) in the models and the magnitude of the regression coefficients seem to be in line with our understanding of the process of constituent mobilization and transport from the catchment into streams. The standardized regression coefficient for the proportion of the catchment covered in shrub (*eff. Shrub*) was positive for TSS, TP, and FRP and negative for EC. Previous studies have identified positive correlations between shrub cover and erosion, likely attributable to the interspaces between shrubs, which are generally nonvegetated and can be prone to weathering and erosion (Eldridge et al., 2011). The negative relationship between EC and the proportion of the catchment covered with shrubs could be because the presence of deep-rooted plants that keep the water table low, preventing salts from being mobilized from soils and later transported into receiving streams. In fact, land clearing has been identified as a key factor in land salinization across Victoria (Cartwright et al., 2004). The fact that the standardized regression coefficient of shrub cover is positive for TSS, TP, and FRP and negative for EC suggests that the flow paths and processes mobilizing TSS, TP, and FRP largely differ to that of EC.

However, it should be noted that the regression coefficients for the effect of shrub area and grass area on TSS, TP, FRP, and EC concentrations are small compared to the other regression coefficients (Figure 4), demonstrating reduced importance of land cover measures for explaining spatial differences in mean water-quality responses.

Hydrology. Hydrologic characteristics (e.g., average daily flow, farm dam area, baseflow index, runoff perennality, and mean 7-day low flow) had weights of evidence greater than 2 for TP, FRP, TKN, NO_x , and EC. However, hydrologic variables did not appear in the statistical models (except for 8% of TP models). This also aligns with the fact that the weights of evidence for hydrological variables were generally lower than those for climate, land use, geology, topography, and land cover (Figure 3). This suggests that once land use, climate, soil properties, and topography are accounted for, hydrologic parameters add little to explain spatial variability in water quality.

Geology and soil characteristics. Geology and soil characteristics appeared in 100% of models for all constituents (Figure 4). The proportion of clay in the catchment appeared in the TSS and TKN models, and the regression coefficients were positive in both constituents' models. When there is a high proportion of clay in soils, hydraulic conductivity can be lower if soil structure is poor. This can lead to a greater

amount of overland runoff compared to subsurface runoff. Particulates, such as TSS and TKN, are largely transported from the catchment into receiving waters via overland flow, and as such greater rates of overland runoff can lead to more particulates being transported over longer distances (Charlton, 2007; Wood, 1977). In addition, the positive relationship of TKN (organic nitrogen plus ammonia and ammonium) to the proportion of clay in the catchment soils may be because these forms of N bind more readily to clay compounds (Bingham & Cotrufo, 2016; Sliva & Dudley Williams, 2001; van der Perk et al., 2007; Varanka et al., 2015), and as such the high clay content of the soil could be indicative of high nitrogen content in soils too.

Soil characteristics (mean TP content of the soil) have a positive effect on TP and FRP concentrations in receiving rivers (Figure 4). This is likely due to the fact that higher concentrations of TP in the soil can lead to a greater store of phosphorus within the catchment, which can then be mobilized and delivered to receiving streams (Drewry et al., 2006). Similarly, the negative regression coefficient of the mean soil TN content to EC could be because the high level of nutrients has a negative correlation to soil salinity ($\rho = -0.46, p < 0.05$; Data Set S1).

The reason for the negative regression coefficient of the mean soil TP content for the TKN and NO_x models is not clear (Figure 4).

Topography. Topographic catchment characteristics had high weights of evidence for all constituents (Figure 3) and appeared in the models for TSS, FRP, and NO_x . Channel slope was the predictor with the greatest explanatory power (i.e., largest absolute value of regression parameter) for FRP and NO_x . This could be due to the cross correlation between slope and land use (Varanka et al., 2015). Streams with shallower slopes are often found on low-lying regions, where the catchment tends to be used for agriculture, grazing, and urban land uses (Chen & Lu, 2014; Varanka et al., 2015; Ye et al., 2009; Yevenes et al., 2016). These land uses all can be sources of sediments, nutrient species, and salts (Arheimer & Lidén, 2000; Drewry et al., 2006; Edwards & Withers, 2008).

Scale effects. Scale is often an important factor in catchment behavior (Blöschl & Sivapalan, 1995). In this study we included two measures of scale: catchment area and total catchment length, as potential predictors of water quality. The weights of evidence for catchment area were greater than 2 for TSS and FRP (Figure 3). Additionally, catchment area is included in all FRP models, and the regression coefficients indicate that the effect of area is comparable to the other catchment characteristics, with concentrations reducing as area increases (Figure 4). This could be indicated that with increasing area (and the subsequent increase in streamflow), there is a dilution, uptake by biota, or changes in sediment characteristics and associated adsorption of the FRP that is present in the catchment. The other constituents are not related to area, and nothing is related to catchment length. These results provide some evidence of scale effects for FRP but not other constituents.

Importance of natural catchment characteristics. It appears that the majority of the spatial variability in mean water quality is explained by natural catchment characteristics. When the anthropogenic catchment characteristics (land use) are removed from the models, model performance remains relatively similar, while when the natural characteristics are removed, the performance drops noticeably (Figure 6). The greatest decrease in performance, when anthropogenic features are removed, is seen for NO_x where the removal of urbanization as a predictor leads to drop in the Nash-Sutcliffe coefficient of 18%. As such, it appears that urbanization is an important factor in NO_x levels in waterways, and reducing NO_x delivery from urban areas (e.g., by better management of stormwater or wastewater) may have an impact on NO_x concentrations. The performance of the EC models seem to be least dependent on anthropogenic catchment characteristics, for there was only a 3% drop (approximately) in model performance when anthropogenic catchment characteristics were removed from the model.

Comparison to previous studies. The catchment characteristics that appear in the models in this study differ slightly to the linear regression models provided in the literature (Table 3). Due to the difference in the catchment characteristics data set for each of the investigations, it is difficult to meaningfully compare and contrast the key catchment characteristic of importance in each of these study regions. The application of the method presented in this paper to other regions may enable us to better understand global variability in key catchment characteristics affecting spatial variability in in-stream constituent concentrations.

Table 3
The Catchment Characteristics Included in Models in the Literature of Spatial Variability in Mean Constituent Concentrations

	Location (number of sites)	Adjusted R^2	Catchment characteristics included				Citation
			Land use	Land cover	Geology/soil type	Topography	
TSS	Motueka River, New Zealand (23)	0.895	■			■	Young et al. (2005)
	SW Finland (22)	0.89		■		■	Ekholm et al. (2000)
	NW England (562)	0.50	■		■	■	Rothwell, Taylor, et al. (2010)
	Han River, South Korea (118) ^a	0.60		■		■	Chang (2008)
	Han River, South Korea (118) ^b	0.39		■		■	Chang (2008)
TP	Motueka River, New Zealand (23)	0.813	■			■	Young et al. (2005)
	SW Finland (22)	0.89		■		■	Ekholm et al. (2000)
	Han River, South Korea (118) ^a	0.75	■		■	■	Chang (2008)
	Han River, South Korea (118) ^b	0.60	■			■	Chang (2008)
FRP	Motueka River, New Zealand (23)	0.851	■		■		Young et al. (2005)
	SW Finland (22)	0.69		■		■	Ekholm et al. (2000)
	NW England (562)	0.23	■			■	Rothwell, Taylor, et al. (2010)
NO _x	Motueka River, New Zealand (23)	0.849	■			■	Young et al. (2005)
	SW Finland (22)	0.62		■		■	Ekholm et al. (2000)
	NW England (562)	0.52	■			■	Rothwell, Taylor, et al. (2010)
EC	Motueka River, New Zealand (23)	0.928	■		■	■	Young et al. (2005)
	Southern catchments Caspian Sea, Iran (23)	0.969	■		■	■	Hasani Sangani et al. (2014)

Note. TSS = total suspended solid; TP = total phosphorus; FRP = filterable reactive phosphorus; NO_x = nitrate/nitrite; EC = electrical conductivity. Highlighted cells indicate inclusion of catchment characteristic type in spatial variability model.

^aData from 1993 to 1995. ^bData from 2000 to 2002.

4.2. Performance of Statistical Models of Spatial Variability in Mean Constituent Concentrations

Overall Performance. There were 1 to 12 likely models identified for the water-quality constituents (Figure 5), and each of these models contains different combinations of catchment characteristics (Table S3). The appearance of the same categories of catchment characteristics in the likely models emphasizes the importance of these characteristics in determining the mean constituent concentration in streams. The appearance of different characteristics in models for the same constituent is likely due to cross correlations between the catchment characteristics.

The performance of the models differs significantly depending on the constituent, with EC and TKN having the best performing models, followed by TSS and TP. FRP and NO_x models do not perform as well as the models for the particulate contaminants and EC (Figure 5). This suggests that while average water-quality conditions are strongly related to catchment characteristics for most constituents (TSS, TP, TKN, and EC), more reactive nutrients such as FRP and NO_x are less predictable using the catchment characteristics included in this study. This may indicate that these constituents are more strongly influenced by other catchment characteristics and processes that were not considered (e.g., catchment coverage of specific vegetation species, microbial populations in catchment soils, or in-stream nutrient dynamics). Indeed, previous studies have highlighted the importance of microbial activity in soils and in the rhizosphere, organic carbon levels, and atmospheric deposition in determining FRP and NO_x stores and transport from the catchment (Ahearn, Sheibley, Dahlgren, Anderson, et al., 2005; Camarero & Catalan, 2012; Fuss et al., 2016; Gardner & McGlynn, 2009; Johnston, 1991; Jones et al., 2001; Rothwell, Dise, et al., 2010). Alternatively, the reactive nature of these compounds may make them more susceptible to changes and transformations that cannot be firmly linked to any landscape feature. Processes such as sediment-water nutrient exchange, and uptake and release by aquatic plants are likely to operate at smaller scales that cannot be readily measured by broad landscape-scale characteristics. Perhaps by accounting for more detailed processes such as transit time, atmospheric deposition, aquatic plant, and microbial activity, FRP and NO_x could be more successfully predicted by statistical models. In particular, we should highlight that we did not consider distance weighting of catchment characteristics in this study. Some previous studies have found that distance of

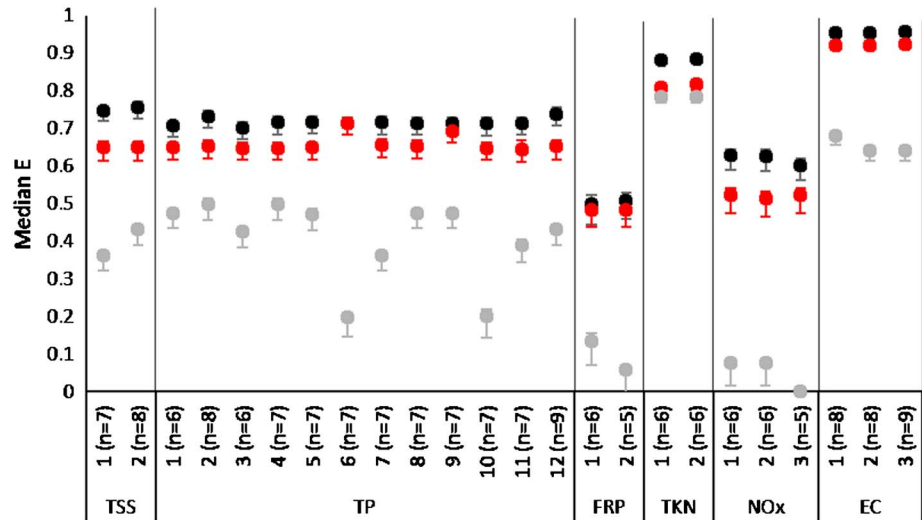


Figure 5. Performance of likely models showing median Nash-Sutcliffe coefficient (E ; error bars represent 2.5th and 97.5th percentiles). Black dots represent performance of models, and red dots represent model performance when only *natural* catchment characteristics are considered. Gray dots represent model performance when only *anthropogenic* catchment characteristics are considered models relating to each model number specified in supporting information Table S3. The x axis shows the model rank order in terms of CAIC. n indicates the number of predictors. TSS = total suspended solid; TP = total phosphorus; FRP = filterable reactive phosphorus; TKN = total Kjeldahl nitrogen; NO_x = nitrate/nitrite; EC = electrical conductivity; CAIC = Complete Akaike Information Criterion.

pollutant sources from the streams, specifically flow weighted distances, can have a significant impact on in-stream constituent concentrations (Baker, 2003; King et al., 2005; Watson & Chang, 2018). In future work, we intend to add complexity to these relatively simple models with average catchment characteristics and assess whether this increased complexity resulting from distance weights sufficiently improves model performance.

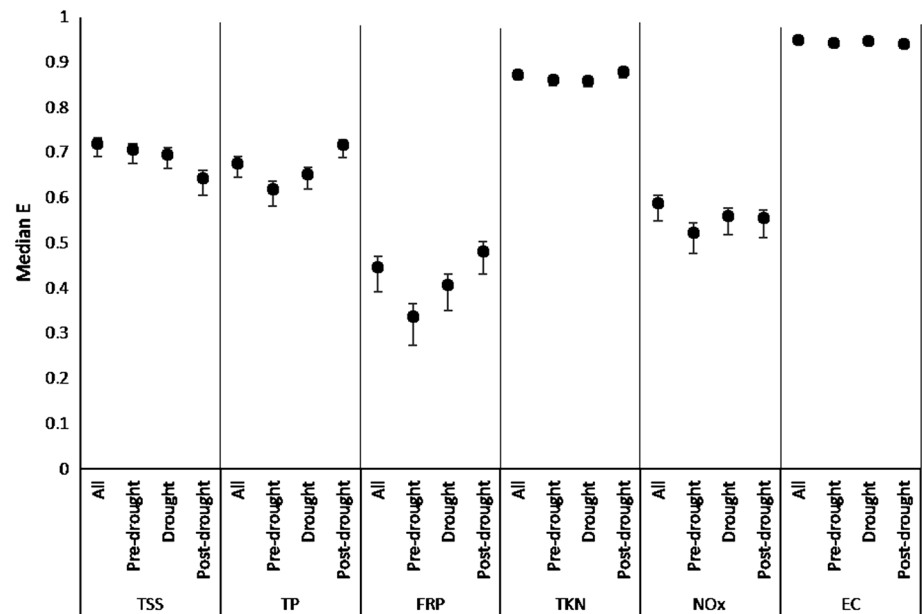


Figure 6. Median Nash-Sutcliffe coefficients (E) for models refitted for specific hydrologic periods (error bars represent the 2.5th and 97.5th percentiles). Models with the lowest difference in CAIC for each constituent are shown. TSS = total suspended solid; TP = total phosphorus; FRP = filterable reactive phosphorus; TKN = total Kjeldahl nitrogen; NO_x = nitrate/nitrite; EC = electrical conductivity; CAIC = Complete Akaike Information Criterion.

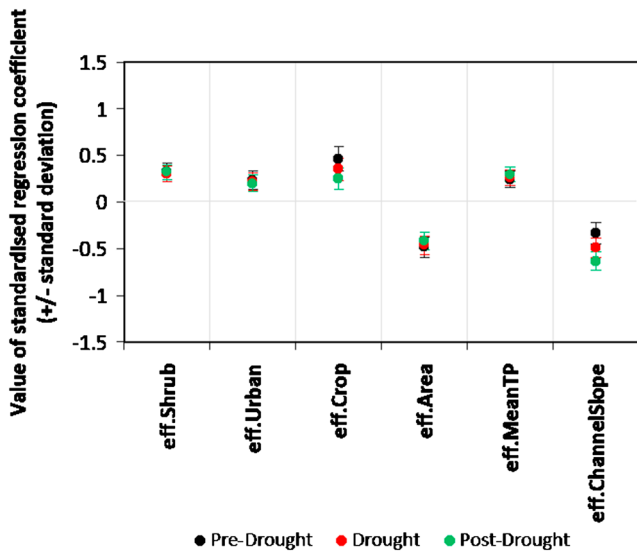


Figure 7. Regression coefficients of predictors (catchment characteristics) for recalibrated models for FRP for the three hydrometeorological periods solved by Bayesian regression. All regression coefficients along x axes have the prefix *eff.* (The regression coefficient abbreviations mean: Shrubs, area covered by shrubs; Crop, area used for cropping; Urban, area urbanized; MeanTP, mean soil TP content; ChannelSlope, mean channel slope; area, catchment area.) See Table S1 in the supporting information for more details of these characteristics. Regression coefficients for recalibrated TKN, NO_x, and EC models are provided in Figure S5 in the supporting information. TP = total phosphorus; FRP = filterable reactive phosphorus; TKN = total Kjeldahl nitrogen; NO_x = nitrate/nitrite; EC = electrical conductivity.

We examined the model residuals to better assess model performance. In general, the models created in this study appear to be capturing well the spatial variability in mean constituent concentrations. The semivariograms indicate minimal spatial autocorrelation in the model residuals (Figure S3).

Performance under varying hydrologic conditions. We examined the performance of the models during predrought (1994–1996), drought (1997–2009), and postdrought (2010–2014) periods in the state of Victoria. It should be noted that there are significant differences in the concentrations in each period only for TSS ($p < 0.05$, one-way analysis of variance, Figure S4 in the supporting information). The TSS concentrations decrease in the drought period and then partially recover in the postdrought period. This correlates with the change in flow that occurs between the three periods, and it is possible that this change in flow is driving the change in TSS occurring across the three periods. The model performance does not vary significantly depending on whether the models are fitted using the average constituent concentrations over the two decades, or whether the models are fitted using average constituent concentrations for the predrought, drought, or postdrought period. The greatest variations in model performance are seen for FRP, where there is a 10% drop in performance when only the predrought water-quality data are used in the model (Figure 6). Similarly, the greatest differences in the regression coefficients between the models recalibrated for the three hydrometeorological periods were evident for FRP (Figure S5, supporting information). However, even for this constituent the difference in regression coefficients was no more than 0.3 (Figure 7). This suggests that there may be some variation in the effect of cropping area and the effect of mean channel slope on FRP concentrations between the three hydrometeorological periods (Figure 7). However, this could just be a spurious effect as the absolute magnitude of the effect of cropping area has decreased, and

the absolute magnitude of the effect of mean channel slope on FRP concentrations has increased. This could be due to the negative cross correlation between the two ($\rho = -0.67$, $p < 0.05$; Data Set S1 in the supporting information).

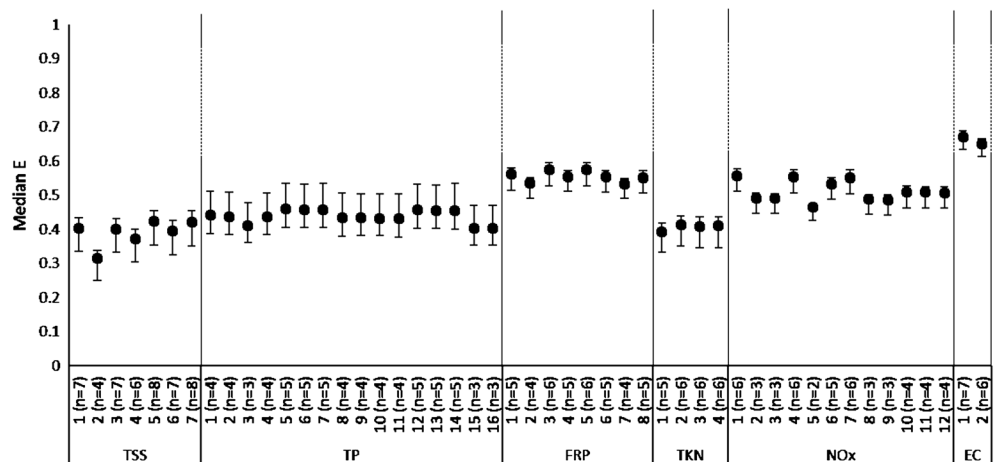


Figure 8. Performance of likely models of constituent standard deviation showing median Nash-Sutcliffe coefficient (E , error bars represent 2.5th and 97.5th percentiles). Models relating to each model number specified in supporting information Table S4. The x axis shows the model rank order in terms of CAIC. n indicates the number of predictors. TSS = total suspended solid; TP = total phosphorus; FRP = filterable reactive phosphorus; TKN = total Kjeldahl nitrogen; NO_x = nitrate/nitrite; EC = electrical conductivity; CAIC = Complete Akaike Information Criterion.

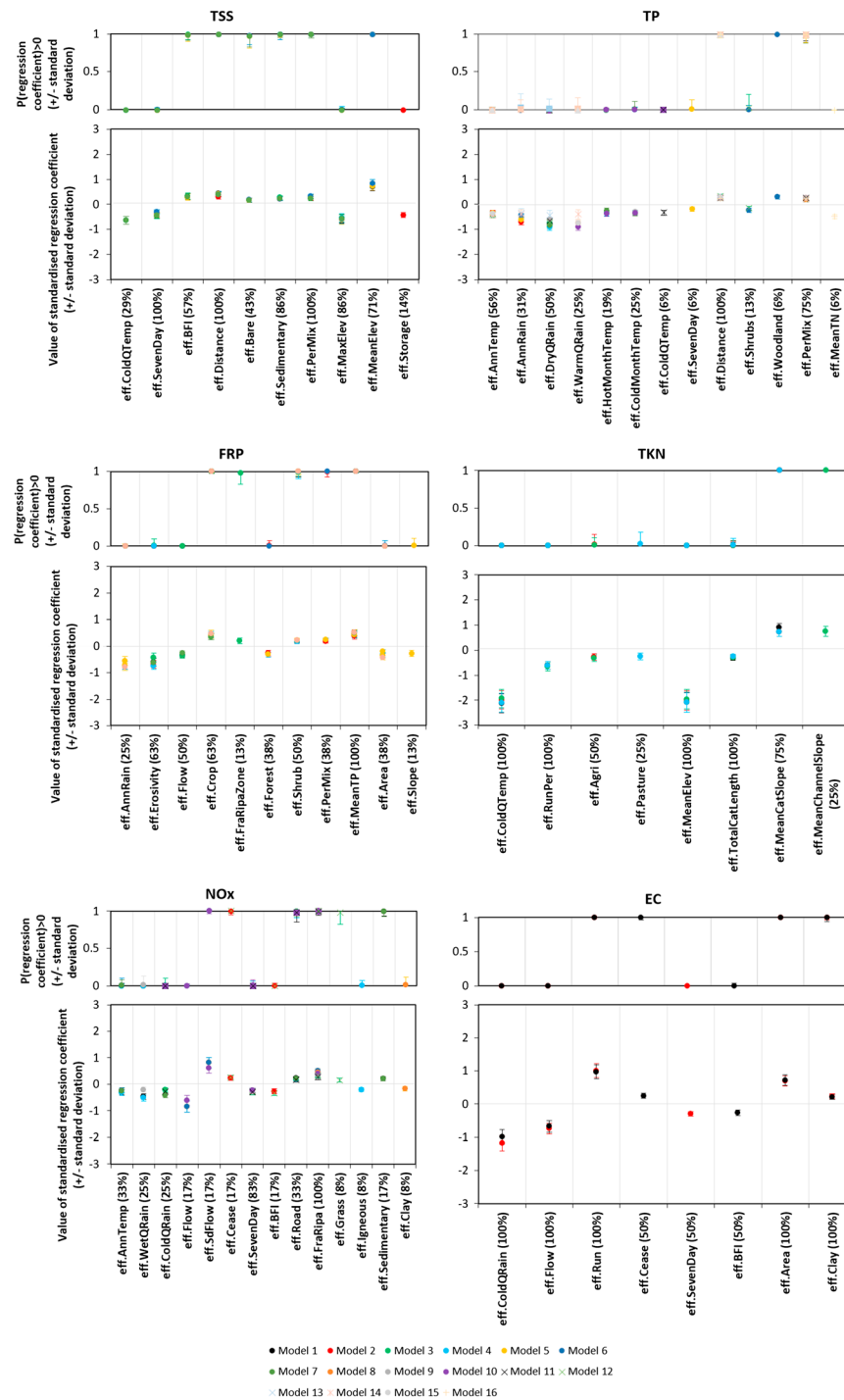


Figure 9. Regression coefficients of predictors (catchment characteristics) for likely models of constituent standard deviation ($\Delta\text{CAIC} < 2$) solved by Bayesian regression. All regression coefficients along x axes have the prefix *eff.* (The regression coefficient abbreviations mean: *ColdQTemp*, coldest quarter temperature; *SevenDay*, mean 7-day low flow; *BFI*, baseflow index; *Distance*, distance upstream to the nearest regulation structure; *Bare*, area of catchment with no vegetation; *Sedimentary*, area of the catchment underlain by sedimentary rock; *PerMix*, area of the catchment underlain by mixed igneous and sedimentary rock; *MaxElev*, maximum catchment elevation; *MeanElev*, mean catchment elevation; *Storage*, area of valley bottoms; *RunPer*, runoff pereniality; *Agri*, area used for agriculture; *Pasture*, area used for pasture; *TotalCatLength*, total length of catchment; *MeanCatSlope*, mean slope of catchment; *MeanChannelSlope*, mean slope of channel; *AnnTemp*, annual average temperature; *WetQRain*, average rainfall in wettest quarter; *ColdQRain*, average rainfall in coldest quarter; *Flow*, average daily flow; *SdFlow*, standard deviation of daily flow; *Cease*, mean number of days with no flow per year; *Road*, area covered by road; *FraRipa*, percentage of riparian zone fragmented; *Grass*, area covered by grass; *Igneous*, area underlain by igneous bedrock; *Clay*, mean clay content; *Run*, annual average runoff; *Area*, catchment area.) See Table S1 in the supporting information for more details of these characteristics. TSS = total suspended solid; TP = total phosphorus; FRP = filterable reactive phosphorus; TKN = total Kjeldahl nitrogen; NO_x = nitrate/nitrite; EC = electrical conductivity; CAIC = Complete Akaike Information Criterion.

4.3. The Effect of the Landscape Characteristics on Variability in Constituent Concentrations at a Particular Site

We briefly assessed whether the variability in constituent concentrations at a site (i.e., the temporal standard deviation of constituent concentrations at each site) could be modeled using catchment characteristics (weights of evidence provided in Figure S6 in the supporting information). The Nash-Sutcliffe coefficients of the standard deviation models range from approximately 0.32 (for TSS) to 0.67 (for EC, Figure 8), which is lower than the range in Nash-Sutcliffe coefficients for the statistical models of mean constituent concentrations, which range from 0.49 (FRP) to 0.96 (EC, Figure 6). This suggests that it is more difficult to model the variability (standard deviation) in constituent concentrations using average catchment characteristics compared to the central tendency (mean) in constituent concentrations. This is an expected result given that the standard deviation is a second moment statistic.

Overall, hydrologic, climatic, and topographic characteristics appear to have an important role in explaining the spatial variability in constituent temporal standard deviations. Land use, land cover, and geologic characteristics appear less frequently as predictors in the models of standard deviation compared to the models of mean concentrations. The difference in these overall trends suggests differences in the catchment characteristics governing the central tendency and the variability in constituent concentrations.

For most constituents, increasing consistency and volume of flow appear to result in a decrease in constituent standard deviation. For example, for TSS and NO_x , average 7-day low flow, and for TKN, runoff pereniality (the proportion of flow occurring in the driest 6 months of the year) has a negative relationship to the standard deviation (Figure 9). It would be expected that as the average 7-day low flow increases and as the flow occurring in drier months increases, there would be a greater temporal consistency in the transport of constituents like TSS, TKN, and NO_x to receiving waters. Previous studies have found fluctuations in constituent concentrations as a result of changes in streamflow between wetter and drier seasons (McKee et al., 2001). In addition, the increase in TSS and TP variability with increasing distance downstream from dam wall or a reservoir suggests that the presence of river regulation structures can make TSS and TP concentrations more consistent by trapping these sediments (Ahearn, Sheibley, & Dahlgren, 2005). There are some exceptions to this however. For EC, average daily flow (i.e., volume) has a negative relationship with EC variability, but average annual runoff (depth) has a positive relationship with the variability in EC. This could be due to the fact that average daily flow (volume) and average annual runoff (depth) are not strongly correlated ($\rho = 0.37$, $p < 0.05$).

The effects of catchment disturbance on variability in constituent concentrations are also apparent in the regression coefficients of the statistical models (Figure 9). There is generally lower variability in constituent concentrations in catchments with higher elevations (e.g., TSS and TKN standard deviations have a negative relationship to maximum catchment elevation and mean catchment elevation). In addition, the variability in NO_x concentrations increases in catchments with a greater extent of fragmentation of the riparian buffer. This suggests that increased catchment disturbance (which tends to occur in lower elevation catchments) results in higher variability in constituent concentrations. This could be due to the fact that humans have intervened by adding additional sources of nutrients or mobilizing sediments with seasonal variability or annual variability (Stutter et al., 2008).

5. Conclusions

Our analyses show that it is not merely human-induced activities in the catchment (i.e., land use) that influence riverine water quality, but other natural catchment characteristics such as climate, hydrology, geology, topography have a significant role. This suggests that natural catchment characteristics need to be considered in conjunction with human influences in the catchment (e.g., land use and land management) when considering the key factors affecting site-to-site variability in water quality. These characteristics are likely to influence constituent source, mobilization, and/or delivery processes within the catchment.

The *best performing* Bayesian models for mean constituent concentrations all performed similarly, despite differences among catchment characteristics included in the models. There was also a high degree of consistency in selected characteristics for a given constituent. The mean TSS, TP, TKN, and EC models

performed better than the models for FRP and NO_x ; spatial variability in average levels of these more reactive compounds is not as well represented by the catchment characteristics investigated in this study and perhaps cannot be represented by whole-of-catchment characteristics. Nevertheless, the models still explained approximately 50% of the spatial variability for the mean of these more reactive constituents. The performance of these models could possibly be further improved by accounting for the internal spatial distribution of catchment characteristics (i.e., distance from the stream and fragmentation of land uses and geological deposits in the catchment), catchment transit times, local stream nutrient dynamics, microbial activities, and localized hot spots with high nutrient levels. The models developed in this study could be applied in the future to explore management and land use change scenarios for these catchments.

Our aim is that the models and understanding of spatial variability in the average and standard deviation of water-quality responses developed in this study could be later integrated with models of temporal variability to create a fully integrated spatiotemporal model of water-quality responses.

Acknowledgments

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