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How Do Terrestrial Determinants Impact the Response of Water Quality to Climate Drivers?—An Elasticity Perspective on the Water–Land–Climate Nexus

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Abstract: Investigating water–land–climate interactions is critical for urban development and watershed management. This study examined this nexus by elasticity and statistical approaches through the lens of three watersheds: The Yukon, Mekong and Murray. Here, this study reports the fundamental characteristics, explanations and ecological and management implications of terrestrial determinant influence on the response of water quality to climate drivers. The stability of the response, measured by climate elasticity of water quality (CEWQ), is highly dependent on terrestrial determinants, with strong impacts from anthropogenic biomes and low impacts from surficial geology. Compared to temperature elasticity, precipitation elasticity of water quality is more unstable due to its possible linkages with many terrestrial determinants. Correlation and linear models were developed for the interaction system, which uncovered many interesting scenarios. The results implied that watersheds with a higher ratio of rangeland biomes have a lower risk of instability as compared to watersheds with a higher proportion of dense settlement, cropland and forested biomes. This study discusses some of the most essential pathways where instability might adversely affect CEWQ parameters and recommends suggestions for policy makers to alleviate the instability impacts to bring sustainability to the water environment.

Keywords: water quality; temperature elasticity; precipitation elasticity; anthropogenic biomes; surficial geology; nexus

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1. Introduction

Nexus thinking mentions the importance of complex linkages among resource sectors, which are useful for management and decision making. The water–land–climate nexus highlights many interconnections among water, land and climate. This nexus is important for science, planning and engineering. Climatic systems and freshwater are closely associated, so alteration in one system impacts the other one [1,2]. Climate change impacts both water quantity and quality. Surface water quality is influenced by multiple factors, which include both climatic and non-climatic drivers [3,4]. Effects of climatic drivers on surface water quality and its relationships with land use are complex and rarely inspected. The influence of climate change on water quality and its correlation with land use is prominent but not fully recognized. Impairment of water quality may affect the functionality of water systems, which includes potable water production, recreation, irrigation, etc. [5]. It is necessary to investigate the response of water quality parameters to climatic drivers and its association with terrestrial determinants.

Climatic drivers, which include air temperature (*T*) and precipitation (*P*), clearly influence stream water quality, but the mechanism is quite complicated. Changes in air temperature and precipitation could influence river flow which affects the transport and dilution of pollutants [6]. Growing air temperature enhances water temperature, which will affect chemical processes (reaction kinetics) in freshwater. Chemical reactions are sped up by rises in water temperature due to increases in molecule activation energy. Warming speeds up nutrient cycling. Increases in water temperature cause a decline in the self-purification capacity of surface waters due to a drop in dissolved oxygen concentration. It decreases the availability of dissolved oxygen for biodegradation [7]. Precipitation plays a positive role in the dilution and mobility of contaminants due to enhanced river flow. Lower flow volume of stream water enhances the concentration of point source (wastewater treatment works) downstream due unavailability of sufficient volume of water for dilution e.g., phosphorous and biochemical oxygen demand (BOD) in summer[3].

Terrestrial determinants including anthropologic biomes [8] and surficial geology are important factors to be considered in land management policy making. The influences of land development on natural ecosystems are quantified extensively by making the relationship between land cover and water quality parameters [9–12]. Land development, in the form of urbanization and intense agricultural activities, has negative impacts on stream health i.e., enhanced surface runoff, heavy metals and nutrients load [13–17]. This association suggests that without abatement efforts, an increase in development leads to a decline in water quality, which affects the availability of safe drinking water, recreational water use and natural habitats [18–21].

To investigate a water–land–climate nexus, these fundamental questions are important: (1) Which terrestrial determinants have the strongest impacts on the response of water quality parameters to climate drivers? (2) How do terrestrial determinants impact response stability at various catchment levels located in different climatic conditions?

To examine the water–land–climate nexus across basins, process-based approaches are data intensive and laborious [22]. Two examples of this are the storm water model (SWMM) in combination with the in-stream water quality model (WASP) which are used to compute non-point pollutant load and water quality responses to precipitation, respectively, based on different land cover scenarios [23]. However, to analyze the temperature influence, many datasets and calibration work are required for a case study. Moreover, process-based water quality models are applicable to small area or a single river owing to the complexity and diversity in the aquatic environment. To contrast, empirical statistical techniques are more beneficial for an elementary analysis of the climate–water quality relationship on a larger scale [24,25]. Therefore, for a preliminary study, statistical approaches have more benefits compared to water quality models [26]. Climate elasticity of water quality (CEWQ), introduced by Jiang et al. [26], is useful for such an investigation.

The concept of bivariate CEWQ was introduced by Jiang et al. [26] based on climate-streamflow relationships [27,28]. Jiang et al. (2014) used extensive data records to compute climate-water quality relationships. The same study looked at impacts of determinants i.e., soil (soil nutrient retention capacity and soil nutrient availability) and land use (cultivated and managed area, bare area, herbaceous cover or shrub cover, and tree cover) which was captured partly using the nonparametric Kruskal-Wallis test. Recently, the sensitivity of CEWQ was assessed on a global scale where precipitation elasticity was found to be highly sensitive to socio-economic and topographic determinants compared to temperature elasticity [29]. The main contributions of this manuscript are to develop linear models using soil texture (sand, silt, clay and gravel) and anthropogenic biomes (dense settlements, villages, croplands, rangelands, forested and wildlands) at three typical watersheds:

The Yukon, Mekong and Murray watersheds. This study investigates the impacts of land use and soil characteristics on the relations between water quality and climate drivers by focusing on precipitation elasticity and temperature elasticity of water quality.

2. Study Area and Methods

2.1. Watersheds Description

Three typical watersheds, the Yukon, Mekong and Murray, were selected as typical basins with long term water quality observations as shown in Figure 1. The Yukon watershed has subarctic climate (Dfc and Dsc), which is characterized by short summers and long cold winters. The Mekong and Murray watersheds both have tropical wet and dry climate (Aw) which is described by high temperature and an extended dry season in winter [30] (Table S1). The Mekong watershed is densely populated compared to both the Murray and Yukon watersheds. Moreover, the Mekong watershed is a developing area. The main purpose of this study is to capture the impacts of terrestrial determinants on the relations between water quality and climatic drivers under different climate conditions, population density and development of the region.

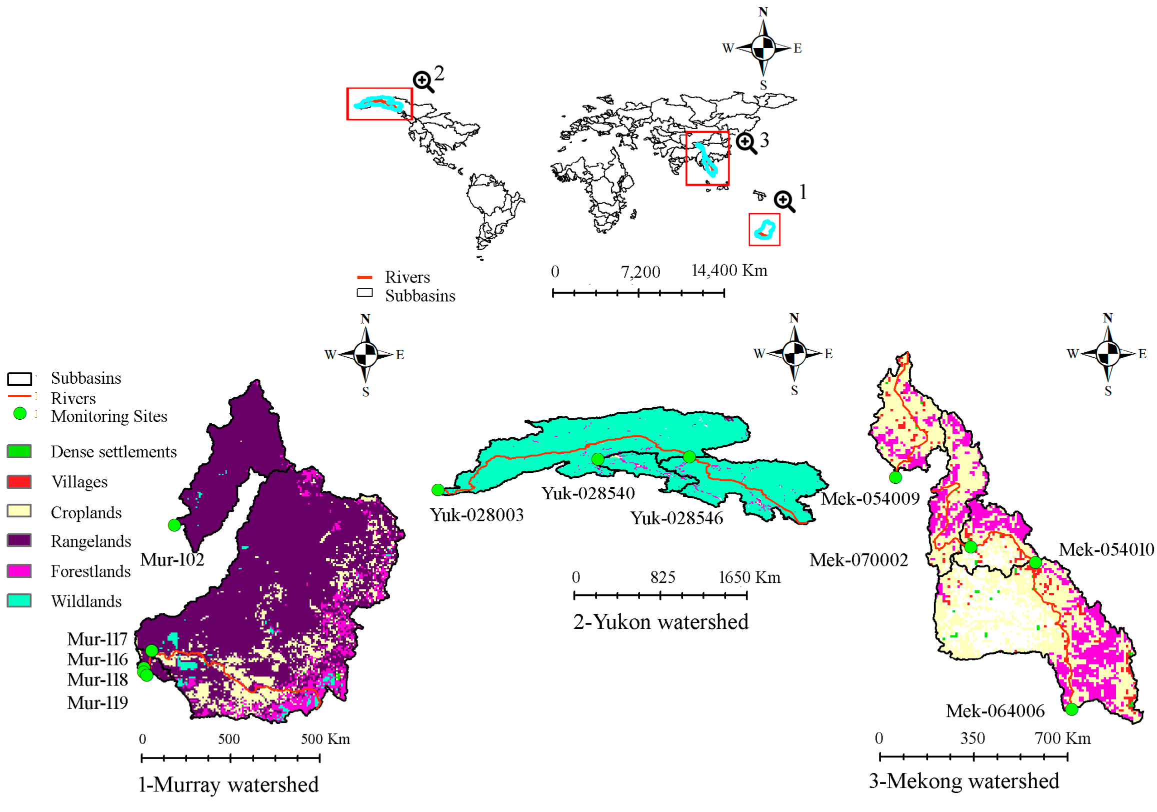

Figure 1. Sub-basin delineated at Yukon, Mekong and Murray watersheds showing its corresponding water sampling stations.

The Yukon River can be found in North America. Its estimated length, average flow and total drainage area are 3190 km, 6430 m^3/s and 832,700 km^2, respectively. The Yukon watershed is relatively small (0.1/km^2). The climate of Yukon is characterized by short warm summers and harsh long cold winters. It has a short growing season. Historically, the Yukon River has been polluted by military installations, gold mining, wastewater, dumps, and some other sources. However, the Yukon River is not listed in impaired watersheds by the Environmental Protection Agency (EPA). According to the U.S. Geological Survey water quality data, the Yukon River has shown relatively better levels of water quality (metals, turbidity, and dissolved oxygen).

The Mekong River is the 12th longest river in the world. Its estimated length, drainage area and annual discharge are 4350 km, 795,000 km^2 and 457 km^3, respectively. It passes through China's Yunnan Province, Myanmar, Cambodia, Laos, Thailand, and Vietnam. The Mekong watershed is large (78/km^2), under developed and close to the equator. The Mekong basin is divided into two parts: the upper basin and the lower basin. The upper basin is steep and approximately 50% of the sediment in the river comes from this part. Forest land cover is greatly reduced owing to high demand for natural resources. The lower basin is also subjected to land use land cover change due to the fast-growing population in the region. Forest lands are converted into agricultural and urban lands to fulfill the requirements of food and accommodation in the region.

The Murray River is in Australia. Average flow, basin area, length of the basin and river are 767 m^3/s, 1,061,469 km^2, 3375 km and 2508 km, respectively. The Murray watershed has a low population density (2/km^2). The Murray watershed is composed of rangeland. It is the most important agricultural region of Australia, where different crops are grown. Sown pastures are used for grazing purposes. This basin consists of more than 30,000 wetlands.

2.2. Data Collection

2.2.1. Water Quality Data

Water quality data were obtained from United Nations Environment Programme (UNEP)/Global Water Quality Data and Statistics (GEMS) [31], except those for Australia. The present study is based on 12 sites with various water quality variables. Details on environmental analytical techniques used for water quality analyses are available on GEMS web page [32]. Water quality records for Australian rivers (Murray-Darling and Cooper Creek) were obtained from the South Australia Environmental Protection Agency (EPA) [33]. It includes 12 main water quality variables with 36–39 years of monthly historical dataset (Table S2).

2.2.2. Climate Data

Monthly mean temperature (°C) and precipitation (mm) datasets are available at a reconstructed 0.5° × 0.5° latitude/longitude global grid (720 × 360) at finer resolution. The above stated variables data were obtained from the National Oceanic and Atmospheric Administration (NOAA) [34]. Climatic variable data were extracted from the grid covering the water quality monitoring stations.

2.2.3. DEM and Terrestrial Determinants Data

The Digital Elevation Model (DEM) was used to delineate sub-watersheds. DEM data was obtained from Shuttle Radar Topography Mission (SRTM) [35]

Twenty-one anthropogenic biomes classes were broadly divided into six major groups [36] which included dense settlements (urban and dense settlements), villages (irrigated villages, cropped and pastoral villages, pastoral villages, rainfed villages and rainfed mosaic villages), croplands (residential irrigated croplands, residential rainfed mosaic, populated irrigated croplands, populated rainfed croplands and remote croplands), rangelands (residential rangelands, populated rangelands and remote rangelands), forested (populated forests and remote forests) and wildlands (wild forests, sparse trees and barren). Anthropogenic biomes data were obtained from Socioeconomic Data and Applications Center (SEDAC) [37].

Surficial geological (sand, silt, clay and gravel) data were extracted from the world harmonized soil database (HWSD) [38].

2.3. Methods

2.3.1. Climate Elasticity of Water Quality

Water quality response to climatic drivers, precipitation and temperature, was based on the concept of climate–streamflow relationships [27,28,39]. Precipitation elasticity, ε_P, (P, WQ) was demonstrated by Equation (1) [26]:

$$\varepsilon_P = median\left(\frac{WQ_t - \overline{WQ}}{P_t - \overline{P}}\frac{\overline{P}}{\overline{WQ}}\right) \tag{1}$$

Based on the above equation, temperature elasticity, ε_T, was developed for air temperature (mean monthly data set):

$$\varepsilon_T = median\left(\frac{WQ_t - \overline{WQ}}{T_t - \overline{T}}\frac{\overline{T}}{\overline{WQ}}\right) \tag{2}$$

where $\overline{WQ}$ = monthly (mean) water quality, $\overline{T}$ = monthly (mean) air temperature and $\overline{P}$ = monthly (mean) precipitation, WQ_t = water quality at any given time t, T_t = air temperature at any given time t and P_t = precipitation at any given time t.

The value of $\left(\frac{WQ_t - \overline{WQ}}{T_t - \overline{T}}\frac{\overline{T}}{\overline{WQ}}\right)$ was computed for each pair of (WQ_t and T_t) using a monthly time series data set. Taking the median of the above stated formula gave the nonparametric estimate of ε_T. The elasticity approach measured the response (direction and strength) of various water quality parameters to precipitation and temperature.

The elasticity approach has some merits over other techniques, which include: The whole function of elasticity is characterized by its median value, which minimizes the impact of outliers (flood and drought). This study focused on general conditions because extreme events happen rarely, and their impacts are severe on biota. To differentiate the effects of general conditions from extreme events only median values were considered for elasticity estimation. Considering the values of average, maximum or minimum etc. of the $\left(\frac{WQ_t - \overline{WQ}}{T_t - \overline{T}}\frac{\overline{T}}{\overline{WQ}}\right)$ time series mixed the effect of general conditions and extreme events. This technique is model independent. It is useful for global studies where it is difficult to define physically based water quality/hydrologic models, which suit large watersheds of the world, and to acquire datasets for such models. Moreover, it is dimensionless which simplifies data analysis.

CEWQ was classified into four broad classes according to the following rule [26]: It was unit elastic, strongly elastic, relatively elastic and inelastic if the absolute value of elasticity was equal to 1, >1, was between 0.1 and 0.5, and <0.1 respectively.

Taking an economic point of view, any element that affects the mathematical value of the price of the elasticity of demand is determinant. This study presented the impacts of land use and soil characteristics on the relations between water quality and climate drivers, by focusing on precipitation elasticity and temperature elasticity of water quality.

2.3.2. Statistical Approaches

Wilcoxon's signed rank test was conducted for pairwise comparison between ε_P and ε_T values to differentiate the response of water quality parameters to temperature and precipitation [40]. The main purpose of this analysis was to compare the sensitivity of temperature and precipitation elasticity.

Trend analysis assessed increasing or decreasing trends in the water quality time series. Trend analysis gained attention in environment studies, especially water quality, owing to the availability of sufficient water quality records [41,42]. Here, monotonic trends in water quality parameters based on rank based nonparametric Spearman's test were assessed [41,43] and fitted to linear, logarithmic, quadratic, power and exponential models [44,45]. The best fitted model was selected for each variable based on coefficient of determination (R^2) value.

Hierarchal cluster analysis (HCA) was carried out to gauge the homogeneity of CEWQ variation tendencies between the examined target water quality monitoring stations located at the Yukon, Mekong and Murray watersheds. The principal motive of this analysis was to check the similarity of water quality parameter responses to climatic drivers within similar watersheds. The HCA was performed using Ward's method, based on squared Euclidean distance [46]. Pearson's correlation and stepwise multiple linear regression (SMLR) was used to make associations of anthropogenic biomes and surficial geology with CEWQ. The main purpose of SMLR analysis was to search independent variables which make the strongest linkage with precipitation and temperature elasticity of water quality parameters [47]. Correlation and SMLR gave an idea about linear relations.

2.3.3. Sub-Watershed Delineation

Sub-watersheds were delineated for each monitoring site (pour point) using Spatial Analyst Tools (Hydrology) in geographic information system (GIS). Each water quality monitoring station was considered the end of the upper sub-watershed or the nutrient load output. Anthropogenic biomes and surficial geological data were extracted for each monitoring station. The percentage proportion of anthropogenic biomes and surficial geology in different sub watersheds is shown in Figure S1.

3. Results and Discussions

3.1. Trends Analysis of Water Quality Parameters and Climatic Drivers

Water quality deterioration is a multifactor context and trends appear due to the implementation of water utilization policy, such as fertilizer application, water abstraction for irrigation and channelization, reservoir building etc. The elasticity will vary among decades and indicate the uncertainty of the CEWQ index, if trends of water quality exist. However, the median value was convincing enough and representative of the given water-climate system for a macroscale study, when the trends were not significantly large. Results of trend analysis at the Mekong, Murray and Yukon, watersheds are shown on Figure 2, and Figures S3 and S4 respectively while best fitted trend models are demonstrated by Figure S2.

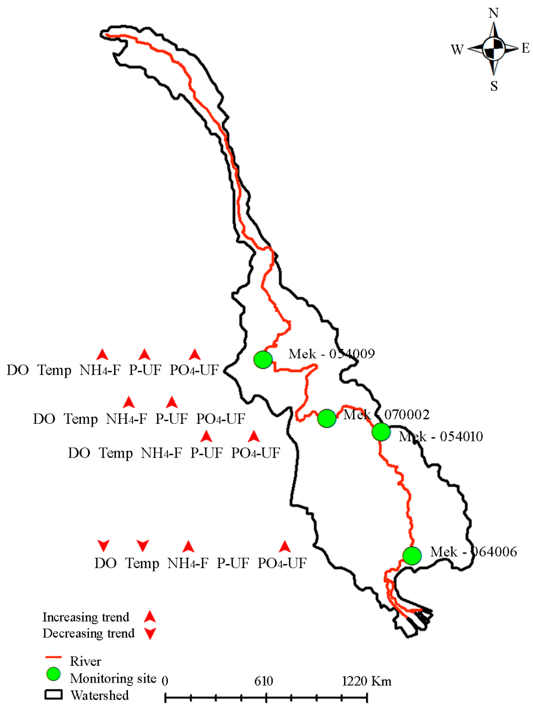

Figure 2. Spatial trend patterns at Mekong monitoring sites.

The total phosphorous (P-UF), total orthophosphate (PO_4-UF) and dissolved ammonia (NH_4-F) displayed uphill trends at various monitoring sites located in the Mekong watershed. A decreasing trend was observed for dissolved oxygen (DO) and water temperature (Temp) at Mek-064006 (e.g., Figure 3). Quadratic and power trend models were followed by various water quality parameters at the Mekong watershed.

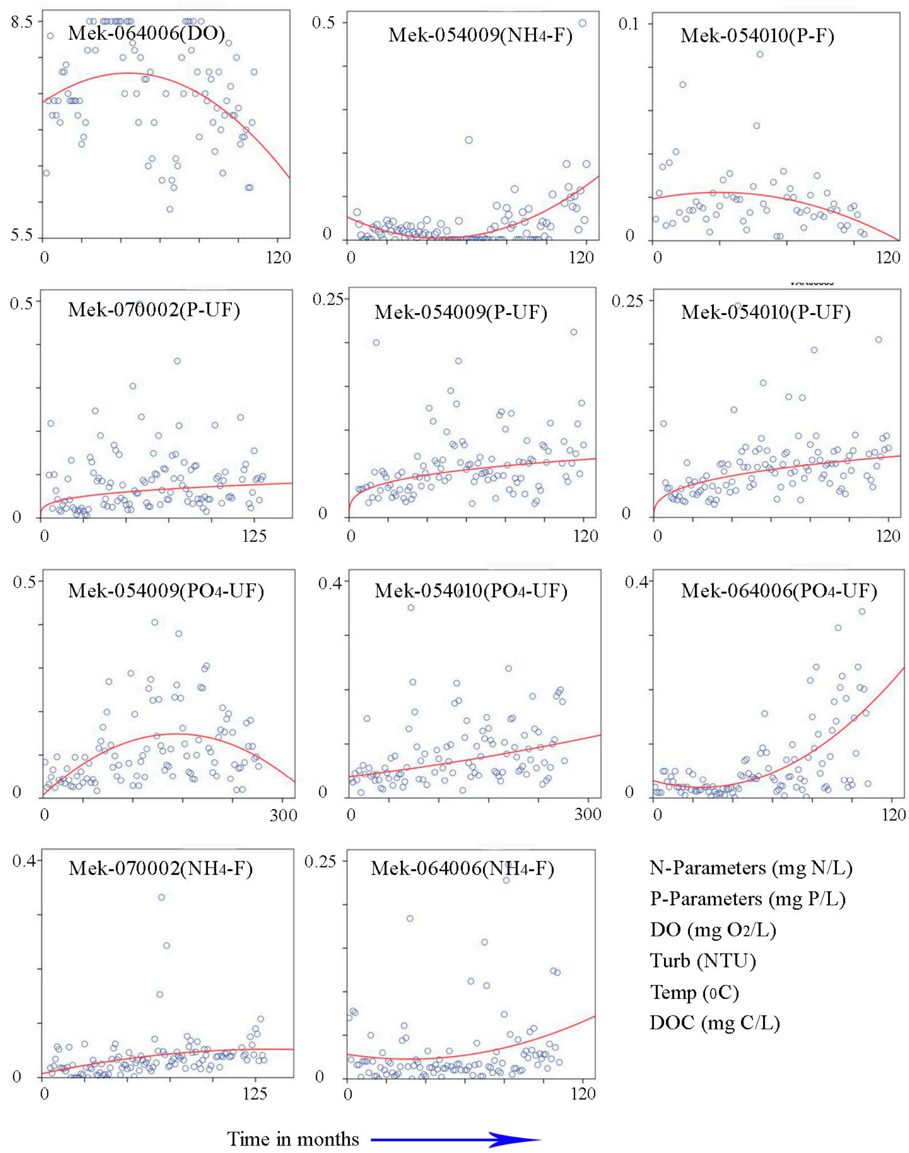

Figure 3. Significant time series trend patterns at Mekong monitoring sites.

The majority of water quality parameters including DO (except Mur-119), dissolved organic carbon (DOC), turbidity (Turb), water temperature, P-UF and total nitrogen (TN-UF) showed decreasing trends at the Mur-116, Mur-117, Mur-118 and Mur-119 monitoring stations. Turbidity and dissolved nitrate + nitrite (NO_X-F) exhibited increasing trends at the Mur-102 and Mur-119 monitoring sites respectively (e.g., Figures S5 and S6). Logarithmic, quadratic, exponential and power time series trend models were adopted by water quality parameters. Water quality parameters adopted various time series trend models, which showed that these stations were different from each other and exposed to different pollution sources.

The turbidity and NO_X-F exhibited an increasing and decreasing trends at the Yuk-028003 and Yuk-028003 monitoring sites respectively. Similarly, the dissolved phosphorus (P-F) showed a decreasing trend at the Yuk-028546 monitoring station (e.g., Figure S7). Additionally, water quality parameters adopted quadratic and power trend models.

No significant trends were observed for both precipitation and temperature except at Mur-102 where precipitation showed a downhill trend. A 20-year time span was not long enough to demonstrate trends of precipitation and temperature variation, obviously. However, at station Mur-102 in Australia, 36 years of observation uncovered changes in rainfall pattern.

During a deicidal analysis in the Yukon River, the elasticity varied and was linked to population density changes. However, to analyze how and why elasticity varied over decades was really challenged due to the unavailability of long historical records (more than 50 year) of water quality parameters and the associated time series of potential impact factors. Conversely, it was more applicable in hydrology due to longer historical records of precipitation, temperature and streamflow.

3.2. Response Pattern of Water Quality to Climatic Drivers in the Three Basins

3.2.1. Order Pattern of ε_P and ε_T

Wilcoxon signed rank test was conducted to investigate whether the impact of precipitation and temperature on a given water quality parameter outweighed each other or not (Table 1). Results showed that only the response of water temperature and TN-UF to air temperature was significantly dominant to that of precipitation ($p < 0.05$). The remaining ten water quality parameters retained the null hypothesis which illustrated that neither the impact of precipitation nor the impact of temperature on the given water quality parameters were dominant.

Table 1. Wilcoxon pairwise testing results for CEWQ.

Pairs	Negative Ranks	Positive Ranks	*p* Value
$\mid\varepsilon_T(T, \text{DO})\mid - \mid\varepsilon_P(P, \text{DO})\mid$	7	4	0.328
$\mid\varepsilon_T(T, \text{Turb})\mid - \mid\varepsilon_P(P, \text{Turb})\mid$	2	6	0.674
$\mid\varepsilon_T(T, \text{DOC})\mid - \mid\varepsilon_P(P, \text{DOC})\mid$	3	4	0.176
$\mid\varepsilon_T(T, \text{TN-UF})\mid - \mid\varepsilon_P(P, \text{TN-UF})\mid$	0	9	0.008
$\mid\varepsilon_T(T, \text{NH}_4\text{-F})\mid - \mid\varepsilon_P(P, \text{NH}_4\text{-F})\mid$	4	2	0.116
$\mid\varepsilon_T(T, \text{NO}_2\text{-F})\mid - \mid\varepsilon_P(P, \text{NO}_2\text{-F})\mid$	1	2	0.285
$\mid\varepsilon_T(T, \text{NO}_X\text{-F})\mid - \mid\varepsilon_P(P, \text{NO}_X\text{-F})\mid$	2	10	0.136
$\mid\varepsilon_T(T, \text{P-F})\mid - \mid\varepsilon_P(P, \text{P-F})\mid$	5	7	0.209
$\mid\varepsilon_T(T, \text{P-UF})\mid - \mid\varepsilon_P(P, \text{P-UF})\mid$	5	6	0.929
$\mid\varepsilon_T(T, \text{PO}_4\text{-F})\mid - \mid\varepsilon_P(P, \text{PO}_4\text{-F})\mid$	2	0	0.180
$\mid\varepsilon_T(T, \text{PO}_4\text{-UF})\mid - \mid\varepsilon_P(P, \text{PO}_4\text{-UF})\mid$	1	3	0.715
$\mid\varepsilon_T(T, \text{Temp})\mid - \mid\varepsilon_P(P, \text{Temp})\mid$	0	10	0.005

Notes: F = Filtered, UF = Unfiltered, P = Precipitation, T = Air Temperature; ε_P = Elasticity of Precipitation, ε_T = Elasticity of Temperature.

It was easy to understand that significant rises in surface water temperature occurred due to the direct effects of atmospheric warming [48–50], while minor rises in water temperature might have happened also, owing to heat transfer from paved surfaces to water bodies via surface runoff [51,52]. The median values of ε_T (T, TN-UF) were strongly positive or relatively elastic [26] which gave an idea about its possible linkage with nitrogen leaching from soil. It is well founded knowledge that a rise in air temperature favors the release of nitrogen from soil, which enhances stream nitrogen concentration with time [53,54].

3.2.2. Spatial Pattern of Precipitation Elasticity

Spatially, all monitoring sites were clustered into three groups based on similar characteristics of precipitation elasticity of water quality parameters. Stations located in the same watershed, not surprisingly, grouped together (Figure 4) except Mur-102, which is located on Cooper River. It denotes that the response of water quality parameters to precipitation was approximately similar within a given watershed. This similarity pattern might be due to exposure of surface waters to the same determinants (for example, land use, soil, etc.) and climatic conditions within a given watershed, which resulted in approximately similar responses of water quality parameters to precipitation caused by dilution and contribution of non-point source pollution (NPS). Moreover, most water quality parameters at the Mekong watershed showed increasing trends. The same trend was observed at Mur-102. It was the reason that Mur-102 clustered with the Mekong watershed monitoring stations.

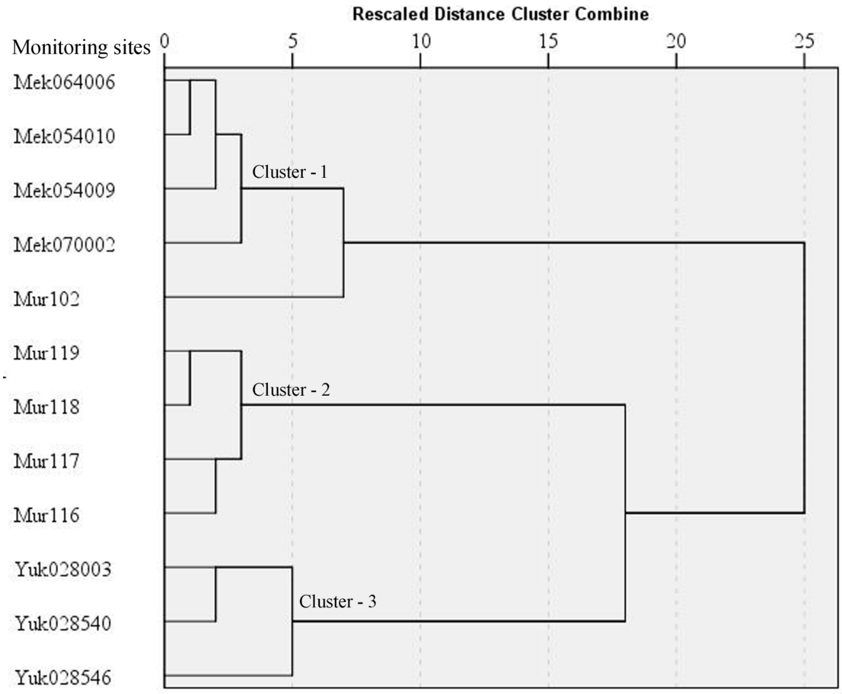

Figure 4. Dendrogram of monitoring stations using HCA based on ε_P values.

3.2.3. Spatial Pattern of Temperature Elasticity

Clustering results of temperature elasticity were quite different from precipitation elasticity. Figure 5 shows cluster 1 was composed of two sub-groups, cluster 1-1 and cluster 1-2. Cluster 1-1 contained the entire monitoring sites of the Murray watershed, while cluster 1-2 consisted of two monitoring sites of the Mekong watershed. Cluster 2 consisted of sub-group 2-1, the Mur-102 and Mek-054010 monitoring sites. Sub group 2-1 was entirely composed of Yukon monitoring sites. Interestingly, approximately all water quality monitoring stations within the Yukon and Murray watersheds showed spatial similarity, while the Mekong watershed monitoring sites showed variability in space. Two monitoring sites (Mek-070002 and Mek-054009) showed similarity with the Murray watershed, while one monitoring site (Mek-054010) showed resemblance to the Yukon watershed. The remaining one site, Mek-064006, remained isolated, perhaps due to an interesting decreasing trend of water temperature at Mek-064006.

The Mekong watershed is wide spread in four countries, namely Cambodia, Laos, Thailand and Vietnam. It is a thickly populated developing area with high anthropogenic activities and diverse cultures. Regional variability in temperature and its related determinants altered the response of water quality parameters to temperature in the Mekong watershed.

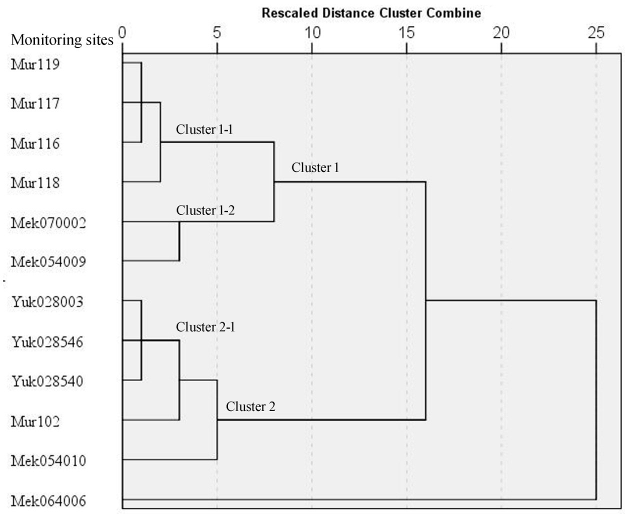

Figure 5. Dendrogram of monitoring stations using HCA based on εT values.

3.3. *Impacts of Terrestrial Determinants on CEWQ*

Pearson's correlation analysis was conducted to develop a relationship between CEWQ, and anthropogenic biomes and surficial geological variables. Significant linear relationships are tabulated in Tables 2 and 3.

Table 2. Correlations between anthropogenic biomes, precipitation and temperature elasticity of water quality.

CEWQ / Anthro-Pogenic Biomes	DOC	TN-UF	NH_4-F	NO_X-F	P-F	P-UF	Temp	
	0/+	+	S	0/+	0/+	0/+	+	**Sign of ε_P [26]**
	S	+	-	-	+	+	+	**Sign of ε_T [26]**
Dense settlements				0.603 *	0.611 *			
Croplands			0.591 *	0.585 *				Precipitation
Rangelands	−0.851 **			−0.637 *				Elasticity, ε_P
Forested		0.649 *		0.612 *				
Dense settlements	−0.714 *							
Croplands	−0.580 *							Temperature
Rangelands						−0.578 *	−0.767 **	Elasticity, ε_T
Forested		0.623 *						

Note: 0, −, +, S in elasticity sign denotes, inelastic, negative elastic, positive elastic, and site specific; * denotes correlation is significant at the 0.05 level (2-tailed); ** denotes correlation is significant at the 0.01 level (2-tailed).

Table 3. Correlations between surficial geology, precipitation and temperature elasticity of water quality.

Surficial Geology	CEWQ					Elasticity Type
	DOC	NH_4-F	P-F	P-UF	Temp	
Gravel	−0.599	0.580				
Silt					0.615	Precipitation Elasticity ε_P
Clay			−0.601			
Gravel				−0.576		Temperature Elasticity, ε_T
Clay				−0.665		

Note: correlation is significant at the 0.05 level (2-tailed).

3.3.1. Relationship between Anthropogenic Biomes and CEWQ

Sensitivity of Precipitation Elasticity to Anthropogenic Biomes

Table 2 displays that ε_P (P, NO_X-F) and ε_P (P, P-F) were sensitive and positively correlated to dense settlement biomes. Dense settlement had intensifying effects on increasing nitrogen loads, phosphorus and other nutrients in surface water [16,55–62] due to high anthropogenic activities and low retention capacity in urban lands [63]. There might be a high nitrogen emission when people practice urban gardening or do not have sewage plants etc. Strong storminess enhanced discharge which drained domestic sewage and nutrients [3] to nearby watercourses. Sub-class dense settlements ratio was higher in the Mekong watershed with annual rainfall (median) of 1051 mm [36]. Precipitation exacerbated the deterioration of surface waters due to high overland flow in dense settlements [63].

Precipitation was reported to cause serious problems of surface water contamination from diffuse sources of croplands[3]. Similar results were found in this study where ε_P (P, NH_4-F) and ε_P (P, NO_X-F) were positively linked with cropland biomes. Agriculture lands had positive impacts on increasing phosphorous and nitrogenous materials [55,61]. It can be attributed to surface runoff, which sweeps all kinds of nitrogenous material produced by cultivation practices (fertilizers application, plough land, etc.) to nearby rivers and streams [64–66]. Generally, the effect of precipitation on nitrogen (N)parameters in rivers were significant compared to temperature [67]. Results of the current study were consistent with previous studies because precipitation increased the overall stream nitrogen loading. Precipitation substantially enhanced nitrogen flux. ε_P (P, NH_4-F) and was site specific. Residential rainfed mosaic, residential irrigated croplands and populated rainfed croplands were comparatively in large proportion at the Mekong watershed, while populated rainfed croplands and remote croplands were abundant at the Murray watershed, which mainly depends upon rainfall for irrigation purposes. The results here were reasonable and consistent with literature because rainfall sweeps pollutants from the rainfed croplands to the nearby surface waters [36].

Rangelands were the agents that played a positive role in controlling non-point source pollution. Here, ε_P (P, DOC) and ε_P (P, NO_X-F) were negatively correlated with rangeland biomes. Rangeland played a positive role in the declining nutrients load [68]. Rangeland biome watersheds retained more nutrients in comparison to lost with surface runoff [69–71]. Degradation of rangeland lead to the degradation of water quality, which showed the importance of rangeland conservation [16,66]. The Murray watershed consists of all the three sub-classes of rangeland, residential rangelands, populated rangelands and remote rangelands, where remote rangeland was in high proportion. Remote rangelands were wild pastures with minor human interference and the lowest annual rainfall of 247 mm, which favored the results.

Like rangelands, forests (having minor human interference) also helped in surface water purification by modulating diffuse pollutants at catchment scale [72]. The ε_P (P, TN-UF) and ε_P (P, NO_X-F) were positively linked with forested biomes. Forest land use was most often negatively linked with degraded water quality [55,73]. Few studies have shown that forest land cover has a positive relation with nitrogenous materials [47,74,75]. It could be attributed to higher water discharge and lower water residence time, which affects the uptake capacity of vegetation [63]. Populated forests with human intrusion (mean population density of 3 persons/km^2) and a higher annual rainfall of 1090 mm, were in higher ratio at the Mekong watershed compared to remote forests. Human settlements and higher rainfall in populated forests supported this study's results whose conceptual model is described in detail by [8]. The Mekong watershed had an increase in the "source" due to deforestation for urbanization and crop growth increased the risk of non-point source pollution which impaired surface water quality [76].

Sensitivity of Temperature Elasticity to Anthropogenic Biomes

Table 2 shows that dissolved organic carbon (DOC) was the representative of organic loadings both in terrestrial processing (within forests, wetlands and soil) and surface waters [77]. Here, ε_T (T, DOC) was sensitive to, and negatively correlated with, dense settlement biomes. The ε_T (T, DOC) was site specific both in intensity and direction, which could be due to complex impacts of precipitation and temperature on DOC solubility, hydrological transport and decomposition [78]. Warming impacted the transport of DOC, depending upon the accompanying rainfall intensity [79]. Due to the complex determinants of DOC, the relationship between ε_T (T, DOC) and dense settlements was strange and difficult to explain.

The ε_T (T, DOC) was negatively associated with cropland biomes, which was reasonable because excessive application of water for crop growth due to rises in air temperature facilitated the infiltration of DOC from top to bottom soil layers due to loose soil structure (plowing) [80]. This reduced DOC contents in the top layer. There were large uncertainties owing to the complex dynamics and biochemical processes controlling soil carbon flux[3].

The ε_T (T, P-UF) and ε_T (T, Temp) were negatively correlated with rangeland biomes. Rangelands had positive effects on decreasing nutrient load [71]. Rises in air temperature favored the uptake of phosphorous by terrestrial vegetation, which lead to lower loading in surface waters [79]. Some other studies have also suggested rangeland conservation at catchment level for better water quality [16,66,68]. Similarly, rangelands had a positive influence on surface water temperature. The availability of vegetation reduced the temperature of water in the topsoil due to indirect exposure to solar radiation. Thus, it regulated the transfer of heat from atmosphere to soil and from soil to river through sub-superficial flow pathways [81]. The Murray watershed mainly consisted of remote rangelands, which were free from human interference supporting this study's results.

Forested biomes were positively linked with TN-UF. Forest land use was most often negatively linked with degraded water quality. Several studies have shown that forest land cover had a positive relation with nitrogenous material [74,82]. Generally, decomposition of leaves resulted in low level nitrogen leaching, but larger forest land use area accounted for higher N fluxes in fall [74]. A rise in air temperature also favored the release of nitrogen from soil, which enhanced stream nitrogen concentration with time [53,54]. Populated forests were in high proportion at the Mekong watershed, which favored this study's output whose conceptual model was explained in detail by Ellis and Ramankutty, 2008 [8].

3.3.2. Relationship between Surficial Geology and CEWQ

Like anthropogenic biomes, heterogeneity of surficial geology is reported to be involved in diffuse water pollution [74]. Results of the current study are tabulated in Table 3. The ε_P (P, DOC) was negatively linked to gravel. This relation was complex and subject to soil texture, vegetation and topographic conditions of the territory [83]. The ε_P (P, P-F) was negatively correlated with clay. The relation between soils and P-F was complex, as high clay content had a low infiltration rate and high sorption capacity, but phosphorous was usually transported into the river with sediments that required different processes (surface runoff and soil erosion rather than base flow). The ε_P (P, Temp) was positively correlated with silt. The temperature of topsoil increased with increasing air temperature due to absorption of solar radiation [81]. Water temperature in stream generally fluctuated in response to variations in air temperature and solar radiation but minor increases occurred due to warm storm water runoff [84,85].

The ε_T (T, P-UF) was negatively correlated with gravel and clay. Generally, high temperature favored the phosphorous conversion to tightly bonded forms, which increased soil phosphorous retention capacity [86].

3.3.3. Physical Insights to the Relationship

The above discussion demonstrates that anthropogenic biomes impacted the stability of CEWQ, which included DOC, water temperature, N-parameters and phosphorous (P)-parameters. Precipitation elasticity of water quality parameters was highly sensitive to anthropogenic biomes compared to temperature elasticity of water quality parameters. Positive elasticity and positive correlation meant that, under the same precipitation (same storm intensity)/temperature (same temperature) conditions, those areas tended to have higher pollutant loads and concentrations in receiving waters due to anthropogenic biomes and vice versa.

Areas with higher dense settlement, cropland and forested biomes (having human interference like deforestation for urbanization and agriculture production) were prone to have larger precipitation elasticity values. Precipitation elasticity values of CEWQ parameters concerned with the above stated land uses were normally positive from the authors' former global study [26]. Under the same precipitation conditions (same storm intensity), those areas tended to have higher pollutant loads and concentration in the receiving waters as a result. Areas with a higher ratio of rangelands were expected to have lower precipitation elasticity values. It would reduce pollutant loads in receiving waters for the same condition of precipitation.

Watersheds with a higher ratio of rangeland biomes were prone to have lower values of temperature elasticity except DOC. Larger rangeland biome area decreased water quality sensitivity to temperature. Conversely, larger forest land use area increased water quality response to temperature.

Like anthropogenic biomes, surficial geology also affected the stability of temperature elasticity of water quality parameters which included DOC, water temperature, N-parameters and P-parameters. Comparatively, precipitation elasticity of water quality parameters was highly sensitive to surficial geology.

Watersheds having comparatively high proportions of clay and gravels reduced temperature and precipitation elasticity values except ε_P (P, NH_4-F). It decreased the response of water quality parameters to precipitation and temperature. Silt enhanced the response of water temperature to precipitation.

Temperature elasticity was complex compared to precipitation elasticity owing to its complex mechanism. Complete interpretation of terrestrial determinants impact on temperature elasticity needs combined multiple climatic and non-climatic variables.

3.4. Linear Models of Terrestrial Determinants and CEWQ

To quantitatively investigate the associations between terrestrial determinants and CEWQ, stepwise regression was applied at sub-basin scale. Linear models with p-values less than 0.05 are demonstrated by Table 4 and Figure 6. It was evident from high values of R^2 that precipitation elasticity had stronger models compared to temperature elasticity for both terrestrial determinants like anthropogenic biomes and surficial geology. Precipitation elasticity of water quality developed many linear empirical equations with determinants compared to temperature elasticity of water quality [29]. Precipitation had stronger links to water quality compared to temperature. Precipitation rapidly drained all kinds of particulate and dissolved materials from the whole catchment into the nearby river [87]. Moreover, anthropogenic biomes were the strong predictors of CEWQ compared to surficial geology because anthropogenic biomes were directly associated with intense human activities. Those interesting equations potentially were useful to make climate change adaptions on a watershed scale like scenario analysis.

Table 4. SMLR models for temperature and precipitation elasticity.

Elasticity Type	*WQ* Parameters	Regression Model	R	R^2	ΔR^2	F-Value	*p*-Value
Temperature Elasticity	DOC	1.041 − 0.915 (Dense settlements)	0.714	0.509		9.348	0.014
		0.646 − 0.735 (Dense settlements) + 0.545 (Rangelands)	0.851	0.725	0.215	10.533	0.006
	TN-UF	0.185 + 0.654 (Forest)	0.623	0.388		5.705	0.041
	P-UF	3.523 − 0.438 (Clay)	0.665	0.443		7.144	0.026
	Temp	1.107 − 0.898 (Rangelands)	0.767	0.589		12.876	0.006
Precipitation Elasticity	DOC	0.979 − 0.813 (Rangelands)	0.851	0.725		23.680	0.001
		1.4 − 0.705 (Rangelands) − 0.014 (Gravel)	0.924	0.854	0.130	23.478	0.000
	TN-UF	0.17 + 0.681 (Forest)	0.649	0.421		6.557	0.031
	NO_X-F	0.321 − 0.653 (Rangelands)	0.637	0.405		6.133	0.035
		0.153 − 0.589(Rangelands) + 0.005 (Croplands)	0.817	0.667	0.262	8.014	0.012
	P-F	−0.411 − 0.798 (Dense settlements)	0.611	0.373		5.360	0.046
		0.872 + 0.730 (Dense settlements) − 0.169 (Clay)	0.818	0.670	0.297	8.117	0.012
	Temp	−0.231 − 0.014 (Silt)	0.615	0.378		5.475	0.044

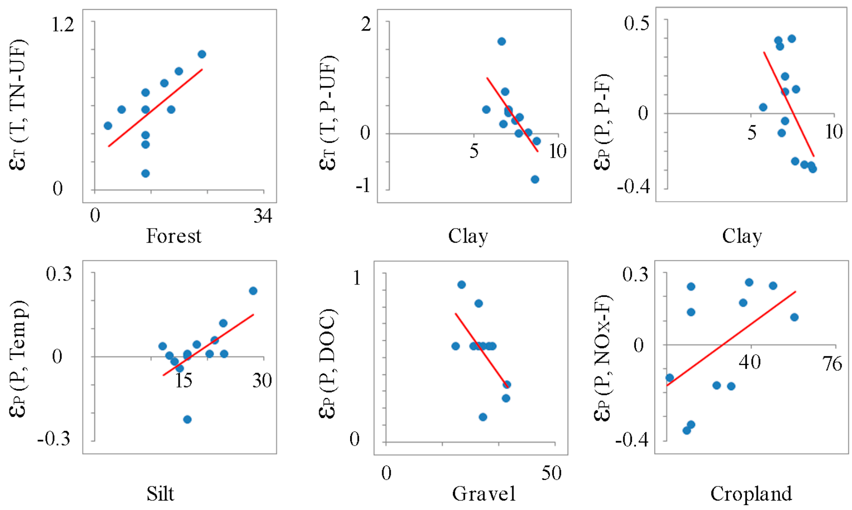

Figure 6. Typical regression models of CEWQ with terrestrial determinants.

The coefficients of the fitted equations did have uncertainty due to the uncertainty of elasticity index, which had many potential impact factors. The wider the distribution of value of $\left(\frac{WQ_t-\overline{WQ}}{T_t-\overline{T}}\frac{\overline{T}}{\overline{WQ}}\right)$, the larger the uncertainty of elasticity.

3.5. Ecological and Management Implications

This study demonstrated that terrestrial determinants significantly impacted the stability of CEWQ at the Yukon, Mekong and Murray watersheds. Furthermore, the developed linear models between terrestrial determinants and CEWQ parameters were helpful for the policy makers in improving stream health in the above-mentioned watersheds. Hence, the nonparametric approach of elasticity provided a good framework for associating water quality, land use and climatic variables.

Model assessment showed that many CEWQ parameters, which included DOC, water emperature, N-parameters and P-parameters, had useful relations with terrestrial determinants. Therefore, watershed managers can take advantage of those useful relationships between CEWQ and terrestrial determinants to improve water quality in the study area. This study shows that different terrestrial determinants impacted the stability of CEWQ parameters differently and people should concentrate on reducing nutrient amounts coming from dense settlement and cropland biomes to surface waters to modulate eutrophication. To maintain the stability of CEWQ, preventive measures should be introduced in the study area, such as rangelands and porous materials to reduce the risk of incoming diffused pollutants to surface waters [76].

The obtained linear models can be used for forecasting the impacts of terrestrial determinants on CEWQ in the study area. Based on the developed linear models, watershed managers can reduce diffused pollution originating from dense settlements and croplands. Besides, it will be helpful in preparing water pollution control plans for the understudy area, which will be helpful in reducing peak discharge and enhancing filtration of sediments and pollutants to protect stream health. Moreover, the acquired linear regression models in combination with GIS will be helpful in developing a land use control plan to maintain the stability of CEWQ by restoring critical ecosystems, protecting natural resources and implementing stormwater management plans that integrate dense settlements with natural environment. A water–land–climate nexus might improve thinking to implement better management options for dense settlements and croplands, and conserve rangelands and forests, to protect natural resources from human intrusion at the Yukon, Mekong and Murray watersheds.

3.6. Limitations

The results of the current study present an overview of the associations between terrestrial determinants and CEWQ. Although there is adequate proof for explaining variations in CEWQ in relation to terrestrial determinants, the quantitative cause-effect associations in different climate types was not reached. Moreover, SMLR and correlation analysis did not capture non-linear relations between CEWQ and terrestrial determinants. Future work is recommended if enough datasets can be collected to differentiate the influences between agricultural activities and anthropogenic wastewater, to uncover the pattern and drivers of deicidal variations of CEWQ, a comparative study between elasticity approach and physical model approach on a local scale for water–land–climate nexus analysis, etc.

4. Conclusions

This research was conducted to uncover the generic relationships among water quality, terrestrial factors and climate drivers based on a direct, data-intensive approach, and climate elasticity of water quality. Three typical watersheds of The Yukon, Mekong and Murray rivers were selected as the study area.

It was shown that 10 out of 12 water quality parameters presented approximately similar responses to temperature and precipitation, except water temperature and total nitrogen. It was also noted that temperature elasticity showed variability in space. Many interesting links were found between precipitation elasticity and anthropogenic biomes for example. Positive association of urban settlements with dissolved phosphorous and nitrate + nitrite. Similarly, the positive relationship of croplands was observed with ammonia and nitrate + nitrite. Negative linkage of rangelands was found with dissolved organic carbon and nitrate + nitrite. Similarly, many useful relationships were found between precipitation elasticity and anthropogenic biomes, for example: A negative linkage of rangelands with total phosphorous and water temperature was found. Some useful correlations of surficial geology were found with precipitation and temperature elasticity, which includes: negative relationship of clay with dissolved phosphorous and total phosphorous based on precipitation and temperature elasticity, respectively. Dense settlements and croplands played negative roles in impairing river water quality while rangelands and clay played a positive role in maintaining river health.

Anthropogenic biomes are superior determinants compared to surficial geology for both temperature and precipitation elasticity of water quality, which might be due to direct exposure of landscape to anthropogenic activities. Precipitation elasticity of water quality parameters has many determinants compared to temperature elasticity of water quality parameters. Precipitation elasticity better explained water quality variations than temperature elasticity. This work will help the decision makers in urban planning, water sensitive city and sponge city under the changing climate.

Supplementary Materials: The following are available online at www.mdpi.com/2071-1050/9/11/2118/s1, Figure S1: Percent anthropogenic biomes and surficial geology at sub watersheds scale for each monitoring station, Figure S2: Best fitted time series trend models for water quality parameters at Yukon, Mekong and Murray monitoring sites, Figure S3: Spatial trend patterns at Murray monitoring sites, Figure S4: Spatial trend patterns at Yukon monitoring sites, Figure S5: Significant time series trend patterns of nitrogen and phosphorous parameters at Murray monitoring sites, Figure S6: Significant time series trend patterns of turbidity, water temperature, DOC and DO at Murray monitoring sites, Figure S7: Significant time series trend patterns at Yukon monitoring sites, Table S1: Summary of rivers and monitoring stations, Table S2: Summary of water quality parameters.

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References

1. Kundzewicz, Z.W.; Mata, L.J.; Arnell, N.; Doll, P.; Kabat, P.; Jimenez, B.; Miller, K.; Oki, T.; Zekai, S.; Shiklomanov, I. *Freshwater Resources and Their Management*; Intergovernmental Panel on Climate Change: Geneva, Switzerland, 2007.
2. Kundzewicz, Z.; Mata, L.; Arnell, N.W.; Döll, P.; Jimenez, B.; Miller, K.; Oki, T.; Şen, Z.; Shiklomanov, I. The implications of projected climate change for freshwater resources and their management. *Hydrol. Sci. J.* **2008**, *53*, 3–10. [CrossRef]
3. Whitehead, P.G.; Wilby, R.L.; Battarbee, R.W.; Kernan, M.; Wade, A.J. A review of the potential impacts of climate change on surface water quality. *Hydrol. Sci. J.* **2009**, *54*, 101–123. [CrossRef]
4. Bricker, O.P.; Jones, B.F. Main factors affecting the composition of natural waters. In *Trace Elements in Natural Waters*; CRC Press: Boca Raton, FL, USA, 1995; pp. 1–5.
5. Bierman, P.; Lewis, M.; Ostendorf, B.; Tanner, J. A review of methods for analysing spatial and temporal patterns in coastal water quality. *Ecol. Indic.* **2011**, *11*, 103–114. [CrossRef]
6. Pińskwar, I. *Projections of Changes in Precipitation Extremes in Poland*; Monografie Komitetu Gospodarki Wodnej PAN: Warsaw, Poland, 2010.
7. Kundzewicz, Z.W.; Krysanova, V. Climate change and stream water quality in the multi-factor context. *Clim. Chang.* **2010**, *103*, 353–362. [CrossRef]
8. Ellis, E.C.; Ramankutty, N. Putting people in the map: Anthropogenic biomes of the world. *Front. Ecol. Environ.* **2008**, *6*, 439–447. [CrossRef]
9. Reimann, C.; Finne, T.E.; Nordgulen, Ø.; Sæther, O.M.; Arnoldussen, A.; Banks, D. The influence of geology and land-use on inorganic stream water quality in the Oslo region, Norway. *Appl. Geochem.* **2009**, *24*, 1862–1874. [CrossRef]
10. Cunningham, M.A.; Menking, K.M.; Gillikin, D.P.; Smith, K.C.; Freimuth, C.P.; Belli, S.L.; Pregnall, A.M.; Schlessman, M.A.; Batur, P. Influence of open space on water quality in an urban stream. *Phys. Geogr.* **2010**, *31*, 336–356. [CrossRef]
11. Tran, C.P.; Bode, R.W.; Smith, A.J.; Kleppel, G.S. Land-use proximity as a basis for assessing stream water quality in New York State (USA). *Ecol. Indic.* **2010**, *10*, 727–733. [CrossRef]
12. Utz, R.M.; Eshleman, K.N.; Hilderbrand, R.H. Variation in physicochemical responses to urbanization in streams between two Mid-Atlantic physiographic regions. *Ecol. Appl.* **2011**, *21*, 402–415. [CrossRef] [PubMed]
13. Wang, X.; Yin, Z.-Y. Using GIS to assess the relationship between land use and water quality at a watershed level. *Environ. Int.* **1997**, *23*, 103–114. [CrossRef]
14. Paul, M.J.; Meyer, J.L. Streams in the urban landscape. *Annu. Rev. Ecol. Syst.* **2001**, *32*, 333–365. [CrossRef]
15. Tsegaye, T.; Sheppard, D.; Islam, K.; Tadesse, W.; Atalay, A.; Marzen, L. Development of chemical index as a measure of in-stream water quality in response to land-use and land cover changes. *Water Air Soil Pollut.* **2006**, *174*, 161–179. [CrossRef]

16. Lee, S.-W.; Hwang, S.-J.; Lee, S.-B.; Hwang, H.-S.; Sung, H.-C. Landscape ecological approach to the relationships of land use patterns in watersheds to water quality characteristics. *Landsc. Urban Plan.* **2009**, *92*, 80–89. [CrossRef]
17. Zeilhofer, P.; Lima, E.B.N.R.; Lima, G.A.R. Land use effects on water quality in the urban agglomeration of Cuiabá and Várzea Grande, Mato Grosso State, central Brazil. *Urban Water J.* **2010**, *7*, 173–186. [CrossRef]
18. Mehaffey, M.; Nash, M.; Wade, T.; Ebert, D.; Jones, K.; Rager, A. Linking land cover and water quality in New York city's water supply watersheds. *Environ. Monit. Assess.* **2005**, *107*, 29–44. [CrossRef] [PubMed]
19. Versace, V.; Ierodiaconou, D.; Stagnitti, F.; Hamilton, A.; Walter, M.; Mitchell, B.; Boland, A.-M. Regional-scale models for relating land cover to basin surface-water quality using remotely sensed data in a GIS. *Environ. Monit. Assess.* **2008**, *142*, 171–184. [CrossRef] [PubMed]
20. Heathwaite, A. Multiple stressors on water availability at global to catchment scales: Understanding human impact on nutrient cycles to protect water quality and water availability in the long term. *Freshw. Biol.* **2010**, *55*, 241–257. [CrossRef]
21. Miserendino, M.L.; Casaux, R.; Archangelsky, M.; Di Prinzio, C.Y.; Brand, C.; Kutschker, A.M. Assessing land-use effects on water quality, in-stream habitat, riparian ecosystems and biodiversity in Patagonian Northwest streams. *Sci. Total Environ.* **2011**, *409*, 612–624. [CrossRef] [PubMed]
22. Giri, S.; Qiu, Z. Understanding the relationship of land uses and water quality in twenty first century: A review. *J. Environ. Manag.* **2016**, *173*, 41–48. [CrossRef] [PubMed]
23. Wang, Q.; Li, S.; Jia, P.; Qi, C.; Ding, F. A review of surface water quality models. *Sci. World J.* **2013**, *2013*, 231768. [CrossRef] [PubMed]
24. Prathumratana, L.; Sthiannopkao, S.; Kim, K.W. The relationship of climatic and hydrological parameters to surface water quality in the Lower Mekong river. *Environ. Int.* **2008**, *34*, 860–866. [CrossRef] [PubMed]
25. Fukushima, T.; Ozaki, N.; Kaminishi, H.; Harasawa, H.; Matsushige, K. Forecasting the changes in lake water quality in response to climate changes, using past relationships between meteorological conditions and water quality. *Hydrol. Process.* **2000**, *14*, 593–604. [CrossRef]
26. Jiang, J.; Sharma, A.; Sivakumar, B.; Wang, P. A global assessment of climate–water quality relationships in large rivers: An elasticity perspective. *Sci. Total Environ.* **2014**, *468*, 877–891. [CrossRef] [PubMed]
27. Sankarasubramanian, A.; Vogel, R.M.; Limbrunner, J.F. Climate elasticity of streamflow in the United States. *Water Resour. Res.* **2001**, *37*, 1771–1781. [CrossRef]
28. Chiew, F.H. Estimation of rainfall elasticity of streamflow in Australia. *Hydrol. Sci. J.* **2006**, *51*, 613–625. [CrossRef]
29. Khan, A.U.; Jiang, J.; Wang, P.; Zheng, Y. Influences of topographic and socio-economic attributes on the climate sensitivity of global river water quality. *Environ. Res. Lett.* **2017**, *12*. [CrossRef]
30. Rubel, F.; Kottek, M. Observed and projected climate shifts 1901–2100 depicted by world maps of the Köppen-Geiger climate classification. *Meteorol. Z.* **2010**, *19*, 135–141. [CrossRef]
31. UNEP/GEMS. United Nations Environment Programme (Unep)/Global Water Quality Data and Statistics (Gems). Available online: www.gemstat.org (accessed on 16 November 2017).
32. GEMSwater. Environmental Analytical Techniques Used for Water Quality Analyses. Available online: http://www.unep.org/gemswater/TechnicalResources/AnalyticalMethodsforEnvironmentalWaterQuality/tabid/78547/Default.aspx (accessed on 16 January 2013).
33. EPA. South Australia Environmental Protection Agency. Available online: http://www.epa.sa.gov.au (accessed on 16 November 2017).
34. NOAA. National Oceanic and Atmospheric Administration. Available online: http://www.esrl.noaa.gov/psd/data/ (accessed on 16 November 2017).
35. DEM. Shuttle Radar Topography Mission Digital Elevation Model Imagery. Available online: http://www.webgis.com/srtm30.html (accessed on 16 November 2017).
36. Ellis, E.C.; Ramankutty, N. *Anthropogenic Biomes of the World, Version 1*; NASA Socioeconomic Data and Applications Center (SEDAC): Palisades, NY, USA, 2008.
37. Ellis, E.C.; Goldewijk, K.K.; Siebert, S.; Lightman, D.; Ramankutty, N. *Anthropogenic Biomes of the World, Version 2: 1700*; NASA Socioeconomic Data and Applications Center (SEDAC): Palisades, NY, USA, 2013.

38. Nachtergaele, F.; van Velthuizen, H.; Verelst, L.; Batjes, N.; Dijkshoorn, J.; van Engelen, V.; Fischer, G.; Jones, A.; Montanarella, L.; Petri, M. *Harmonized World Soil Database (Version 1.0)*; Food and Agriculture Organization of the UN (FAO): Rome, Italy; International Institute for Applied Systems Analysis (IIASA): Laxenburg, Austria; ISRIC-World Soil Information: Wageningen, The Netherlands; Inst of Soil Science-Chinese Acad of Sciences (ISS-CAS): Beijing, China; EC-Joint Research Centre (JRC): Ispra, Italy, 2008.
39. Yang, Z.; Liu, Q. Response of streamflow to climate changes in the Yellow river basin, China. *J. Hydrometeorol.* **2011**, *12*, 1113–1126. [CrossRef]
40. Sheskin, D.J. *Handbook of Parametric and Nonparametric Statistical Procedures*; CRC Press: Boca Raton, FL, USA, 2003.
41. Antonopoulos, V.Z.; Papamichail, D.M.; Mitsiou, K.A. Statistical and trend analysis of water quality and quantity data for the Strymon river in Greece. *Hydrol. Earth Syst. Sci.* **2001**, *5*, 679–692. [CrossRef]
42. Antonopoulos, V.; Papamichail, D. Trend analysis of water quality parameters for two transboundary rivers in Northern Greece. In Proceedings of the International Conference Protection and Restoration of the Environment VI, Skiathos, Greece, 1–5 July 2002.
43. Helsel, D.R.; Hirsch, R.M. *Statistical Methods in Water Resources*; US Geological Survey: Reston, VA, USA, 2002; Volume 323.
44. Dahmen, E.; Hall, M.J. *Screening of Hydrological Data: Tests for Stationarity and Relative Consistency*; ILRI: Nairobi, Kenya, 1990.
45. Naddafi, K.; Honari, H.; Ahmadi, M. Water quality trend analysis for the Karoon river in Iran. *Environ. Monit. Assess.* **2007**, *134*, 305–312. [CrossRef] [PubMed]
46. Jung, K.Y.; Lee, K.-L.; Im, T.H.; Lee, I.J.; Kim, S.; Han, K.-Y.; Ahn, J.M. Evaluation of water quality for the Nakdong river watershed using multivariate analysis. *Environ. Technol. Innov.* **2016**, *5*, 67–82. [CrossRef]
47. Xiao, R.; Wang, G.; Zhang, Q.; Zhang, Z. Multi-scale analysis of relationship between landscape pattern and urban river water quality in different seasons. *Sci. Rep.* **2016**, *6*. [CrossRef] [PubMed]
48. Maheu, A.; Poff, N.; St-Hilaire, A. A classification of stream water temperature regimes in the conterminous USA. *River Res. Appl.* **2015**, *32*, 896–906. [CrossRef]
49. Hill, R.A.; Hawkins, C.P.; Carlisle, D.M. Predicting thermal reference conditions for USA streams and rivers. *Freshw. Sci.* **2012**, *32*, 39–55. [CrossRef]
50. Van Vliet, M.T.; Franssen, W.H.; Yearsley, J.R.; Ludwig, F.; Haddeland, I.; Lettenmaier, D.P.; Kabat, P. Global river discharge and water temperature under climate change. *Glob. Environ. Chang.* **2013**, *23*, 450–464. [CrossRef]
51. Putro, B.; Kjeldsen, T.; Hutchins, M.G.; Miller, J. An empirical investigation of climate and land-use effects on water quantity and quality in two urbanising catchments in the Southern United Kingdom. *Sci. Total Environ.* **2016**, *548*, 164–172. [CrossRef] [PubMed]
52. Roa-Espinosa, A.; Wilson, T.; Norman, J.; Johnson, K. Predicting the impact of urban development on stream temperature using a thermal urban runoff model (turm). In Proceedings of the National Conference on Urban Stormwater: Enhancing Programs at the Local Level, Chicago, IL, USA, 17–20 February 2003; pp. 17–20.
53. Whitehead, P.; Wilby, R.; Butterfield, D.; Wade, A. Impacts of climate change on in-stream nitrogen in a lowland chalk stream: An appraisal of adaptation strategies. *Sci. Total Environ.* **2006**, *365*, 260–273. [CrossRef] [PubMed]
54. Arheimer, B.; Andréasson, J.; Fogelberg, S.; Johnsson, H.; Pers, C.B.; Persson, K. Climate change impact on water quality: Model results from Southern Sweden. *AMBIO J. Hum. Environ.* **2005**, *34*, 559–566. [CrossRef]
55. Ahearn, D.S.; Sheibley, R.W.; Dahlgren, R.A.; Anderson, M.; Johnson, J.; Tate, K.W. Land use and land cover influence on water quality in the last free-flowing river draining the Western Sierra Nevada, California. *J. Hydrol.* **2005**, *313*, 234–247. [CrossRef]
56. Galbraith, L.M.; Burns, C.W. Linking land-use, water body type and water quality in Southern New Zealand. *Landsc. Ecol.* **2007**, *22*, 231–241. [CrossRef]
57. Haidary, A.; Amiri, B.J.; Adamowski, J.; Fohrer, N.; Nakane, K. Assessing the impacts of four land use types on the water quality of wetlands in Japan. *Water Resour. Manag.* **2013**, *27*, 2217–2229. [CrossRef]
58. Liu, W.; Zhang, Q.; Liu, G. Influences of watershed landscape composition and configuration on lake—Water quality in the Yangtze river basin of China. *Hydrol. Process.* **2012**, *26*, 570–578. [CrossRef]
59. Tu, J. Spatially varying relationships between land use and water quality across an urbanization gradient explored by geographically weighted regression. *Appl. Geogr.* **2011**, *31*, 376–392. [CrossRef]

60. Tu, J. Spatial variations in the relationships between land use and water quality across an urbanization gradient in the watersheds of Northern Georgia, USA. *Environ. Manag.* **2013**, *51*, 1–17. [CrossRef] [PubMed]
61. Wan, R.; Cai, S.; Li, H.; Yang, G.; Li, Z.; Nie, X. Inferring land use and land cover impact on stream water quality using a Bayesian hierarchical modeling approach in the Xitiaoxi river watershed, China. *J. Environ. Manag.* **2014**, *133*, 1–11. [CrossRef] [PubMed]
62. Chang, H. Water quality impacts of climate and land use changes in Southeastern Pennsylvania. *Prof. Geogr.* **2004**, *56*, 240–257.
63. Ding, J.; Jiang, Y.; Fu, L.; Liu, Q.; Peng, Q.; Kang, M. Impacts of land use on surface water quality in a subtropical river basin: A case study of the Dongjiang river basin, Southeastern China. *Water* **2015**, *7*, 4427–4445. [CrossRef]
64. King, R.S.; Baker, M.E.; Whigham, D.F.; Weller, D.E.; Jordan, T.E.; Kazyak, P.F.; Hurd, M.K. Spatial considerations for linking watershed land cover to ecological indicators in streams. *Ecol. Appl.* **2005**, *15*, 137–153. [CrossRef]
65. Unwin, M.; Snelder, T.; Booker, D.; Ballantine, D.; Lessard, J. *Predicting Water Quality in New Zealand Rivers from Catchment-Scale Physical, Hydrological and Land Cover Descriptors Using Random Forest Models*; National Institute of Water and Atmospheric Research: Christchurch, New Zealand, 2010.
66. Tong, S.T.; Chen, W. Modeling the relationship between land use and surface water quality. *J. Environ. Manag.* **2002**, *66*, 377–393. [CrossRef]
67. Correll, D.L.; Jordan, T.E.; Weller, D.E. Effects of precipitation and air temperature on nitrogen discharges from Rhode river watersheds. *Water Air Soil Pollut.* **1999**, *115*, 547–575. [CrossRef]
68. Bateni, F.; Fakheran, S.; Soffianian, A. Assessment of land cover changes & water quality changes in the Zayandehroud river basin between 1997–2008. *Environ. Monit. Assess.* **2013**, *185*, 10511–10519. [PubMed]
69. Olness, A.; Smith, S.; Rhoades, E.; Menzel, R. Nutrient and sediment discharge from agricultural watersheds in Oklahoma. *J. Environ. Qual.* **1975**, *4*, 331–336. [CrossRef]
70. Menzel, R.; Rhoades, E.; Olness, A.; Smith, S. Variability of annual nutrient and sediment discharges in runoff from Oklahoma cropland and rangeland. *J. Environ. Qual.* **1978**, *7*, 401–406. [CrossRef]
71. Ritter, W.F. Water quality of agricultural coastal plain watersheds. *Agric. Wastes* **1986**, *16*, 201–216. [CrossRef]
72. Li, S.; Gu, S.; Tan, X.; Zhang, Q. Water quality in the Upper Han river basin, China: The impacts of land use/land cover in riparian buffer zone. *J. Hazard. Mater.* **2009**, *165*, 317–324. [CrossRef] [PubMed]
73. Zhao, J.; Lin, L.; Yang, K.; Liu, Q.; Qian, G. Influences of land use on water quality in a reticular river network area: A case study in Shanghai, China. *Landsc. Urban Plan.* **2015**, *137*, 20–29. [CrossRef]
74. Sliva, L.; Williams, D.D. Buffer zone versus whole catchment approaches to studying land use impact on river water quality. *Water Res.* **2001**, *35*, 3462–3472. [CrossRef]
75. Boeder, M.; Chang, H. Multi-scale analysis of oxygen demand trends in an urbanizing Oregon watershed, USA. *J. Environ. Manag.* **2008**, *87*, 567–581. [CrossRef] [PubMed]
76. Jiang, M.; Chen, H.; Chen, Q.; Wu, H. Study of landscape patterns of variation and optimization based on non-point source pollution control in an estuary. *Mar. Pollut. Bull.* **2014**, *87*, 88–97. [CrossRef] [PubMed]
77. Kirchman, D.L.; Suzuki, Y.; Garside, C.; Ducklow, H.W. High turnover rates of dissolved organic carbon during a spring phytoplankton bloom. *Nature* **1991**, *352*, 612–614. [CrossRef]
78. Futter, M.; Butterfield, D.; Cosby, B.; Dillon, P.; Wade, A.; Whitehead, P. Modeling the mechanisms that control in—Stream dissolved organic carbon dynamics in upland and forested catchments. *Water Resour. Res.* **2007**, *43*. [CrossRef]
79. George, G. The impact of climate change on European lakes. In *The Impact of Climate Change on European Lakes*; Springer: New York, NY, USA, 2010; pp. 1–13.
80. Jiao, Y.; Xu, Z.; Zhao, J. Effects of grassland conversion to cropland and forest on soil organic carbon and dissolved organic carbon in the farming-pastoral ecotone of Inner Mongolia. *Acta Ecol. Sin.* **2009**, *29*, 150–154. [CrossRef]
81. Binkley, D.; Fisher, R. *Ecology and Management of Forest Soils*; John Wiley & Sons: New York, NY, USA, 2012.
82. Chang, H. Spatial analysis of water quality trends in the Han river basin, South Korea. *Water Res.* **2008**, *42*, 3285–3304. [CrossRef] [PubMed]

83. Awad, J.; Van Leeuwen, J.; Abate, D.; Pichler, M.; Bestland, E.; Chittleborough, D.J.; Fleming, N.; Cohen, J.; Liffner, J.; Drikas, M. The effect of vegetation and soil texture on the nature of organics in runoff from a catchment supplying water for domestic consumption. *Sci. Total Environ.* **2015**, *529*, 72–81. [CrossRef] [PubMed]
84. Jones, M.P. Effect of Urban Stormwater BMPs on Runoff Temperature in Trout Sensitive Regions. 2008. Available online: https://repository.lib.ncsu.edu/handle/1840.16/4980 (accessed on 16 November 2017).
85. Morrill, J.C.; Bales, R.C.; Conklin, M.H. Estimating stream temperature from air temperature: Implications for future water quality. *J. Environ. Eng.* **2005**, *131*, 139–146. [CrossRef]
86. Silveira, M.L.; O'Connor, G.A. Temperature effects on phosphorus release from a biosolids-amended soil. *Appl. Environ. Soil Sci.* **2013**, *2013*, 981715. [CrossRef]
87. Coulliette, A.D.; Noble, R.T. Impacts of rainfall on the water quality of the Newport river estuary (Eastern North Carolina, USA). *J. Water Health* **2008**, *6*, 473–482. [CrossRef] [PubMed]