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### Application of Multivariate Statistical Methods and Water Quality Index for the Evaluation of Surface Water Quality in the Cunas River Basin, Peru

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**Abstract:** Watershed management requires information that allows the intervention of possible sources that affect aquatic systems. Surface water quality in the Cunas river basin (Peru) was evaluated using multivariate statistical methods and the CCME-WQI water quality index. Twenty-seven sampling sites were established in the Cunas River and nine sites in the tributary river. Water samples were collected in two contrasting climatic seasons and the CCME-WQI was determined based on physicochemical and bacteriological parameters. The PCA generated three PC with a cumulative explained variation of 78.28 %. The generalised linear model showed strong significant positive relationships (p < 0.001) of *E. coli* with Fe, nitrate, Cu and TDS, and a strong significant negative relationship (p < 0.001) with pH. Overall, the CCME-WQI showed the water bodies in the upper reaches of the Cunas River as good water quality (87.07), in the middle reaches as favourable water quality (67.65) and in the lower reaches as poor water quality (34.86). In the tributary, the CCME-WQI showed the water bodies as having good water quality (82.34).

Key words: Water quality, Cunas River, CCME-WQI, watershed management, surface water.

#### Introduction

Rivers are essential systems for society because they provide freshwater for agriculture, fish farming, human needs, industry and transportation (Nong et al., 2020). However, their quality varies according to environmental and anthropogenic factors generating great heterogeneity (Custodio and Chanamé, 2016). Anthropogenic impact on water bodies is associated with changes in the water flow regime and water quality due to pollutant discharges from point sources (wastewater treatment plants) and diffuse sources. In

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addition, other threats to water quality include climate change, atmospheric deposition and soil management (El-Alfy et al., 2020; Kedra, 2020) accompanied by more frequent extreme weather phenomena, especially heat waves and prolonged drought, may pose a serious threat to the river environment and native river ecosystems. Therefore, reliable and up-to-date information on current and anticipated changes in river flow and thermal conditions is necessary for adaptive water resource management and planning. This study focuses on semi-natural mountain river systems to reliably assess the magnitude of water temperature change in the Polish Carpathians in response to climatic warming. The Mann-Kendall test was used to detect trends in water temperature series covering the last 35 years (1984-2018).

In recent decades, concern about the quality of water bodies has increased significantly (Yurova and Shirokova, 2020). Many studies reveal that drinking water quality is associated with source quality and human-induced impacts (Villena, 2018). Globally, 0.007 % of the 2.5 % of fresh water that exists on Earth is potable, a value that is decreasing due to contamination year after year. In Peru, there is undoubtedly an unequal distribution of water resources, 38% of the population has 98% of the resource and 62% has access to 1.8% (Calla and Cabrera, 2010). In addition, water quality is aggravated by the transport and distribution of sediments characteristic of the watershed and those from anthropogenic activities (Calizaya-Anco et al., 2013).

Nowadays, water quality is assessed by individual indicators and more complex comprehensive approaches. In different parts of the world, indices have been generated for application in a river basin (Mohebbi et al., 2013). In other regions, water quality is assessed using multimetric indices based on numerical and biological criteria. Water quality indices (WQI) integrate information from several parameters, allowing the transformation of large amounts of data into a single scale of water quality measurement (Howladar et al., 2017). In addition, WQIs are a fundamental management tool; they reduce the number of measurements and simplify the process of communicating measurement results.

In Peru, water quality assessment has been carried out for several decades by conventional methods using mainly individual physical and chemical parameters. Currently, the National Water Authority has adopted the CCME-WQI water quality index to monitor the water quality of Peru's aquatic systems; however, it is not yet in frequent use. In this context and considering the importance of the implications of water quality on human welfare and aquatic systems, this study was conducted to evaluate surface water quality in the Cunas river basin (Peru) using multivariate statistical methods and the CCME-WQI water quality index.

#### **Materials and Methods**

#### **Study Area**

The selected study area is located in the sub-basin of the Cunas River in the central highlands of Peru, on the right bank of the Mantaro River. It is located between 11° 45' and 12° 20' south latitude, 75° 15' and 75° 45' west longitude. The Cunas River is 101.80 km long, starting at the highest elevation at 4,797 masl and the lowest at the mouth at 3,190 masl (Figure 1).

The sampling sectors defined in the Cunas and Consac rivers were established in the upper, middle and lower parts of the course of each river. In the Cunas



Figure 1: Map showing the location of the sampling sites in the Cunas River and its main tributary, Consac.

river, the sampling sectors were located in the upper part of the river at an altitude of 3759 masl (459051.15E, 8653974.93N) where grasslands predominate. In the middle part, the sampling sectors were located at an altitude of 3423 masl (457165.25E, 8669616.76N), which are characterised by dispersed human settlements. In the lower part, the sampling sectors were located at an altitude of 3226 masl (470632.08E, 8666832.25N), characterised by nucleated and high-density human settlements. In the tributary zone, there are scattered human settlements with agricultural and livestock activities.

Water Sample Collection and Laboratory Analysis Water samples were collected during the dry season (July to September 2019) and the rainy season (December 2019 to February 2020), according to the monitoring protocols of the National Water Authority (ANA, 2016). In situ, dissolved oxygen (DO)  $(mgL^{-1})$ , total dissolved solids (TDS)  $(mgL^{-1})$  and pH were determined using Hanna Instruments portable equipment (HI 991301 Microprocessor pH/temperature, HI 9835 Microprocessor Conductivity/TDS and HI 9146 Microprocessor dissolved oxygen). Previously, the instruments were calibrated in the respective sampling sector. Water samples for physicochemical determinations were collected at a depth of approximately 20 cm in plastic bottles previously treated with hydrochloric acid and rinsed with river water. Samples for bacteriological determinations were collected in sterile bottles against the current. All samples were transported under refrigerated conditions to the Water Research Laboratory of the National University of Central Peru.

# Calculation of the Water Quality Index (CCME-WQI)

The CCME-WQI consists of three factors, each of which has been scaled between 0 and 100. In the CCME-WQI, the values of the three variance measures of the selected objectives for water quality are combined to create a vector in an imaginary space of "objective exceedance". In the index, "objectives" refer to water quality guidelines across Canada or site-specific water quality objectives (De Rosemond et al., 2009). The length of the vector is then scaled to range between 0 and 100, and subtracted from 100 to produce an index which is 0 (or close to 0) for very poor water quality, and close to 100 for excellent water quality (María Custodio, 2019). The CCME-WQI consists of three factors, equation (1).

CCME - WQI = 100 - 
$$\left[\frac{\sqrt{(F_1)^2 + (F_2)^2 (F_3)^2}}{1.732}\right]$$
 (1)

where:

F1 (Scope) is the percentage of variables that exceed the standard.

$$F_1 = \frac{\text{Number of failed variables}}{\text{Total Number of variables}} \times 100$$

F2 (Frequency) is the percentage of individual tests for each parameter that exceeds the standard.

$$F_2 = \frac{\text{Number of failed tests}}{\text{Total Number of tests}} \times 100$$

F3 (Amplitude) is the magnitude by which each parameter that does not comply exceeds the norm.

$$F_3 = \frac{\text{nse}}{0.01 \text{ nse} + 0.01}$$
  
nse =  $\frac{\sum \text{nse}}{0.01 \text{ nse} + 0.01}$ ; Excursion =  $\frac{\text{Failed tests}}{\text{Guideline value}} - 1$ 

The maximum and minimum CCME-WQI values were 100 and 0, respectively, and scores with high values represented good water quality status. According to the CCME-WQI values, the water quality status was divided into five categories: poor (0-44), marginal (45-64), fair (65-79), good (80-94) and excellent (95-100), based on the maximum acceptable concentrations in Canada (Health Canada, 2020).

#### **Statistical Analysis**

The data obtained from the water samples for each parameter were evaluated for normality of the data in the rainy and dry seasons using the Shapiro-Wilk test. Kruskal-Wallis one-way ANOVA was used for the comparison of four sectors based on significant differences (p < 0.05) in the two seasons.

#### **Results and Discussion**

## Spatio-Temporal Distribution of Water Quality Parameters

The values of the water quality parameters of the Cunas and Consac rivers were compared with Peruvian water quality standards (PWQS)(MINEN, 2015) and with the aquatic life criteria of the Canadian Council of Ministers of the Environment (CMME, 2007). Along the Cunas River, pH values of between 6.6 and 7.8 were reported, but the difference is given due to the climatological season and the sampling sector. In the dry season, the high sector obtained a mean of 7.11, tending to increase in the middle sector to 7.37, and decreasing to 7.13 in the low sector. While in the rainy season the mean of the high sector was 7.16, medium sector 7.30 and in the low sector 7.03. The trend towards water alkalinity would be related to natural factors (photosynthetic activity occurring during the day) and anthropogenic factors (edaphic characteristics, agricultural activities and domestic and industrial wastewater discharges).

The highest TDS values were recorded in the lower reaches of the Cunas River ( $\mu = 406.99 \text{ mg/L}$ ) during the dry season, while the lowest TDS values were recorded in the Consac River ( $\mu = 172 \text{ mg/L}$ ) during the wet season. These values tend to be similar to those reported in the upper Cunas River, without any disturbance (µ = 199.26 for the dry season and increase in the rainy season with a  $\mu = 264.44$  mg/L). The comparison of TDS levels in waters from the upper part of the Cunas River with waters from the lower part of the river showed a significant increase in both study seasons. This result reveals that the sampling sites in the lower sector were below the natural ranges for aquatic life, drinking water production and other uses, according to the PWQS and CCME guidelines. Similarly, Custodio and Chávez (2019) observed in the lower sector decreases in DO when assessing the quality of the Cunas River. DO is one of the key water quality parameters (Matta et al., 2020). Low DO negatively influences fish development and growth. The maximum BOD<sub>5</sub> values were well above the PWQS (10 mg/L) in both climatic seasons for the Cunas River. While in the tributary river, BOD<sub>5</sub> values were below the standard value.

Nutrient levels in the Cunas and Consac rivers depend mainly on anthropogenic sources and runoff from agricultural areas, mainly. The maximum phosphorus levels that exceeded the PWQS were recorded in the lower sector of the Cunas River, characterised by the urban area with concentrated human settlements and wastewater discharges. The maximum values of trace elements such as Cu, Fe and Zn evaluated in the sampling sectors did not exceed the water quality standards. However, an increasing trend is observed as the course of the Cunas River advances for Fe and Zn. For the Fe, in the upper part and both climatological epochs, a mean of 0.83 was obtained for the dry season and 0.73 in the rainy season in the lower part. Meanwhile, the upper part obtained a mean of 0.24 for the dry season and 0.18 mg/L for the rainy season, with a slight increase in the dry season, probably due to a reduction in flow and precipitation. The values reported for Zn showed similar behaviour with minimum values in the upper sector with means of 0.035 and 0.034 for the dry and rainy seasons, respectively.

These results reveal that the concentration of metals depends on natural (soil type, climate, weathering and dilution capacity) and anthropogenic (discharges of domestic, industrial and agricultural wastewater loaded with metals) factors (Barik et al., 2017). Natural factors can vary at different spatial and temporal scales, and these variations affect the concentration of metals and consequently cause water quality to fluctuate (Albagawi, 2019). Cu is one of the most abundant trace metals and is an essential micronutrient for almost all organisms. The increase of Cu in aquatic systems can be attributed to geological weathering, atmospheric deposition, municipal and industrial wastewater, mining waste discharge, and pesticide runoff (Tchounwou et al., 2012).

The bioavailability of heavy metals in the aquatic environment is influenced by physical (temperature, phase association, adsorption and sequestration) and chemical factors that influence speciation, complexation, solubility and partition coefficients (Li et al., 2017). Bacteriological indicators of *E. coli* exceeded the Canadian standards for the lower sector of the Cunas River significantly (p < 0.05). These indicators reveal the process of water quality degradation that the Cunas River has been experiencing, especially in its course through urban areas, in the lower part of the Cunas River. Their presence in the water indicates the occurrence of faecal contamination due to the discharge of untreated livestock and urban wastewater into the river.

Table 1 shows the correlation analysis of physicochemical and bacteriological indicators of the water of the Cunas River and tributary. It was found that DO is negatively and significantly correlated with TDS, nitrate, P, BOD<sub>5</sub>, Cu, Fe, Zn and E. coli, denoting the importance of DO in healthy aquatic environments, since the lower the DO concentration, the higher the level and concentration of these elements or parameters. Furthermore, at a significant level (p < 0.05) there is no effect of pH on the concentrations and levels of the other parameters under study. In the case of TDS, a positive and significant correlation was observed with nitrates, P, BOD<sub>5</sub>, Cu, Fe, Zn, and E. coli. Nitrate has a significant and positive correlation with P, BOD<sub>5</sub>, Cu, Fe, Zn, and E. coli. P concentrations correlate positively and significantly with BOD<sub>5</sub>, Cu, Fe, Zn and E. coli; as do trace elements such as Cu, Fe and Zn, with each other and with E. coli concentrations.

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Parameters	рН	TDS	DO	Nitrate	Р	BOD <sub>5</sub>	Си	Fe	Zn
TDS	-0.131 -0.055								
DO	0.003 0.962	-0.242 0.000							
Nitrate	-0.051 0.454	0.500 0.000	-0.551 0.000						
Р	-0.071 0.300	0.435 0.000	-0.607 0.000	0.883 0.000					
BOD <sub>5</sub>	0.000 0.999	0.591 0.000	-0.634 0.000	0.653 0.000	0.663 0.000				
Cu	0.102 0.135	0.375 0.000	-0.474 0.000	0.256 0.000	0.234 0.001	0.569 0.000			
Fe	0.000 0.997	0.696 0.000	-0.575 0.000	0.604 0.000	0.555 0.000	0.821 0.000	0.727 0.000		
Zn	-0.125 0.068	0.445 0.000	-0.494 0.000	0.463 0.000	0.415 0.000	0.522 0.000	0.416 0.000	0.558 0.000	
Escherichia coli	-0.024 0.724	0.560 0.000	-0.484 0.000	0.728 0.000	0.701 0.000	0.576 0.000	0.272 0.000	0.602 0.000	0.355 0.000

 Table 1: Spearman's rank correlations of physicochemical indicators and *Escherichia coli*. Entries in each cell are Spearman's rho values and significance level. Significant correlations are in bold italics

The principal component analysis (PCA) generated three principal components with a cumulative explained variation of 78.28%, with the first component (PC1) obtaining the most significant value of 52.93% and an eigenvalue of 5.29, followed by 14.87% and 10.48%

for the second (PC2) and third (PC3) components, respectively (Figure 2). PC1 shows a strong positive loading for TDS, nitrates, P, BOD<sub>5</sub>, Fe and *E. coli*, moderate positive loading for Cu and Zn and moderate negative loading for DO. This distribution is explained



Figure 2: Bi plots for principal component analysis 1 + 2 of water quality parameters.

by anthropogenic pressure along the river and corroborates the effect of cultivated and urban areas in the lower sector. The changes in nitrate concentration from the upper to the lower sector could be explained by the use of nitrogen fertiliser, which undergo nitrification processes (Shrestha and Kazama, 2007). The presence of significant *E. coli* in the lower sector is due to the fact that the drainage systems of drains and productive activities (animal processing centers) of the cities go directly to the river.

PC2 showed moderate negative Cu and weak negative pH loads and PC3 showed weak negative TDS, DO and Cu loads. The inverse relationship between nitrates, P and *E. coli* versus DO is a natural process. In addition, viable *E. coli* counts are related to nutrient levels (Carrillo et al., 1985) and higher TDS concentration in the water (Sikder et al., 2013). PC2 tends to explain the effect of climatic season on trace elements, especially Cu and Fe.

To explain the nature and magnitude of the relationships between physicochemical parameters and *E. coli* frequencies, the functional significance of the interactions was calculated, and the significant ones were plotted. The concentrations of most variables increased with increasing MPN values of *E. coli* (Figure 3). The results of the statistical analysis with the generalised linear model showed strong significant positive relationships (p < 0.001) of *E. coli* with Fe, nitrates, Cu and TDS. While the water pH showed a strong significant negative relationship (p < 0.001), denoting a higher concentration of *E. coli* to waters with an acidic tendency (Table 2).

The water quality index (CCME-WQI) showed that the water bodies in the upper part of the Cunas River were of good quality (87.07), in the middle part as favourable water quality (67.65) and the lower part as poor water quality (34.86) during the dry season. In the tributary, the CCME-WQI showed the water quality as good (82.34) in the low water period, which indicates that the degree of threat from exogenous anthropogenic factors is lower. During the rainy season, in the upper part of the Cunas River, the CCME-WQI showed that the water bodies as good water quality (89.44), in the middle part as favourable water quality (76.21) and the lower part as fair water quality (45.54). In the tributary, the CCME-WOI showed the water quality as good (82.34). The results also indicate that in the lower part of the Cunas River the water bodies show a certain tendency to qualify as poor quality water, due to the anthropic activity that exists in this area. The results obtained are supported by Custodio and Amesquita (2017) who evaluated the quality of the Cunas River from the middle part towards the lower part, finding good quality water in the middle part of the river and poor quality water in the lower part.

#### Conclusions

The Cunas River in the central region of Peru is one of the key rivers for the nourishment and development of agricultural activities and fish farming, whose food products are used for external and internal consumption. In the current state, most of the water quality parameters in the upstream sectors of the Cunas River were below

Term	b	SE	Т	<i>p(T)</i>
(Intercept)	-16.856	7.259	-2.32	0.021
рН	8.646	3.173	2.72	0.007
TDS	1.132	0.460	2.46	0.015
DO	-0.372	0.503	-0.74	0.460
Nitrates	3.586	0.738	4.86	0.000
Р	-0.273	3.449	-0.08	0.937
$BOD_5$	-0.228	0.295	-0.77	0.440
Cu	-579.385	138.389	-4.19	0.000
Fe	3.527	1.061	3.33	0.001
Zn	-12.714	9.366	-1.36	0.176

Table 2: Generalised linear model analysis to explain the nature and magnitude of the relationship between water physicochemical parameters and the *E. coli* response variable (explanatory variables account for 79.1% and pseudo-F = 86.7, P = 0.002



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Figure 3: Plots of water quality parameters and PC1 as a generalised linear model with *Escherichia coli* like response variable.

the natural ranges for aquatic life, drinking water production, irrigation and animal drinking, according to the PWQS and CCME guidelines. However, because none of the physicochemical parameters provide a complete picture of water quality, multivariate statistical methods and water quality index were used in this study. The CCME-WQI integrates the results of the evaluated parameters into a single score in time and space, which makes it possible to view water quality in terms of a numerical value and classify it for possible water use. The PCA revealed the importance of certain physicochemical parameters for water quality. Also, the generalised linear model showed strong significant positive relationships (p < 0.001) of *E. coli* with Fe, nitrate, Cu and TDS. While the water pH showed a strong significant negative relationship (p < 0.001), denoting a higher concentration of E. coli to waters with acidic tendency.

In general, the CCME-WQI showed the water bodies in the upper reaches of the Cunas River as good water quality (87.07), in the middle reaches as favourable water quality (67.65), and in the lower reaches as poor water quality (34.86). In the tributary, the CCME-WQI showed the water bodies as having good water quality (82.34). The results of this research can be of great use for the adoption of measures to control the level of pollution in the urban sector of the Cunas River. They also reflect the applicability and necessity of the water quality index in water quality monitoring.

#### **Conflict of Interest**

The authors declare that they have no conflicts of interest.

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