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Assessment of the Water Quality Index of Amazon River Using Chemometrics Method

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ABSTRACT

The objective of this work was to determine a water quality index (WQI), considering the spatial and seasonal variations of the Peixe-Boi River watershed using chemometrics methods. Twenty-eight sampling sites were selected. The elements Ag, Al, B, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Si, Ti, V, and Zn were determined using optical emission spectrometry with inductively activated plasma. (ICP-OES) and physicochemical parameters were evaluated using different techniques. The WQI values in the wet season indicated that 39.3 % of the samples collected had good quality and 60.7 % had excellent quality. In the dry season, the WQI values ranged from “Regular” (10.7 %), “Good” (67.9 %), and “Excellent” (21.4 %). The parameters evaluated were found, on average, by the standards of CONAMA resolution 357/2005 for class 2 freshwater rivers. The WQI are among the most effective ways of communicating water quality information to the public or quality managers.

Keywords - advanced statistical methods, Amazon, water monitoring.

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I. INTRODUCTION

Watersheds are often studied to characterize impacts on surface water quality for human health and/or ecosystem health deficiencies that may be associated with various land-use practices or diffuse sources of contamination [1, 2, 3]. Rivers and streams are the main water resources in the interior for domestic, industrial, and irrigation use, and regular monitoring studies are important to prevent and control water pollution and to have reliable information on the quality of these resources in view of spatial and temporal variations. in surface water hydrochemistry [4, 5, 3].

Multivariate statistical techniques, such as hierarchical cluster analysis (AAH) and principal component analysis (PCA), have been used to characterize and assess surface water quality, because they facilitate the interpretation of complex data matrices and are useful in verifying temporal and spatial variations caused by natural and anthropogenic disasters and factors linked to seasonality [6, 7, 8]. In many studies, these techniques have been effectively used to classify water quality data and detect similarities between samples and variables [9, 4, 10].

In water quality assessment, decision-making based on quality data is a crucial issue that can be compromised by the number of parameters. In general, researchers have compared individual parameters with reference values. However, this language is very technical and does not provide a complete picture of water quality [11]. To solve this problem, it was made a pioneering attempt to describe water quality as a Water Quality Index (WQI), which was improved by the National Sanitation Foundation (NSF) using the Delphi technique [12]. The WQI is a mathematical tool that integrates complex data into a numerical score that describes water quality under different environmental conditions. Subsequently, considerable advances were made on the basis of the WQI principle using slightly modified [13, 14, 15].

The basic differences between these indices are the path for their development, the sub-index, and the aggregation function. However, these indices may exhibit discrepancies, allowing the assignment of a quality value with a limited number of parameters. These discrepancies are the failure to deal with uncertainty and imprecision in decision-making and the limitations of aggregation functions that can occasionally mask the development of problems associated with trends in one of the quality measures in the index [13, 16].

In the present work, the objective was to apply chemometric methods for the elaboration of the surface water quality index of the Peixe-Boi River, evaluating the spatial and seasonal variations of chemical, physical-chemical parameters, and trace elements.

II. METHODOLOGY

2.1 Study area

The study area belongs to the Northeast Amazon, State of Pará Mesoregion in the Bragantina microregion (Fig. 1).

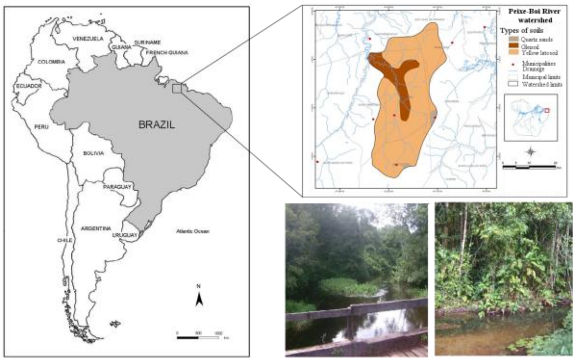

Figure 1. Location map of the Peixe-Boi River watershed [17, 18].

The Peixe-Boi River has a hydrographic system whose main drainage is the Peixe-Boi River, which is about 70 km long, and it has sufficient potential for the expansion of ecotourism and leisure, in addition to serving public supply, and for these reasons, it is characterized as a rural watershed [19, 20].

2.2 Sampling and laboratory procedures

Twenty-eight sampling sites were selected from the rivers and streams that make up the Peixe-Boi River, carried out from May to November 2010, including the wet and dry seasons. The sampling locations were managed through the GPS (Global Positioning System).

In the field, temperature, electrical conductivity (EC), total dissolved solids (TDS), salinity, chlorides, dissolved oxygen (DO), turbidity, and chlorophyll-a data were obtained using an YSI 6600 multiparameter probe.

The pH was measured using a Handylab 1 potentiometer. To determine the chemical oxygen demand (COD) the closed reflux method was used - titration according to NBR 10357 of the Brazilian Association of Technical Standards [21].

The chemical elements (Ag, Al, B, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Si, Ti, V, and Zn) were analyzed simultaneously using the ICP-OES (Vista Pro - Varian) with axial configuration. Before the analysis, analytical programs were developed to determine all elements of interest using the analytical curve method through the use of multi-element standard solutions.

The quality control of the determinations was performed by analyzing the reference sample with the NIST⁄SRM-1640 (National Institute of Standard and Technology) certificate of trace elements in natural water to evaluate the accuracy of the method. The standard recovery showed that the method is adequate in the analysis of the evaluated elements with recoveries ranging from 76.3% (Mn) to 103.2% (Na).

2.3 Statistical analysis

The data obtained were analyzed by descriptive statistics and multivariate (PCA and HCA) with the help of SPSS (Statistical Package for the Social Sciences) and Minitab 14 computer applications.

2.4 Water Quality Index - WQI

To calculate the WQI, three steps were followed [13]. In the first step, each of the 29 parameters was assigned a weight (wi) according to its relative importance in the overall water quality. The maximum weight of five was assigned to parameters with great importance in the quality of the water assessment. Minimum weight of one was assigned to parameters that played a less significant role in the assessment of water quality.

In the second step, the relative weight (Wi) was calculated using equation below (1), where Wi is the relative weight, wi is the weight that was assigned to each parameter and n is the number of parameters.

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i}$$

In the third step, a quality assessment scale (qi) was assigned to each parameter, dividing the concentration of each water sample by its standard according to the respective orientation established in CONAMA resolution nº 357/200522, and the result was multiplied by 100 as shown in equation below (2), where qi is the quality assessment, Ci is the concentration of each chemical parameter in each water sample in mg.L^{-1}, and Si is the water quality standard for each parameter chemical in mg.L^{-1}.

$$q_i = (C_i / S_i) \times 100$$

To calculate WQI, SIi was first determined for each chemical parameter (3) and then used to determine WQI by (4) where SIi is the subscript of parameter i.

$$SI_i = W_i \times q_i$$

$$IQA = \sum SI_i$$

The calculated WQI values were classified into five categories as shown in Table 1.

Table 1. Water quality classification [13]

WQI	Water quality
< 50	Excellent
50-100	Good
100-200	Regular
200-300	Poor
> 300	Very poor

III. RESULTS AND DISCUSSION

3.1 Descriptive statistical analysis

The results of the statistical analyzes for all water quality parameters measured during the wet and dry seasons are shown in Table 2, together with the values established for some parameters by CONAMA Resolution 357/2005.

The results found in this work for pH are compatible with several studies in rivers in the Amazon region that show a tendency toward slightly acidic pH, without damage to the aquatic environment [23, 24, 3], revealing a need to make the adoption of parameters and quality standards compatible with the characteristics of Amazonian ecosystems more flexible.

The increase in conductivity, turbidity, and TDS may be related to domestic sewage discharges and/or sediment resuspension.

The decrease in dissolved oxygen near the spring may be due to the large presence of aquatic plants that consume dissolved oxygen from the liquid medium. Aquatic plants increase the productivity of the water body causing an increase in the concentration of heterotrophic bacteria, which feed on organic matter and other dead microorganisms [25].

Table 2. Results of the descriptive statistical analysis for the parameters (wet and dry season).

Variables	**Wet season**			**Dry season**			**Conama 357/2005**
	Mín.	**Max.**	**Mean±SD**	**Mín.**	**Max.**	**Mean±SD**	
Temperature	24.9	31.3	26.8±1.98	24.4	33.7	27.4±1.79	-
Electric conductivity	5.10	522	97.5±90.0	12.8	1071	134±191	-
Salinity	0.010	0.340	0.050±0.052	0.010	**0.530**	0.060±0.093	≤0.5
Turbidity	0.100	**359**	11.7±40.3	0.100	**917**	30.8±122	≤100
Chlorophyll a	0.010	**562**	17.0±85.5	0.010	**563**	**39.4±135**	≤30
pH	**4.18**	7.67	6.06±0.810	**4.44**	7.57	6.30±0.865	6.0 - 9.0
Total Dissolved Solids	16	339	61.5±56.3	8.00	**696**	82.3±122	≤500
Dissolved oxygen	**1.33**	14.4	6.90±2.26	**3.03**	14.16	5.64±1.43	≥5.0
Chlorides	0.001	12.7	1.42±2.52	0.001	0.540	0.167±0.079	≤250
Chemical oxygen demand	2.88	155	24.6±31.0	9.13	293	26.1±42.45	-
Ag	0.002	**0.052**	**0.014±0.013**	0.002	**0.025**	0.004±0.005	≤0.01
Al	0.002	**0.152**	0.030±0.030	0.002	**0.400**	0.072±0.053	≤0.1
B	0.0002	0.205	0.008±0.028	0.0002	0.387	0.157±0.073	≤0.5
Ca	0.000001	0.990	0.390±0.302	0.042	0.994	0.361±0.233	-
Co	0.020	0.038	0.020±0.004	0.0008	0.050	0.015±0.015	≤0.05
Cr	0.0001	0.022	0.0006±0.003	0.0001	0.008	0.005±0.002	≤0.05
Cu	0.00007	**0.047**	**0.010±0.010**	0.00007	**0.019**	0.007±0.003	≤0.009
Fe	0.007	**0.416**	0.090±0.086	0.003	**0.390**	0.067±0.078	≤0.3
K	0.029	0.965	0.310±0.195	0.043	0.906	0.260±0.174	-
Mg	0.000003	0.976	0.350±0.269	0.100	0.920	0.420±0.236	-
Mn	0.020	0.059	0.020±0.005	0.000002	0.020	0.004±0.008	≤0.1
Na	0.000001	0.996	0.320±0.330	0.101	0.990	0.519±0.318	-
Ni	0.002	**0.028**	0.006±0.005	0.002	**0.035**	0.004±0.005	≤0.025
P	0.012	**0.185**	0.060±0.033	0.012	**0.358**	0.096±0.079	≤0.1
Pb	0.0096	**0.052**	**0.020±0.013**	0.010	**0.370**	**0.095±0.107**	≤0.01
Si	0.000003	0.856	0.410±0.170	0.015	0.825	0.241±0.145	-
Ti	0.026	0.154	0.030±0.014	0.009	0.033	0.013±0.007	-
V	0.036	0.052	0.040±0.002	0.015	0.042	0.021±0.008	≤0.1
Zn	0.0007	**0.275**	0.010±0.039	0.0007	**0.806**	0.014±0.088	≤0.18

The COD is widely used to determine the concentrations of residues and is applied primarily to mixtures of pollutants, in this work there was no increase of the parameter beyond the maximum values allowed, indicating the little influence of organic matter in the Peixe-Boi River.

Other parameters such as Chloride, Salinity, Chlorophyll and the chemical elements evaluated did not present high values and show that the Peixe-Boi River presents characteristics of a preserved location.

3.2 Multivariate analysis

3.2.1 Principal Component Analysis (PCA)

The plot of weights for the selected principal components is illustrated in Fig. 2a and PC1 can be interpreted as a gradient between conductivity (0.964), TDS (0.956), and salinity (0.940). PC2 represents Mn (0.893) and V (0.913) at the negative end. The first component (PC1) explained 98.64% of the total variance, while the second component (PC2) explained 1.36%.

The ordering diagram from the scores obtained from the PCA for the 168 samples (Fig. 2b), reveals a separation of the samples, with the PC1 scores at the positive end corresponding to the samples collected during the dry season and the PC2 scores in the negative end, corresponding to the samples analyzed in the wet season.

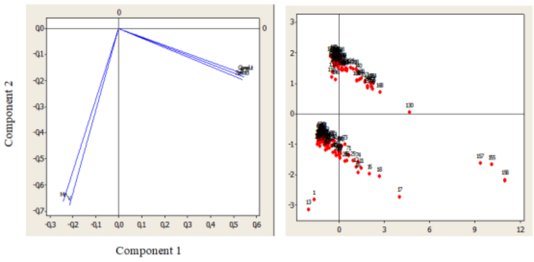

Figure 2. (a) Weights of variables in the first two principal components and (b) Ordering diagram in the first two principal components.

3.3 Hierarchical Cluster Analysis (HCA)

Hierarchical clustering was performed using Euclidean distance as a measure of similarity. The dendrogram for the variables selected by the PCA is illustrated in Fig. 3 which was divided into two groups. Cluster 1 corresponded to the analyzes carried out in the wet season, while cluster 2 included the samples collected in the dry season.

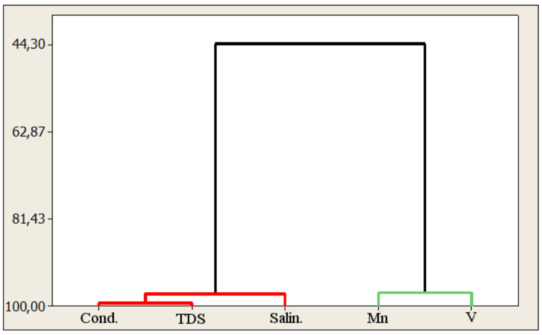

Figure 3. Dendrogram based on hierarchical clustering based on PCA scores. Legend: Cond.: Conductivity; TDS: Total Dissolved Solids; Salin.: Salinity

Cluster analysis revealed different properties at each site concerning chemical variables and metals.

Thus, it became evident that the hierarchical clustering technique is reliable in classifying surface waters throughout the region and it is possible to design a sampling strategy in the best possible way. In this way, the sampling frequency and the number of monitoring sites can be reduced without losing any meaning of the result. Several reports have successfully applied this approach in water quality assessment program [26, 10, 15].

3.2.2 Water Quality Index of the Peixe-Boi River

Table 3 shows the relative weights of the physical-chemical parameters and chemical elements used to calculate the water quality index.

The maximum weight of 5 was assigned to parameters such as electrical conductivity, salinity, total dissolved solids (TDS), manganese, and vanadium because they are of great importance in the assessment of water quality for the region in question.

Parameters such as chlorophyll a, copper, and nickel were given the minimum weight of 1, as they demonstrated an insignificant role in the assessment of local water quality. The other parameters weighted 1 and 5 depending on their importance in determining water quality.

Table 3. Relative weights of physical-chemical parameters and chemical elements.

Parameters	**Weights (wi)**	**Relative weights**	**Parameters**	**Weights (wi)**	**Relative weights**
TDS	5	0.089	Co	2	0.036
Salinity	5	0.089	Cr	2	0.036
OD	3	0.054	Cu	1	0.018
Turbidity	2	0.036	Fe	3	0.054
Chlorides	3	0.054	Mn	5	0.089
Chlorophyll a	1	0.018	Ni	1	0.018
pH	2	0.036	P	2	0.036
Ag	4	0.071	Pb	2	0.036
Al	4	0.071	V	5	0.089
B	2	0.036	Zn	2	0.036
				$\sum w_i = 56$	$\sum W_i = 1.000$

Table 4. Results of the WQI and Water Quality

Wet season			**Dry season**		
Location	**WQI**	**Quality**	**Location**	**WQI**	**Quality**
APS1	71.2	Good	APS1	66.6	Good
ABS	56.2	Good	ABS	61.6	Good
AFS	47.9	Excellent	AFS	31.0	Excellent
ANS	48.1	Excellent	ANS	54.2	Good
APS2	44.3	Excellent	**APS2**	**152**	**Regular**
BFS	48.8	Excellent	BFS	74.4	Good
BGS	61.4	Good	BGS	34.1	Excellent
BIS	52.8	Good	BIS	95.9	Good
CNR1	43.4	Excellent	CNR1	70.5	Good
CNR2	51.5	Good	CNR2	53.4	Good
CPR	51.1	Good	CPR	89.1	Good
JBR	40.1	Excellent	JBR	93.4	Good
LGN	47.2	Excellent	LGN	74.7	Good
PBR1	42.9	Excellent	PBR1	31.3	Excellent
PBR2	33.5	Excellent	**PBR2**	**110.6**	**Regular**
PBR3	40.5	Excellent	PBR3	32.2	Excellent
PBR4	36.3	Excellent	PBR4	62.9	Good
PBR5	44.2	Excellent	**PBR5**	**103**	**Regular**
PBR6	47.9	Excellent	PBR6	68.3	Good
PDR1	55.7	Good	PDR1	60.4	Good

PDR2	50.2	Good	PDR2	54.3	Good
PNS	39.0	Excellent	PNS	57.6	Good
SNS	50.2	Good	SNS	91.2	Good
TBS	62.3	Good	TBS	58.3	Good
TTS	37.5	Excellent	TTS	39.0	Excellent
UBS	41.1	Excellent	UBS	65.3	Good
UCS1	45.3	Excellent	UCS1	77.5	Good
UCS2	50.4	Good	UCS2	49.8	Excellent

The results for the water quality index proposed for the Peixe-Boi River are shown in Table 4. WQI values were obtained in the range of 33.54 to 71.23 (wet period) and from 30.97 to 152 (dry period) and, therefore, classified into three types of water according to quality: excellent, good, and regular.

In all sampling locations, the water quality was good or excellent in both seasonal periods, except for points APS2 (WQI=152) and PBR5 (WQI=103) which in the dry period presented regular water quality.

In most of the samples, about 60.7% showed “Excellent” quality water and 39.3% of the collected samples showed “Good” quality in the wet season. This situation can be attributed to the dilution effect that occurs due to the increase in the flow of water courses and the consequent reduction in the concentration of contaminants27. In the dry season, the WQI values ranged from “Regular” (10.7%), “Good” (67.9%), and “Excellent” (21.4%).

Because of the results, it can be considered that the water courses evaluated presented satisfactory characteristics in terms of water quality, except in three sampling sites that presented WQI greater than 100.

It was possible to verify through multivariate analysis the importance of some water quality parameters and how they interfere with the WQI.

The water quality index (WQI) has proved to be a good tool for interpreting variations in water quality in various seasonal seasons and has been widely used by other author [13, 28, 15].

IV. CONCLUSIONS

In this study, different multivariate statistical techniques were used to assess variations in surface water quality in the Peixe-Boi River. Cluster analysis of the 28 sampling sites resulted in five groups according to similar water quality characteristics. Based on the information obtained from this study, it is possible to devise an ideal sampling strategy, resulting in a reduced number of sampling sites. PCA helped to identify the factors responsible for water quality variations. The water quality of the evaluated watercourses was, in general, acceptable, as the WQI values varied between 30.97 and 152.02 during the monitoring period. The results obtained showed a punctual increase in WQI values during the dry season.

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