Chemometrics Applied in the Development of a Water Quality Indicator System for the Brazilian Amazon

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ABSTRACT: The objective of this work was to develop a method to calculate the water quality index (WQI) using chemometric methods. The study was carried out at the Cururú-Una hydroelectric power plant in the state of Pará in the Brazilian Amazon. Eight collection stations in four periods (winter, intermediate I, summer, and intermediate II) and 29 parameters were selected. Multivariate analysis was applied to the results to verify the quality of the data and to select the most sensitive variables to be used as indicators for the WQI calculation. The 10 parameters selected were $E_{h}$, dissolved oxygen, total dissolved solids, chlorophyll $a$, phosphate, Ba, Ca, Fe, Na, and Sn. The WQI proposed herein was effective in the classification of water quality for the periods analyzed.

1. INTRODUCTION

Rivers and lakes near urban areas undergo continuous, daily contamination from a significant amount of effluents produced in the nearby regions, generating a high environmental risk for all life types that depend on water matrices.1 The introduction of pollutants such as toxic elements, hydrophobic organic compounds, and pathogenic organisms is a major environmental concern worldwide and thus a problem for the finite freshwater resources existing on our planet.2

The Amazon, about two-thirds of which lies in Brazilian lands, is being extensively used for the construction of hydroelectric dams, with plans in place to construct large and medium reservoirs on nearly all the tributaries of the Amazon River.3,4 Because of the way in which dams are built in the Amazon, these ventures cause significant socioenvironmental problems, which are compounded by the fact that the Amazon is a crucial biome for biodiversity conservation and global climate balance. Several of the problems arising directly and indirectly from the anthropogenic activity in these environments are caused by flooding without forest clearing, which results in the release of large amounts of greenhouse gases into the atmosphere, mercury methylation in water,5 contamination of fauna and flora,6 displacement of indigenous populations, and more.7

As a result of the anthropogenic pressure placed on this region, more and more studies are being conducted to monitor environmental impacts and to find ways to minimize these impacts.8 Because of the significant increase in the demand for water for human consumption, one of the most threatened ecosystems is inland waters. This has created the need to find improved ways of preserving these ecosystems, which are essential to biodiversity conservation. One way to evaluate the influence of anthropogenic actions on water resources is through the water quality index (WQI). Here, we suggest the use of a series of WQIs, coupled with mathematical and statistical methods, to provide a better analysis of the situation faced by inland waters, which are the most diverse water bodies found. With this, many important decisions are being made to protect these resources and better distribute them all over the planet.9

One of the first review papers was that of Ott (1978),10 which described the WQIs used in the USA and included detailed discussions on the practices and theories of environmental indices. Also, in the USA, in partnership with the National Sanitation Foundation (NSF), Brown et al. (1970)11 developed an index that was widely accepted until the end of the 1980s. The variables used for calculating the index were

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The objective of this work was to develop a methodology for creating a WQI in the evaluation of Amazonian water bodies based on the chemometric analysis of chemical and physicochemical parameters in water samples collected in the reservoir of the hydroelectric power plant, Curuá-Uná in Santarém-PA.

2. RESULTS AND DISCUSSION

Construction of the WQI for the Curuá-Uná hydroelectric power plant (HPP) required illustrating how the principal components (PCs) would be formed by verifying the results obtained and thus selecting the most significant parameters using two fundamental factors: correlation of the most significant parameters and the analysis through the new method. Using these, it was possible to define which parameters would have a greater influence on the construction of the PCs and thus on the construction of the WQI for the UHE Curuá-Uná. Table 2 shows data from the single-factor analysis of variance (ANOVA) test.

| parameter | p value | parameter | p value |
|-----------|---------|-----------|---------|
| transparency (m) | 0.030 | chlorides (mg L$^{-1}$) | 0.731 |
| temperature (°C) | 0.131 | nitrate (mg L$^{-1}$) | 0.549 |
| pH | 0.717 | chlorophyll a (mg L$^{-1}$) | 0.505 |
| $E_h$ (mV) | 0.915 | phosphate (mg L$^{-1}$) | 0.450 |
| DO (mg L$^{-1}$) | 0.907 | apparent color (Pt–Co) | 0.517 |
| turbidity (NTU) | 0.040 | true color (Pt–Co) | 0.373 |
| TDS (mg L$^{-1}$) | 0.844 | COD (mg L$^{-1}$) | 0.978 |
| conductivity ($\mu$S cm$^{-1}$) | 0.740 | NH$_4^+$ (mg L$^{-1}$) | 0.744 |

**Note:** DO: dissolved oxygen; TDS: total dissolved solids; COD: chemical oxygen demand; NTU: nephelometric turbidity units; and Pt–Co: platinum–cobalt units.

2.1. Principal Component Analysis. Principal component analysis (PCA) is widely used to facilitate the interpretation of certain complex data. Thus, it is possible to summarize the statistical correlation among certain physicochemical variables and metal concentrations where the type and magnitude of results can vary widely and where very large results can possibly influence how the WQI can be constructed. These large values are normalized to decrease their influence amongst the remaining variables and present equivalent amounts. Table 3 shows the eigenvalue correlation matrix, variance, and total variance of the PCs with all parameters evaluated for the locality.

Table 4 shows the values of the weights obtained by the analysis of the main components for all parameters evaluated in the surface water samples collected at the Curuá-Uná HPP in four periods.

With these results, a graph of the weights of all 29 parameters evaluated by PCA and applied for the water samples of the Curuá-Uná HPP was produced (Figure 1).
Through the PCA analysis, results obtained by the correlations, and ANOVA tests, it was possible to determine the most important parameters. The factors with the greatest influence on these tests, except those determined during the weight and score evaluations in the first two components (PC1 and PC2), were chosen. Parameters which did not provide significant information, including those which overlapped the most important elements, were removed from the analysis, as they illustrated the same information as the elements that provided the most significant information. Thus, 10 parameters were determined in the surface samples from the Curuá-Una HPP and used to perform a new PCA test with the aim of demonstrating the correlation matrix of eigenvalues, variance, and total variance. With this, it was possible to obtain a new PCA statistic with 71.1% of information on the first two components shown in Table 5.

It was concluded that the 10 parameters selected provided the same information as the 29 previously selected parameters for the collected water samples. Table 6 shows the variance in the parameters selected by the multivariate analysis in Curuá-Una.

Figure 2 shows the weights of the 10 parameters selected by the PCA applied to the dataset. A similar behavior was observed for the analysis performed with the 29 parameters. It was further observed that the analyzed parameters presented a difference in their values, presenting a significant dispersion, which can be an indication that seasonality is a factor of great relevance for the water dynamics in the region.

2.2. WQI for UHE Curuá-Una. The quality index proposed in this work was calculated from a point of view that matches the present reality in the locality with the use of the Curuá-Una HPP. Although all the analysis results were analyzed by the PCA, the WQI calculations only considered the 10 most

Table 3. Eigenvalue Correlation Matrix

|   | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
|---|------|------|------|------|------|------|------|------|------|
| eigenvalues | 7.7580 | 4.6275 | 4.2386 | 2.5537 | 1.8023 | 1.2367 | 1.1581 | 0.9337 | 0.6273 |
| variance    | 0.227 | 0.165 | 0.151 | 0.091 | 0.064 | 0.044 | 0.041 | 0.033 | 0.6273 |
| cumulative variance | 0.227 | 0.442 | 0.594 | 0.685 | 0.749 | 0.793 | 0.835 | 0.905 | 0.905 |
| eigenvalues  | 0.6273 | 0.4241 | 0.3719 | 0.3127 | 0.2048 | 0.1810 | 0.1330 | 0.1044 | 0.137 |
| variance    | 0.022 | 0.015 | 0.013 | 0.011 | 0.007 | 0.006 | 0.005 | 0.004 | 0.051 |
| cumulative variance | 0.928 | 0.943 | 0.956 | 0.967 | 0.975 | 0.981 | 0.986 | 0.990 | 0.990 |
| eigenvalues  | 0.0914 | 0.0719 | 0.0451 | 0.0286 | 0.0260 | 0.0145 | 0.0086 | 0.0052 | 0.051 |
| variance    | 0.003 | 0.003 | 0.002 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.019 |
| cumulative variance | 0.993 | 0.995 | 0.997 | 0.998 | 0.999 | 0.999 | 1.000 | 1.000 | 1.000 |

Table 4. Weights of the Parameters Evaluated by the PCA

| variables | PC1 | PC2 | variables | PC1 | PC2 |
|-----------|-----|-----|-----------|-----|-----|
| transparency | −0.133 | −0.222 | COD | 0.137 | −0.148 |
| temperature | −0.244 | −0.169 | NH₄⁺ | 0.051 | 0.110 |
| pH | 0.227 | −0.012 | Ag | 0.119 | −0.063 |
| Eh | −0.028 | 0.362 | Ba | 0.322 | −0.113 |
| DO | 0.083 | −0.371 | Be | 0.160 | −0.253 |
| turbidity | 0.255 | 0.011 | Ca | 0.218 | 0.110 |
| TDS | 0.071 | 0.434 | Fe | 0.307 | −0.042 |
| conductivity | 0.093 | 0.419 | K | −0.029 | −0.039 |
| chlorides | −0.030 | 0.175 | Mg | −0.037 | −0.036 |
| nitrate | 0.101 | −0.102 | Mn | −0.063 | 0.026 |
| chlorophyll a | −0.215 | 0.039 | Na | 0.179 | 0.266 |
| phosphate | 0.314 | −0.018 | Sn | 0.283 | 0.006 |
| apparent color | 0.268 | −0.055 | Sr | −0.063 | −0.048 |
| true color | 0.312 | −0.061 | Ti | −0.177 | −0.153 |

**DO**: dissolved oxygen; **TDS**: total dissolved solids; and **COD**: chemical oxygen demand.

Through the PCA analysis, results obtained by the correlations, and ANOVA tests, it was possible to determine the most important parameters. The factors with the greatest influence on these tests, except those determined during the weight and score evaluations in the first two components (PC1 and PC2), were chosen. Parameters which did not provide significant information, including those which overlapped the most important elements, were removed from the analysis, as they illustrated the same information as the elements that provided the most significant information. Thus, 10 parameters were determined in the surface samples from the Curuá-Una HPP and used to perform a new PCA test with the aim of demonstrating the correlation matrix of eigenvalues, variance, and total variance. With this, it was possible to obtain a new PCA statistic with 71.1% of information on the first two components shown in Table 5.

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2.2. WQI for UHE Curuá-Una. The quality index proposed in this work was calculated from a point of view that matches the present reality in the locality with the use of the Curuá-Una HPP. Although all the analysis results were analyzed by the PCA, the WQI calculations only considered the 10 most
important parameters. Parameters that presented greater importance (a greater percentage of variance) during the PCA analysis received the maximum weight value of "5", while those that presented a role of lesser importance (lower percentage of variance) were less determining during the statistical treatment and received the minimum weight of "1". Parameters with intermediate importance were weighted between 1 and 5, depending on their importance (percentage of veracity) in the determination of water quality.

Table 7 shows the weights (w) and relative weights (W) attributed to the physicochemical parameters and the limits of CONAMA Resolution no. 357/2005, which were used to calculate the surface WQI of the Curuá-Una reservoir. The results obtained for the proposed quality index for the Curuá-Una reservoir are presented in Table 8. According to Sahu and Sikdar (2008), the quality index can be classified as excellent (WQI ≤ 50), good (50 < WQI ≤ 100), regular (100 < WQI ≤ 200), and bad (200 < WQI ≤ 300).

The results of this study suggest that the WQI values varied from 37.7 to 106.26, corresponding to three types of water quality: excellent, good, and regular. The samples from the winter and intermediate I periods showed good water quality, with only one season (J1) being of regular quality in both journals. It is possible that runoff caused by rains can transport pollutants from the land to rivers. In addition, the displacement of the soil due to the rain influences the silting of the rivers, further damaging the water quality.

The summer and intermediate II periods corresponded to good and excellent WQIs. This was especially true for the intermediate II collections, where five collection points had an excellent WQI. Because of the seasonal reduction of rain, a reduction in river flow occurred, and we observed an increase in the concentration of the analyzed parameters, which directly influenced our results. These observations suggest that seasonality is an important parameter for the water quality of the Curuá-Una HPP.

These results suggest that the water quality of the samples analyzed from the Curuá-Una HPP exhibited satisfactory characteristics. Not only are aquatic environments that present WQI evaluations between good and excellent able to sustain a great diversity of aquatic life but their waters can also be satisfactorily used for all forms of use, including human consumption. The water that was evaluated as being of regular quality in the winter and intermediate I periods may harbor reduced diversity and may also present an increased algal population.

3. CONCLUSIONS

Based on our results, we were successful in developing a method to effectively calculate the WQI of the waters of the Amazon River using the chemical and physicochemical parameters presented here. Analysis of the main components helped us to identify the primary parameters responsible for variations in water quality. The PCA, ANOVA tests, and
Table 7. Weights ($w_i$) and Relative Weights ($W_i$) Assigned to the Variables Used in the Calculation of the WQI

| parameters | CONAMA 357/2005 (assigned values) | weights ($w_i$) | relative weights <keep-together-$W_i = w_i/\sum w_i$> |
|------------|----------------------------------|-----------------|-----------------------------------------------|
| transparency | 3                                | 0.034091        |
| temperature | 4                                | 0.045455        |
| pH         | 7                                | 0.045455        |
| $E_h$      | 4                                | 0.045455        |
| DO         | >0.5 mg L$^{-1}$                 | 5               | 0.056818                                      |
| turbidity  | 100 UNT                          | 3               | 0.034091                                      |
| TDS        | 500 mg L$^{-1}$                  | 5               | 0.056818                                      |
| conductivity | 3                                | 0.034091        |
| chlorides  | <250 mg L$^{-1}$                 | 2               | 0.022727                                      |
| nitrate    | <10 mg L$^{-1}$                  | 2               | 0.022727                                      |
| chlorophyll $a$ | <30 μg L$^{-1}$       | 4               | 0.045455                                      |
| phosphate  | 5                                | 0.056818        |
| apparent color | <75 mg pt L$^{-1}$          | 3               | 0.034091                                      |
| COD        | 2                                | 0.022727        |
| NH$_4^+$   | 2                                | 0.022727        |
| Ag         | <0.01 mg L$^{-1}$                | 1               | 0.011364                                      |
| Ba         | 0.7 mg L$^{-1}$                  | 5               | 0.056818                                      |
| Be$^+$     | 0.04 mg L$^{-1}$                 | 3               | 0.034091                                      |
| Ca         | 5                                | 0.056818        |
| Fe         | 0.3 mg L$^{-1}$                  | 5               | 0.056818                                      |
| K          | 1                                | 0.011364        |
| Mg         | 1                                | 0.011364        |
| Mn         | 0.1 mg L$^{-1}$                  | 1               | 0.011364                                      |
| Na         | 4                                | 0.045455        |
| Sn         | 4                                | 0.045455        |
| Sr         | 1                                | 0.011364        |
| Ti         | 3                                | 0.034091        |

$\sum w_i = 88 \quad \sum W_i = 1.000$

“DO: dissolved oxygen; TDS: total dissolved solids; and COD: chemical oxygen demand.

correlations were able to identify the essential parameters needed to construct a quality index for the region. Therefore, we suggest that the parameters selected here for the construction of the WQI were representative of an environmental analysis of the study area.

The WQI proposed in this study proved to be effective, as it was able to perform an analysis of the quality of the water resources present in the Curuá-Una HPP region, where it was possible to classify the waters as excellent, good, and regular. Results from the summer and intermediate II periods showed an improvement in the water quality of the region compared to the winter and intermediate I periods, in which there was a decrease in water quality, suggesting that the seasonality of the locality directly influences the quality of the waters in the region.

4. METHODS

4.1. Study and Sampling Area. The Curuá-Una HPP is located 70 km south of the city of Santarém on the Curuá-Una River, a tributary of the right bank of the Amazon River. The UHE Curuá-Una is about 850 km straight to the west of the state capital. Its geographic coordinates are 2°24′52″ S and 54°42′36″ W.

The Curuá-Una River provides several uses; the predominant activity is the generation of energy. Most of the populations in the evaluated area do not use river water but use well water for consumption, personal hygiene, cooking, and other uses. Small riverside communities use the river water for consumption, with simplified treatment, usually filtering and use of sodium hypochlorite; they also use it for irrigation and other uses.

The Curuá-Una HPP is located in the Amazonian plateau, on tertiary clastic sedimentary terrains of the barrier and quaternary formation. Water collection was performed quarterly according to periods of high and low rainfall and during two intermediate periods for the North region, in eight collection stations (winter, intermediate I, summer, intermediate II), as recommended by Standard Methods. The samples were collected in a 5 L vertical Hale bottle and georeferenced through a global positioning system, as shown in Figure 3. After collection, the samples were filtered on GPF (Millipore 0.45 μm) membranes using vacuum filtration. Samples for metal testing were acidified to pH < 2 with

Table 8. WQI by the Collection Station—Curuá-Una HPP

| sampling station | WQI | water quality | sampling station | WQI | water quality |
|------------------|-----|---------------|------------------|-----|---------------|
| Winter           |     |               | Summer           |     |               |
| amount 1 (M1)    | 97.47 | good         | amount 1 (M1)    | 68.40 | good         |
| amount 3 (M3)    | 78.94 | good         | amount 3 (M3)    | 91.18 | good         |
| amount 4 (M4)    | 90.50 | good         | amount 4 (M4)    | 79.60 | good         |
| amount 7 (M7)    | 80.92 | good         | amount 7 (M7)    | 97.70 | good         |
| amount 8 (M8)    | 96.34 | good         | amount 8 (M8)    | 82.14 | good         |
| escape channel (CF) | 89.92 | good         | escape channel (CF) | 71.25 | good         |
| downstream 1 (J1) | 106.26 | regular      | downstream 1 (J1) | 83.24 | good         |
| downstream 2 (J2) | 90.08  | good         | downstream 2 (J2) | 76.32 | good         |
| Intermediate I   |     |               | Intermediate II  |     |               |
| amount 1 (M1)    | 98.27 | good         | amount 1 (M1)    | 53.75 | good         |
| amount 3 (M3)    | 87.02 | good         | amount 3 (M3)    | 45.57 | excellent    |
| amount 4 (M4)    | 85.22 | good         | amount 4 (M4)    | 44.14 | excellent    |
| amount 7 (M7)    | 94.91 | good         | amount 7 (M7)    | 59.62 | good         |
| amount 8 (M8)    | 87.71 | good         | amount 8 (M8)    | 54.41 | good         |
| escape channel (CF) | 56.89  | good         | escape channel (CF) | 42.97 | excellent    |
| downstream 1 (J1) | 104.50 | regular      | downstream 1 (J1) | 37.70 | excellent    |
| downstream 2 (J2) | 65.34  | good         | downstream 2 (J2) | 43.29 | excellent    |

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Suprapur (Merck) concentrated nitric acid for further analysis in the Laboratory of Analytical and Environmental Chemistry—LAQUANAM/UFPA.

4.2. Analysis of Environmental Parameters. The following measurements were made at the sampling site using the Hanna multiparameter probe: pH, oxidation potential ($E_h$), temperature, conductivity, total dissolved solids, and DO. Phosphate, apparent color, and true color were determined with Hanna colorimeters. True color was determined after filtration on GFF (Millipore 0.45 μm) membranes using vacuum filtration. The turbidity was assessed using a Policontrol turbidimeter (model Ap2000), and transparency was measured with a Secchi disk. Chloride and nitrate were determined using a potentiometer (Hanna).

Phytoplankton biomass was measured in terms of chlorophyll $a$ (μg m$^{-3}$) by the method suggested in Technical Standard L5.306/2014 via acetone extraction and spectrophotometric readings at 664, 665, and 750 nm. COD and NH$_4^+$ were also determined using methods recommended by Standard Methods. Metal concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

4.3. Quality Control of ICP-OES Analyses. Accuracy of measurements was assessed with the river water standard reference material, NIST SRM 1640. The certified value of elements was compared to the average result obtained from 10 measurements, which gave 92.36–108.00% of recovery. The relative standard deviation was obtained similarly and was between 1.54 and 4.66%. The method was sensitive to the limits of detection (3s level) and quantification limits of elements analyzed at levels of parts per billion (ppb) obtained from measurements of 15 blanks under different conditions. The method was linear in the range of 0.00–2000.00 μg L$^{-1}$ for major elements and 0.00–200.00 μg L$^{-1}$ for the minor and trace elements, with a linear correlation coefficient of 0.9995–0.9999.

4.4. Statistical Treatment. The results obtained were processed according to chemometric methods using software.
Minitab 18. Calculation of the WQI followed three steps. In the first step, a weight (\(w_i\)) was assigned to each of the 29 parameters according to their relative importance to the general quality of water. A maximum weight of “5” was assigned to parameters with great importance in the evaluation of water quality. A minimum weight of 1 was assigned to parameters that played a less-significant role in the assessment. In the second step, this variable was used to calculate the relative weight (\(W_i\)) from eq 1 below, where \(n\) is the number of parameters.

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

(1)

In the third step, a quality assessment scale (\(q_i\)) was assigned to each parameter according to eq 2, where \(C_i\) is the concentration of each chemical parameter in each water sample in mg L\(^{-1}\) and \(S_i\) is the water quality standard of CONAMA Resolution 357/2005,\(^{32}\) with each chemical parameter in mg L\(^{-1}\).

\[
q_i = \left(\frac{C_i}{S_i}\right) \times 100
\]  

(2)

To calculate the WQI, the SI was first determined for each chemical parameter (eq 3), and this value was used to determine the WQI with eq 4, where SI\(_i\) is the subscript of the parameter \(i\).

\[
SI_i = W_i \times q_i
\]  

(3)

\[
IQA = \sum SI_i
\]  

(4)

The calculated WQI values were based on the classification of five categories, as shown in Table 9.

| WQI  | water quality |
|------|--------------|
| <50  | great        |
| 50–100 | good      |
| 100–200 | regular   |
| 200–300 | bad      |
| >300 | terrible    |

“Source: Sahu and Sikdar, 2008.\(^{33}\)"

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**Notes**  
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