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Evaluation of the water quality of the Verde River, Ponta Grossa, PR: a study on the conditions of aquatic life maintenance and the eutrophication process

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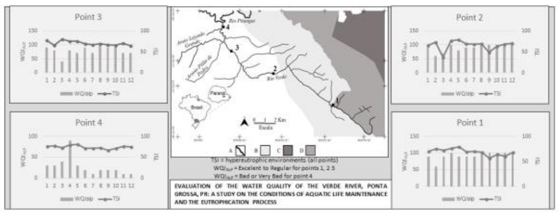
ABSTRACT: This study was to evaluate the physicochemical parameters that express the water quality of the Verde River, in the city of Ponta Grossa, Paraná. Multivariate Analysis was used, and quality indexes were obtained, such as the Trophic State Index (TSI) and the Water Quality Index for Aquatic Life Protection (WQI_{ALP}). River samples were collected at 4 points along the Verde River for 12 months. The results indicated that, at point 4, downstream from the Sewage Treatment Plant (STS), the aquatic environment is very poor for the biota. The calculation of the WQI_{ALP} showed BAD to VERY BAD quality, and the disposal of the effluent was indicated as the cause. It was also concluded that points 1 and 2 correspond to more preserved sites but are not totally favourable to aquatic life either because they receive surface drainage from agricultural areas in the basin. Point 3, of urban character, suffers an impact caused by irregular connections of sewers, and contribution of streams that flow into the river. For all sampling points, TSI > 67 for more than 90% of the samples, indicating hypereutrophic environments throughout the river. The quality indexes applied in this work were faithful to the reality found for the water of the Verde River.



1. Introduction

Even if water is considered a renewable natural resource, the growing impact on natural sources, due to the disordered increasing population density and the many interferences resulting from it, have made the degradation of water resources a public health problem. Improper disposal of domestic and industrial effluent, large-scale use of agricultural input and destruction of riparian forests are examples of anthropogenic pressure which contribute to their degradation[1]. However, when a water body is monitored, there is a great number of parameters to be analyzed, and the interpretation of this data set requires technical knowledge as well as awareness of the current law. Therefore, aiming to help disseminate water quality data, indices can be employed, which represent the consolidation of information from different analyses[2]. Among the quality indices, this work employed WQI_{ALP} (Water Quality Index for Aquatic Life Protection), based on ammoniacal nitrogen and dissolved oxygen (DO), and the TSI (trophic state index) based on phosphorous and chlorophyll concentrations. The integrated evaluation of Verde River also included the determination of 14 physicochemical parameters, studied individually, and their set submitted to multivariate analysis.

Verde River is one of the main tributaries of Pitangui River, a source of water supply to Ponta Grossa, and is in an area classified as “high to extremely high” importance for conservation[3], with its course including the Environmental Preservation Area (EPA) of the Devonian Escarpment and the National Park of Campos Gerais. Therefore, it plays a relevant role in the city of Ponta Grossa. However, it still suffers with the disposal of raw sewage, STS effluents, domestic waste irregular disposal, degradation of the riparian forest and intensive farming activities on its margins. All these activities potentially affect water quality and biodiversity, they decrease the diversity of ecological niches available in the environment and provoke serious damage to the ichthyofauna.

The objective of this work was to express the water quality of the Verde River through quality indexes, calculated from the physicochemical parameters obtained experimentally. We also promote simplified data dissemination and encourage environmental protection actions.

1.1 WQI_{ALP} and TSI

The commonly adopted surface water quality indicators are not directed to the aquatic life maintenance, they usually refer to drinkability criteria and the different uses of water by the population. Taking into consideration the importance of parameters such as DO and ammoniacal nitrogen, Silva and Jardim[4] proposed the WQI_{ALP} in which the numerical value of the index is the lowest normalized value of such parameters. Ammoniacal nitrogen, for example, presents concentrations accepted by the regulations which can be lethal to many aquatic organisms, since legal limits do not consider toxicity to the biota. On the other hand, the biota requires minimum DO levels. According to the United States Environmental Protection Agency (USEPA), a 0 to 2 mg L^{-1}concentration is not enough to keep aquatic life and between 2 and 4 mg L^{-1} DO few fish species can survive[5]. In Brazil, according to the Resolution CONAMA nº 357/05[6] the minimum DO concentration set forth for water Class 2 is 5 mg L^{-1}, which is not enough for many species of the ichthyofauna.

TSI is an indicator of eutrophication, a phenomenon that is characterized by the increase in the nutrient concentration, mainly phosphorous and nitrogen, in aquatic ecosystems, resulting in problems such as algae growth, increase in the organic matter decomposition rate with reduction of dissolved oxygen, and, consequently, water quality deterioration[7, 8]. This index is obtained from the total phosphorous and chlorophyll analyses and was developed to evaluate water quality regarding its enrichment by nutrients and the consequent effect, revealed by the growth of algae or macrophytes, obtaining a classification in different degrees of trophic status. The TSI determination might aid the management of hydric resources, favouring the control of eutrophication, a phenomenon that is of global concern[7, 8, 9].

1.2 Physicochemical parameters and Multivariate analysis

The physicochemical parameters that are used to characterise water quality present great variability over time and space, and it is necessary to keep a continuous monitoring program when the actual quality of superficial water is to be evaluated. From monitoring programs, data sets containing several parameters are obtained, which are measured in different scales and units, which makes their interpretation complex. The Multivariate Analysis is made up by a set of statistical methods able to analyse simultaneously the measures of *n* variables, providing useful results for the understanding of large and complex data sets. Among the multivariate analysis techniques, the Principal Component Analysis, PCA, is widely used in environmental data base analyses[10, 11]. The PCA objective is to reduce the complexity of data making its interpretation easier.

2. Experimental

Searching for differentiated characteristics along the Verde River, this study established four sampling points. Monthly collection of surface water was carried out from May 2016 to April 2017. Polyethylene bottles (1 L) were used and three bottles were collected in each point. The bottles were packet in plastic bags, in portable cool box with ice and transported to the laboratory where they were stored at 4 °C. Aliquots of water samples were immediately filtered in a reduced pressure device, using 0.45 μm cellulose acetate membranes. Analyses regarding DO, temperature, conductivity and turbidity were carried out *in situ*,

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with a portable analyser Lutron, and in the laboratory, following the techniques described in the Standard Methods for the Examination of Water and Wastewater[12], the analyses performed were: total alkalinity, dissolved chloride, total suspended solids (TSS), chlorophyll-a, oxygen biochemical demand (OBD), total phosphorous, total nitrogen and ammoniacal nitrogen. Analytical grade reagents and ultrapure water were used in all analyses.

3. Results and Discussion

The data analysed covered 14 physicochemical parameters, obtained monthly for one year from 4 monitoring points, resulting in 48 samples. Initially, the principal component analysis of the monitored data was carried out aiming at identifying which water quality parameters were more significant in the characterization of the water quality in Verde River.

Table 1. Eigenvalues and total variance explained by the principal components.

Principal component	Eigenvalue	Explained variance (%)	Accumulated explained variance (%)
1	5.956	42.540	42.540
2	1.946	13.900	56.439
3	1.462	10.440	66.879
4	0.995	7.108	73.987
5	0.819	5.851	79.837
6	0.681	4.868	84.705
7	0.576	4.115	88.820
8	0.446	3.186	92.006
9	0.423	3.019	95.025
10	0.247	1.764	96.789
11	0.228	1.626	98.415
12	0.120	0.854	99.269
13	0.064	0.454	99.723
14	0.039	0.277	100.000

To calculate the principal components, the Kaiser criterion was employed, in which the components with eigenvalues higher than 1 were retained[13]. Eigenvalues obtained from the correlation matrix are presented in Table 1 in descending order and define the importance of the principal components, since they correspond to the variance explained by each of them. When the variables present different units and/or when they present magnitude difference, self-scaling is recommended to minimize the dominant effect that one variable might have[14]. Data pre-treatment is fundamental for the success of the multivariate analysis and, it seems relevant to emphasise that for PCA when the correlation matrix is employed, self-scaling can be dismissed. The Program *Statistica*, version 13 was used to analyse the data.

The number of principal components to be retained according to the Kaiser criterion (eigenvalues higher than 1 are retained) were four and, together they explain approximately 74% variance. It seems important to highlight that for the fourth component the eigenvalue 0.995 was considered as 1. This study considered that a correlation equal or over 0.5 would be reasonable to state that the parameters correlated, since this type of data presents natural variability.

The variables influencing each of the 4 principal components are shown in Table 2. The table also shows the total variance explained by the components, so that the evaluation of the importance of each one is presented when explaining the data set collected. When considering one important variable for the composition of the component, the numerical value of the correlation is recommended to be over 0.7.

In the first component, the outstanding variables were total nitrogen, ammoniacal nitrogen, OBD, TSS, alkalinity, total chloride and conductivity, all with a negative signal. This component reflects the water quality for these parameters, lower values indicate better quality. In this component, DO did not reach a correspondence value over 0.7 presenting 0.525 with a positive signal. However, this opposition of signals is justified by the fact that an increase in the OBD and ammoniacal nitrogen

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variables is associated to the presence of organic matter, that is, higher DO consumption. The DO concentration is important for the self-clearing capacity, which is the recovery of balance in the aquatic environment through natural mechanisms. In this sense, the self-clearing capacity of Verde River is related to the characteristic relief, which includes several rapids. Component 1 can be considered an indication of aspects related to organic matter degradation.

Table 2. Weight of the variables in the composition of principal components.

Variable	Factor 1	Factor 2	Factor 3	Factor 4
Water temperature	-0.207	-0.548	0.575	0.093
DO	0.525	-0.478	-0.092	0.251
Cond	-0.825	-0.091	0.163	0.032
Environment temperature	0.175	0.100	0.833	-0.054
Chl	-0.879	0.163	-0.142	0.123
Alkalinity	-0.951	-0.062	0.005	0.030
Turbinity	-0.440	-0.385	-0.430	-0.106
TSS	-0.705	-0.156	0.356	0.001
OBD	-0.855	0.071	-0.097	-0.118
Chlorophyll	-0.185	0.614	-0.004	-0.558
P	-0.073	0.719	0.231	0.115
Total N	-0.946	-0.046	-0.010	0.129
Ammoniacal N	-0.941	-0.079	-0.016	0.005
pH	0.075	-0.538	0.079	-0.733
eigenvalue	5.956	1.946	1.462	0.995
Explained variance (%)	42.5	13.9	10.4	7.1

Component 2 was only formed by the total P content following the correlation criterion over 0.7 and positive. If a value over 0.6 is to be accepted, the variable chlorophyll-a can be aggregated to this component. Component 2 can be considered to express the influence of the farming activity in the neighbourhood of the river and the higher the P content is, the higher the resulting impact is. In component 3, there is also a single variable with correlation over 0.7, which was the environmental temperature. In this component, the hypothesis of accepting a value over 0.6 can also be considered, which would mean that the variable water temperature would also be aggregated. The fourth component presented moderate influence of the variable pH. However, since the data set under analysis involved parameters of natural variability it does not seem reasonable to affirm that the relations between the parameters are strong or weak.

Figure 1 presents the scores for the components 1 and 2 and the samples collected from 4 distinct monitoring points and the formation of some groups as a function of these components can be observed. In component 1, the growing impact in the quality of the Verde River water was verified in all points in the spring-mouth direction. Point 1 is located closer to the spring, in a place called "Capão da Onça", and point 2 in a place called "curva do cemitério", both present preserved margins and clear water. Samples 1-24 (Figure 1) collected from these points, generally presented the highest DO concentrations (> 6 mg L^{-1}) and the lowest dissolved chloride concentrations (< 8 mg L^{-1}), total nitrogen and ammoniacal nitrogen, as well as the lowest OBD, conductivity and total alkalinity (< 24 mg L^{-1}) values, exactly as indicated in the data obtained from the PCA. These are in fact less impacted when compared to points 3 and 4, but still present total phosphorous concentration above the limit set forth in the law, which is 0.1 mg L^{-1}. Despite the river presenting margins apparently preserved in these points, the basin is characterized by farming activities, suggesting that the input of this nutrient in the water body occurs via surface drainage.

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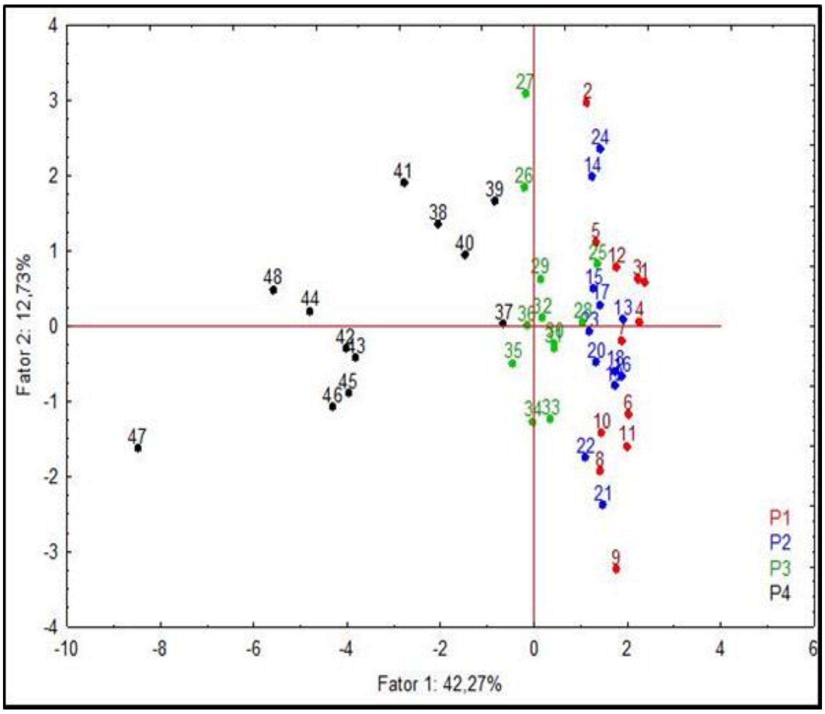

Figure 1. CP1 x CP2 scores of the samples collected in Verde River. ●Collection point 1; ● Collection point 2; ● Collection point 3 and● Collection point 4.

Point 3 (samples 25-36, Figure 1) is located in the place called "Passadouro", in the urban area, after Verde River receives the input of the stream Pilão de Pedra, which crosses the city centre, through an underground gallery, but where irregular links provoke leaking resulting in high pollution indices. This point, according to the parameters, is only less impacted than point 4. It presented, for example, OBD over 3mg L^{-1} in more than 50% of the collections, that is, over the legal limit CONAMA 357/05 for rivers Class 2, in addition to higher turbidity and conductivity than points 1 and 2. The analysis shows that component 1 can differentiate from them by the parameters that indicate the worse quality of the river, considering the way the samples from Point 3 were distributed in the score graph presented in Figure 1. Sample 27 in point 3 was collected in July 2016 and presented high chlorophyll-a content (52.45 µg L^{-1}), for this reason it was separated from the remaining samples of this point in relation to component 2.

Point 4 is located downstream to the Verde River effluent treatment station, around 50 m from the local where the effluent flow into the river, and close to the river mouth which is tributary to the Pitangui River. It is, undoubtedly, the most impacted place in the whole course, with DO below 5 mg L^{-1} in most of the samples and organic matter, represented by the ODB, over 4 mg L^{-1}, even reaching 11.5 mg L^{-1} in December 2016 (sample 44, Figure 1). For the same point 4, the samples collected from June 2016 and September 2016 (samples 38 to 41, Figure 1) presented total P content three times higher on average than samples (42-48, Figure 1) collected in the period from October 2016 to April 2017, being grouped in higher scores in relation to component 2, which represented exactly the P content in the samples.

One characteristic of Verde River, throughout its course, is the presence of rock paved bottom and small rapids, factors that dissimulate the impact when analysed regarding parameters such as DO, turbidity and TSS, and which can also interfere when used to calculate quality indices. Numerous studies have shown that multivariate statistical analysis is useful for the assessment of the spatial water quality variations in a river[15, 16, 17].

3.1 TSI – Trophic state index calculation

Considering the trophic status of its aquatic ecosystem, Verde River is classified, practically in all its points, as eutrophic or superior, with predominance of hypereutrophic features (Table 3). Undoubtedly, the presence of phosphorous was

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determining for this condition. The total phosphorous concentration was mainly above the regulations (0.1 mg L^{-1}) for lotic environments, such as the Verde River. This fact is due to the characteristics of the neighborhood of this river. In points 1 and 2, the presence of farming activities in the basin, and the surface drainage carrying phosphorous into the water. While for the urban area, corresponding to points 3 and 4, the raw sewage and the treatment station effluent in a volume that supersedes its flow and dissolution capacity.

Table 3. Trophic state index for Verde River within 12 months (May-2016 to April-2017).

Points	2016								2017			
	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
P1	70	75	72	76	79	69	70	68	56	64	60	68
P2	66	73	37	77	79	69	68	69	49	63	68	71
P3	78	66	80	75	75	69	67	69	67	66	70	64
P4	76	77	73	80	81	71	72	73	67	71	76	75

Legend: Ultra oligotrophic TSI ≤ 47; Oligotrophic 47 < TSI ≤ 52; Mesotrophic 52 < TSI ≤ 59; Eutrophic 59 < TSI ≤ 63; Super eutrophic 63 < TSI ≤ 67; Hypereutrophic TSI > 67.

As well as the phosphorous, the chlorophyll-a concentration is high in Verde River, close to the limit value 30 µg L^{-1}, or even higher than this limit set forth by the Resolution CONAMA nº 357/05. The results corresponding to chlorophyll-a are considered as a measure of response from the water body to the causing agent, therefore, indicating the level of algae growth in the place. According to Cunha *et al.*[18], eutrophication in would be unusual, due to the characteristics of this system, such as the turbulence, low residence time and continuous community transportation phytoplankton downstream.

3.2 WQI_{ALP}– Water Quality Index for aquatic life protection

When evaluating the parameters used to calculate the WQI_{ALP}, the ammoniacal concentrations of all points were seen to be within the legal limits set forth for rivers Class 2 (3.7 mg L^{-1} para pH ≤ 7.5), since they were below 1.3 mg L^{-1}. However, even in low concentrations, this compound might cause impacts to the biota, regarding chronic toxicity with effects on the reproduction capacity, growth as well as biochemical and physiological changes. In this study, the ammoniacal nitrogen was seen to increase along the river, in the spring-mouth direction, mainly after the STS, where it was up to 100 times higher than the concentrations in Point 3. It is possible to promote the biological removal of nitrogen in treatment systems; however, the efficacy of the removal depends on the efficiency of the STS treatment. Regarding DO, it is a variable whose reduction might affect significantly the aquatic biota, and that in surface waters suffers influence of factors such as temperature and natural oxygenation, as well as the impact of organic matter[19]. The reduction in DO concentrations in point 4 is related to the input of the STS, which impacts the river both for its organic charge and for the disparity between the effluent flow and the river capacity. Despite Verde River having small rapids throughout its course, which increase OD concentration, some samples presented concentrations below 5 mg L^{-1}, that is, this fact can be associated to oxidation processes that consume oxygen, indicating the presence of organic matter associated to the impact in the water body.

The calculation of the WQI_{ALP} (Table 4), where 100 represents the best environmental quality, showed between EXCELLENT and REGULAR quality for points 1 and 2, which were less impacted, but also for point 3, since despite several parameters having pointed its low quality, it presented increased DO qualities due to the river oxygenation. On the other hand, downstream the STS, point 4, presented variation from BAD to VERY BAD, clearly indicating the effluent impact even after treatment. The case study of Wu *et al.*[20] confirmed the hypothesis that water remediation pollutants based on replanting vegetation can alleviate increased pollution and enable rehabilitation of the degraded aquatic ecosystem.

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Table 4. Water quality index for aquatic live preservation in Verde River (May-2016 to Apr-2017).

POINTS	2016								2017			
	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr
P1	90	60	90	100	90	90	90	100	100	100	100	100
P2	100	60	70	100	80	90	90	100	100	100	100	100
P3	90	80	40	80	70	90	70	100	90	100	70	70
P4	30	30	40	90	30	20	10	20	20	20	10	10

The critical situation of Verde River, at this point, in terms of aquatic life maintenance capacity should be highlighted. Its ranking as a Class 2 river requires that the water presents physicochemical characteristics that favor the presence of the river natural biota. The input of the STS is the main cause of the impact, since even if the data gathered indicated that there is monitoring of the effluent in the STS, so that it is following the legal disposal regulations, the impact faced by the river is evident, suggesting that the STS flow is above the river capacity to receive input without changing its class.

4. Conclusions

The trophic state index (TSI) at the points evaluated in Verde River indicated that its eutrophication status tends to hypereutrophication. The highest phosphorous concentrations in the water are associated to the domestic effluent load and the farming activity. The phosphorous and chlorophyll concentrations were over the legal limit set forth by the Resolution CONAMA n° 357 de 2005, for fresh water courses class 2. The results also revealed that the STS represent an impact factor to the Verde River, in conditions that might change the ecological balance, both for the species that occupy the river as their habitat and for other predator species that feed from other living organisms in this river. The WQI_{ALP} results showed the critical situation of the river regarding its capacity of aquatic life maintenance, mainly downstream the effluent treatment station, which disagrees with the law that include the protection of aquatic life among the features of Class 2 waters.

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