

Environment

Water quality of the Atibaia river in the city of Paulínia/SP: evaluation of the Electrical Conductivity and Chloride variables

Qualidade da água do rio Atibaia no município de Paulínia/SP: avaliação das variáveis Condutividade Elétrica e Cloretos

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ABSTRACT

The present study aimed to evaluate the characteristics that most influenced the water quality variability of the Atibaia river in the city of Paulínia/SP, the coordinates of the water collection point are given by 22°44'23"(S) and 47°07'40"(W), in the dry and rainy seasons, from 2006 to 2016. The data used in this study come from the monitoring of parameters carried out in the spring by a research team, accompanied by periodic collections of surface water samples and analyzes laboratory tests. The parameters addressed included: precipitation, temperature, Hydrogenionic potential (pH), turbidity, thermotolerant coliforms (*Escherichia coli* (*E. coli*)), dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total nitrogen (N_{total}), total phosphorus (P_{total}), total dissolved solids (TDS), electrical conductivity (EC) and chlorides (Cl⁻). Water quality was assessed using linear correlation analysis, using the Pearson Correlation coefficient (r), and Multivariate Analysis, using Principal Component Analysis (PCA). The results obtained highlight the influence of EC, Cl⁻, P_{total}, DO, pH, COD, turbidity and temperature on the water quality variability of the Atibaia river in the dry season, and EC, Cl⁻, N_{total}, BOD and COD in the rainy season. The presence of EC, Cl⁻ and COD in both periods indicates quality characteristics related to the mineralization of organic compounds present in the water and the eutrophication process.

Keywords: Atibaia river; PCA; Water quality; Pollution

RESUMO

O presente estudo teve o objetivo de avaliar as características que mais influenciaram a variabilidade da qualidade das águas do rio Atibaia no município de Paulínia/SP, as coordenadas do ponto de coleta de água são dadas por 22°44'23"(S) e 47°07'40"(W), nas estações seca e chuvosa, no período de 2006 a 2016. Os dados utilizados neste estudo são provenientes do monitoramento de parâmetros realizado no manancial por uma equipe de pesquisa, acompanhado de coletas periódicas de amostras de água superficial e análises laboratoriais. Os parâmetros abordados compreenderam: precipitação, temperatura, potencial Hidrogeniônico (pH), turbidez, coliformes termotolerantes (*Escherichia coli* (*E. coli*)), oxigênio dissolvido (OD), demanda bioquímica de oxigênio (DBO), demanda química de oxigênio (DQO), nitrogênio total (N_{total}), fósforo total (P_{total}), sólidos totais dissolvidos (STD), condutividade elétrica (CE) e cloretos (Cl^-). A qualidade da água foi avaliada empregando-se análises de correlação linear, através do coeficiente de Correlação de Pearson (r), e Análise Multivariada, mediante Análise de Componentes Principais (ACP). Os resultados obtidos ressaltam a influência de CE, Cl^- , P_{total} , DO, pH, DQO, turbidez e temperatura na variabilidade da qualidade das águas do rio Atibaia na estação seca, e CE, Cl^- , N_{total} , DBO e DQO na estação chuvosa. A presença de CE, Cl^- e DQO em ambos os períodos indica características de qualidade relacionadas à mineralização de compostos orgânicos presente na água e ao processo de eutrofização.

Palavras-chave: Rio Atibaia; ACP; Qualidade da água; Poluição

1 INTRODUCTION

Water is an indispensable natural resource for the survival of animals, plants, and humans, however, its physical, chemical, and microbiological conditions have been largely impacted by anthropogenic activities, causing concerns and reflecting on the characteristics of rivers and water quality. Several factors affect surface freshwater, which makes monitoring the quality of water in water bodies essential, including accidents with spills of compounds, natural changes resulting from climate change, discharges of domestic and/or industrial effluents without appropriate treatment, among others (DURIGON *et al.*, 2015; RAMOS *et al.*, 2016; TAOUFIK *et al.*, 2017).

Water quality monitoring is used to classify water bodies in classes that ensure multiple uses of water and, in the state of São Paulo, it is carried out by the São Paulo State Environmental Company (CETESB), a government agency responsible for the control, inspection, monitoring and licensing of pollution-generating activities, which also uses the Water Quality Index (WQI) to assess and classify the water quality of the springs. The WQI was adapted from the National Sanitation Foundation in the United States and nine parameters are analyzed:

temperature, Hydrogenionic potential (pH), dissolved oxygen (DO), biochemical oxygen demand (BOD), total dissolved solids (TDS), thermotolerant coliforms (*Escherichia coli* (*E. coli*)), total nitrogen (N_{total}), total phosphorus (P_{total}) and turbidity (LEITE *et al.*, 2013, RAMOS *et al.*, 2016).

Among important variables, precipitation, chemical oxygen demand (COD), electrical conductivity (EC), and chlorides (Cl⁻) do not configure the index, but are usually analyzed additionally to complement the quality determination analysis of the water body (LEITE *et al.*, 2013, RAMOS *et al.*, 2016).

The temperature reflects the degree of heating in the water bodies. This parameter is associated with the season and is affected by seasonality. It can be used as an indicator of thermal pollution (PIRATOBA *et al.*, 2017). Through the presence of hydrogen ions (H⁺) the pH indicates whether the medium has an acidic or alkaline condition, being of utmost importance for the maintenance of aquatic life. The changes may have natural origins such as rock dissolution and photosynthesis, or anthropogenic via domestic and/or industrial effluents (GASPAROTTO, 2011).

Numerous aquatic organisms, including zooplankton and most fish species, do not tolerate low DO concentrations, as hypoxia conditions are created. DO is significant for several chemical reactions, reproduction, and diet of aquatic beings (DUBUC *et al.*, 2017; NULL *et al.*, 2017). The BOD indicates the amount of oxygen consumed by aerobic microorganisms to degrade the biodegradable organic matter while in the COD the oxygen consumption occurs via chemical oxidation. The closer the BOD value approaches the COD value, the more biodegradable the compounds present in the analyzed water will be (FRANCE, 2009).

TDS are particles smaller than 10⁻³ µm that, after filtration, remain in solution. They are mainly composed of carbonates, bicarbonates, chlorides, sulfates, phosphates, calcium, magnesium and potassium nitrates (GASPAROTTO, 2011).

The group of thermotolerant coliforms comprises bacteria of the genus *Escherichia* which are considered biological indicators of fecal contamination since

they are present in the gastrointestinal system of humans and warm-blooded animals (GASPAROTTO, 2011).

N_{total} is an important element for aquatic life, but in excess, it causes damage to the environment. This parameter comprises the forms ammonia (NH_3^+), nitrates (NO_3^-), nitrites (NO_2^-), and organic nitrogen. Its origin can be in domestic effluents, fertilizers, proteins, chlorophyll, and several other biological compounds (MARCONE, 2006). Total phosphorus, like N_{total} , is an essential element for plants and animals, however, it is an impurity in surface freshwaters when it is present in excess, causing eutrophication and fish mortality. It may come from natural causes, like the dissolution of soil compounds and the decomposition of organic matter, or anthropogenic, when it comes from domestic and/or industrial effluents, detergents, animal excrement, insecticides, and pesticides (SILVA JÚNIOR *et al.*, 2017).

Turbidity indicates the concentrated and/or recent release of effluents into water bodies. In rainy periods, this variable can change due to erosion of the river banks. It is a significant parameter since it influences the amount of light that penetrates the aquatic environment (FRANCE, 2009; PIRATOBA *et al.*, 2017). Precipitation directly influences the water quality of the water body, as the decrease results in a reduction of surface runoff and ion dilution (RIBEIRO *et al.*, 2005; PIRATOBA *et al.*, 2017).

The EC represents the ability of water to conduct electrical energy. According to França (2009), the EC *"originates from the presence of salts dissolved in water in the form of electrolytically dissociated ions"*. The Cl^- ion can be anthropogenic in origin, through domestic and/or industrial effluents, and geological, through leaching of rocks. It is extremely important for the aquatic ecosystem since it participates in physiological processes such as the exchange and transport of other ions to the intracellular and extracellular media. Its high concentrations in freshwater can provide a salty taste to the water, in addition to having properties under these conditions (PIRATOBA *et al.*, 2017).

Thus, the objective of this study was to identify the physical-chemical and/or microbiological characteristics with greater individual participation in the surface water quality of the Atibaia river and observe the effect of the sampling period (dry and rainy) using the linear correlation tools, through Pearson's Correlation coefficient (r), and Multivariate Analysis, through Principal Component Analysis (PCA).

2 MATERIAL AND METHODS

2.1 Study area

The Atibaia river is formed by the confluence of the Atibainha and Cachoeira rivers, between the municipalities of Atibaia and Bom Jesus dos Perdões in the state of São Paulo, with springs located in the municipalities of Joanópolis, Piracaia and Nazaré Paulista (LOCATELLI, 2011; LEITE *et al.*, 2013; CAMPOS, 2014; GONÇALVES, 2015; OLIVEIRA, 2016).

It is inserted in the Water Resources Management Unit 5 - Piracicaba/Capivari/Jundiaí (UGRHI-5 - PCJ), in the Atibaia sub-basin, characterized as an industrial unit. The hydrographic sub-basin covers an area of 2,816.11 km² and 397.56 km of perimeter. The river has an average flow of 31.38 m³.s⁻¹ and 182.00 km in length (LOCATELLI, 2011; LEITE *et al.*, 2013; CAMPOS, 2014, GONÇALVES, 2015, OLIVEIRA, 2016).

2.2 Sample collection

The data presented in this study come from monitoring and collecting samples of surface water from the Atibaia river in the period from 2006 to 2016.

The coordinates of the water collection point on the Atibaia river are given by 22°44'23"(S) and 47°07'40"(W), 800 m from the wastewater discharge point of a company in the city of Paulínia/SP (Figure 1).

Figure 1 – Location of the surface water sampling point on the Atibaia river



Source: GOOGLE MAPS, 2020

In total there are 183 samples of surface water and 2,196 analyzes following the methodologies indicated in the Standard Methods for the Examination of Water and Wastewater, 20th edition, with the results made available for this study (APHA, 1995).

The collected samples were analyzed for the variables recommended by CETESB, through the WQI, plus three other variables considered ecologically important, making a total of twelve monitoring variables: DO, BOD, COD, *E. coli*, pH, Cl⁻, EC, temperature, turbidity, TDS, N_{total} and P_{total}.

Precipitation data were obtained from reports issued by the Agrometeorology Information Center (CIIAGRO). Because there are no records of precipitation over the entire period (2011, 2012, 2013, 2014, and from February 2015 to January 2016) for the municipality of Paulínia/SP, data from the municipality of Campinas/SP were used to complement the information board.

2.3 Data analysis

The results of the analysis of these variables generated a large, important and complex set of data that was analyzed using statistical tools of correlation via

the Pearson Correlation coefficient (r) and Multivariate Statistics via Principal Component Analysis (PCA) (FINKLER *et al.*, 2020; TAOUFIK *et al.*, 2017).

Such analysis techniques were applied in order to favor the interpretation of the data and the identification of the variables that most contributed to the state of degradation of the water quality of the Atibaia river in the aforementioned period. Once the main variables were identified, it was possible to eliminate those that least contributed to water pollution.

These techniques can also be applied to identify sources of pollution, to manage water resources, and to reduce the time and costs of analysis (TAOUFIK *et al.*, 2017).

Then two large data matrices were obtained and the data were divided between the dry season (autumn and winter) and the rainy season (spring and summer). Each matrix was composed of thirteen columns, represented by the analyzed variables.

For tabulation, data treatment, and calculation of Pearson Correlation, the software Calc, an electronic spreadsheet of the package Libre Office version 6.3.3.2, was used. Pearson's correlation coefficient is an r value such that $r < |1|$ that assesses the correlation between two variables, regardless of the unit of measurement. This coefficient can be positive or negative. The positive linear correlation indicates that the variables are directly proportional, while the negative linear correlation indicates that the variables are inversely proportional to each other (MAIA *et al.*, 2019).

The criteria used in this study to classify Pearson's Correlation coefficient followed those used by Callegari-Jacques (2003), weak correlation for r between 0.00 to 0.30, moderate for r between 0.30 to 0.60, strong for r between 0.60 and 0.90, and very strong for r between 0.90 to 1.00.

Regarding the study of multivariate correlation, PCA analysis was used, which allows variables to be analyzed simultaneously. In this analysis, the dimension of the original data set, with possibly correlated variables, is reduced, giving rise to a

new data set with unrelated variables called principal components (PC) without considerable loss of information (FINKLER *et al.*, 2016).

This analysis was performed in a computational environment using the Palaeontological Statistics (PaSt) version 3.24 software, where we chose to use the correlation matrix to eliminate the effects of scale and units since the variables have different units of measurement (FRANCE, 2009 ; BERTOSSI *et al.*, 2013; MAIA *et al.*, 2019).

For the selection of the number of main components, the Kaiser Criterion, or Latent Root Criterion, was used, where only the PCs with an eigenvalue (λ_i) greater than one (HONGYU *et al.*, 2016) are considered.

Resolutions of the National Environment Council (CONAMA) nº 357/2005 (BRASIL, 2005) and CONAMA nº 430/2011 (BRASIL, 2011) were used to verify that the results were within the limits established for surface freshwater framed in the Class 2, given the role of the preponderant uses, current and future, and the level of water quality of the Atibaia river.

3 RESULTS AND DISCUSSION

The limits established by CONAMA nº 357/2005 and CONAMA nº 430/2011, minimum, maximum, average, and standard deviation of the physical-chemical and microbiological analyzes of the waters of the Atibaia river in the dry and rainy seasons are shown in Table 1.

According to the results in Table 1, it appears that the parameters Cl^- , pH, and temperature were fully within the maximum limits established in legislation, CONAMA nº 357/2005 and CONAMA nº 430/2011. Cl^- ranged from 3.45 to 110.74 mg.L^{-1} in the dry season and from 0 to 164.71 mg.L^{-1} in the rainy season and the resolution establishes a limit $< 250 \text{ mg.L}^{-1}$. The pH varied between 7.06 and 8.93 in the dry season and between 6.84 and 8.03 in the rainy season, being within the expected limits of 6.00 to 9.00. The temperature fluctuated between 15 and 30°C

and between 17 and 30°C in the dry and rainy seasons, respectively, remaining < 40°C.

Table 1 – Limits, minimum and maximum values verified in the collections, average and standard deviation of the values obtained in the physical-chemical and microbiological analyzes of the waters of the Atibaia river in the dry and rainy seasons, period 2006 to 2016

| | Limit* | Dry season | | | Rainy season | | |
|--------------------|--------------------------------------|------------|------------|----------------------------|--------------|------------|----------------------------|
| | | Minimum | Maximum | Average \pm SD | Minimum | Maximum | Average \pm SD |
| EC | < 100.00 $\mu\text{S.cm}^{-1}$ | 93.00 | 1,087.00 | 342.05 \pm 192.40 | 76.40 | 1,364.00 | 293.15 \pm 249.92 |
| Cl ⁻ | < 250.00 mg.L ⁻¹ | 3.45 | 110.74 | 27.79 \pm 19.54 | ** | 164.71 | 27.54 \pm 29.67 |
| TDS | < 500.00 mg.L ⁻¹ | 21.79 | 1,346.00 | 310.61 \pm 211.34 | 59.20 | 770.00 | 275.54 \pm 130.60 |
| pH | 6.00 a 9.00 | 7.06 | 8.93 | 7.56 \pm 0.28 | 6.84 | 8.03 | 7.55 \pm 0.25 |
| BOD | < 5.00 mg.L ⁻¹ | 2.00 | 32.90 | 12.92 \pm 6.18 | 1.10 | 61.00 | 13.63 \pm 7.39 |
| COD | - | 2.16 | 75.44 | 18.88 \pm 11.91 | 1.68 | 64.96 | 19.64 \pm 8.86 |
| DO | > 5.00 mg.L ⁻¹ | 0.73 | 9.59 | 6.23 \pm 1.97 | 0.34 | 9.55 | 5.14 \pm 2.22 |
| N _{total} | < 0.10 mg.L ⁻¹ | 0.35 | 36.93 | 8.18 \pm 7.72 | ** | 68.22 | 8.64 \pm 11.91 |
| P _{total} | < 0.10 mg.L ⁻¹ | 0.01 | 1.35 | 0.29 \pm 0.30 | 0.01 | 0.97 | 0.19 \pm 0.16 |
| Turbidity | < 100.00 UNT | 5.47 | 132.00 | 31.94 \pm 26.63 | 6.00 | 263.00 | 56.96 \pm 56.78 |
| Precipitation | - | ** | 218.20 | 54.02 \pm 52.20 | 6.70 | 438.00 | 159.69 \pm 100.00 |
| Temperature | < 40°C | 15.00 | 30.00 | 21.90 \pm 3.46 | 17.00 | 30.00 | 23.14 \pm 2.76 |
| E. coli | < 1,000.00 NMP(100 mL) ⁻¹ | 200.00 | 900,000.00 | 50,252.97 \pm 142,362.15 | 200.00 | 900,000.00 | 35,573.62 \pm 113,585.93 |

In were: * Limits established by CONAMA n° 357/2005 and CONAMA n° 430/2011; ** Result below the detection limit of the analysis method performed.

The average concentrations of the variables: EC, TDS, BOD, DO, N_{total}, P_{total}, turbidity, and *E. coli* were higher than those recommended by CONAMA Resolution n° 357/2005, in both periods. For the EC, the mean value \pm the standard deviation evaluated was 342.05 \pm 192.40 $\mu\text{S.cm}^{-1}$ in the dry season and 293.15 \pm 249.92 $\mu\text{S.cm}^{-1}$ in the rainy season, the maximum limit being established < 100.00 $\mu\text{S.cm}^{-1}$. For TDS the mean value \pm the standard deviation evaluated was 310.61 \pm 211.34 mg.L⁻¹ in the dry season and 275.54 \pm 130.60 mg.L⁻¹ in the rainy season, with the maximum limit established < 500.00 mg.L⁻¹. The BOD presented mean \pm the standard deviation of 12.92 \pm 6.18 mg.L⁻¹ in the dry season and 13.63 \pm 7.39 mg.L⁻¹ in the rainy season, the limit being set to values < 5.00 mg.L⁻¹. The DO evaluated was 6.23 \pm 1.97 mg.L⁻¹ in the dry season and 5.14 \pm 2.22 mg.L⁻¹ in the rainy season and the one indicated by the Resolution is > 5.00 mg.L⁻¹. The N_{total} evaluated was 8.18 \pm 7.72 mg.L⁻¹ in the dry season and 8.64 \pm 11.91 mg.L⁻¹ in the rainy season and that indicated by the Resolution is < 0.10 mg.L⁻¹. The P_{total} obtained in the samples

was $0.29 \pm 0.30 \text{ mg.L}^{-1}$ and $0.19 \pm 0.16 \text{ mg.L}^{-1}$ in the dry and rainy seasons, respectively, with the indication $< 0.10 \text{ mg. L}^{-1}$. *Escherichia coli* had an average concentration of $50,252.97 \pm 142,362.15 \text{ NMP}(100 \text{ mL})^{-1}$ in the dry season and $35,573.62 \pm 113,585.93 \text{ NMP}(100 \text{ mL})^{-1}$ in the rainy season and the Resolution establishes $< 1,000.00 \text{ NMP}(100 \text{ mL})^{-1}$ (BRASIL, 2005).

The correlations between the thirteen variables in the dry season and in the rainy season were determined using Pearson Correlation matrix and are presented, respectively, in Tables 2 and 3.

According to the results presented in Table 2, it is observed, regarding the data in the dry season, that the variables: EC and Cl^- ($r = 0.88$), EC and P_{total} ($r = 0.61$), and EC and DO ($r = -0.62$) were strongly correlated.

The parameters Cl^- and P_{total} ($r = 0.59$), Cl^- and DO ($r = -0.54$), Cl^- and precipitation ($r = -0.33$), and DO and P_{total} ($r = -0.48$) are moderately correlated.

The results presented in the rainy season (Table 3), indicate that the highly correlated variables are: EC and Cl^- ($r = 0.82$), EC and N_{total} ($r = 0.69$), and Cl^- and N_{total} ($r = 0.71$).

In the rainy season, the variables EC and BOD ($r = 0.33$), EC and P_{total} ($r = 0.31$), Cl^- and BOD ($r = 0.37$), TDS and BOD ($r = 0.32$), BOD and COD ($r = 0.53$), N_{total} and P_{total} ($r = 0.36$), turbidity and precipitation ($r = 0.42$), EC and DO ($r = -0.35$), EC and turbidity ($r = -0.40$), and N_{total} and turbidity ($r = -0.35$).

Based on the Correlation matrix between the variables, the data were submitted to the analysis of main components, PCA, the same being normalized due to the variety of units of measurement between the parameters. The outliers resulting from the analyzes were not discarded because the information had been obtained from a database, which does not allow to identify the reasons for the divergences.

Based on the results obtained for the main components, their respective eigenvalues (λ_i) and percentages of variance (% PCV) (Table 4), it has nine (39.52%) of the thirteen main components, PCs, presented eigenvalue less than one in the

dry season while, in the rainy season, eight (29.58%) had an eigenvalue of less than one.

Of the thirteen PC generated, PC 1 and 2 were selected because they presented variance (eigenvalue) greater than one. The composition of each PC varies according to the weighting coefficient (eigenvector) assigned to each variable (Table 5).

From the results of the PCA, it was observed that a model with two PC was adequate to represent the characteristics of the variables analyzed in the waters and explain 40.38% of the total variance in the dry season and 40.14% in the rainy season (Table 6).

Table 2 – Pearson's Correlation Matrix - dry season

| | EC | Cl ⁻ | TDS | pH | BOD | COD | DO | N _{total} | P _{total} | Turbidity | Precipitation | Temperature | E. coli |
|--------------------|-------|-----------------|-------|-------|-------|-------|-------|--------------------|--------------------|-----------|---------------|-------------|---------|
| EC | 1.00 | | | | | | | | | | | | |
| Cl ⁻ | 0.88 | 1.00 | | | | | | | | | | | |
| TDS | 0.18 | 0.07 | 1.00 | | | | | | | | | | |
| pH | -0.15 | -0.21 | 0.13 | 1.00 | | | | | | | | | |
| BOD | 0.27 | 0.17 | -0.01 | -0.11 | 1.00 | | | | | | | | |
| COD | 0.14 | 0.07 | 0.05 | 0.15 | 0.28 | 1.00 | | | | | | | |
| DO | -0.62 | -0.54 | -0.12 | 0.02 | -0.22 | -0.15 | 1.00 | | | | | | |
| N _{total} | 0.26 | 0.28 | -0.20 | -0.25 | 0.06 | -0.09 | -0.05 | 1.00 | | | | | |
| P _{total} | 0.61 | 0.59 | 0.27 | -0.12 | 0.07 | -0.07 | -0.48 | 0.09 | 1.00 | | | | |
| Turbidity | -0.21 | -0.22 | 0.09 | 0.19 | 0.18 | 0.12 | 0.21 | -0.23 | -0.18 | 1.00 | | | |
| Precipitation | -0.29 | -0.33 | -0.08 | -0.04 | 0.04 | 0.01 | 0.28 | -0.07 | -0.23 | 0.15 | 1.00 | | |
| Temperature | -0.01 | -0.01 | -0.09 | -0.30 | 0.09 | -0.13 | -0.07 | 0.08 | 0.06 | -0.28 | 0.23 | 1.00 | |
| E. coli | -0.14 | -0.20 | -0.04 | 0.17 | 0.09 | 0.17 | 0.03 | -0.09 | -0.13 | 0.23 | 0.25 | -0.11 | 1.00 |

Table 3 – Pearson's Correlation Matrix - rainy season

| | EC | Cl ⁻ | TDS | pH | BOD | COD | DO | N _{total} | P _{total} | Turbidity | Precipitation | Temperature | E. coli |
|--------------------|-------|-----------------|-------|-------|-------|-------|-------|--------------------|--------------------|-----------|---------------|-------------|---------|
| EC | 1.00 | | | | | | | | | | | | |
| Cl ⁻ | 0.82 | 1.00 | | | | | | | | | | | |
| TDS | -0.01 | 0.01 | 1.00 | | | | | | | | | | |
| pH | 0.07 | 0.02 | -0.02 | 1.00 | | | | | | | | | |
| BOD | 0.33 | 0.37 | 0.32 | 0.03 | 1.00 | | | | | | | | |
| COD | -0.15 | -0.04 | 0.28 | 0.11 | 0.53 | 1.00 | | | | | | | |
| DO | -0.35 | -0.28 | 0.06 | -0.18 | 0.08 | 0.18 | 1.00 | | | | | | |
| N _{total} | 0.69 | 0.71 | -0.02 | -0.06 | 0.27 | -0.07 | -0.09 | 1.00 | | | | | |
| P _{total} | 0.31 | 0.26 | 0.23 | -0.19 | 0.08 | -0.01 | 0.01 | 0.36 | 1.00 | | | | |
| Turbidity | -0.40 | -0.28 | 0.17 | -0.10 | -0.03 | 0.16 | 0.10 | -0.35 | -0.09 | 1.00 | | | |
| Precipitation | -0.24 | -0.22 | -0.04 | -0.08 | -0.08 | 0.22 | 0.04 | -0.29 | 0.08 | 0.42 | 1.00 | | |
| Temperature | 0.17 | 0.20 | -0.11 | -0.22 | 0.08 | -0.15 | 0.11 | 0.22 | -0.07 | -0.25 | -0.12 | 1.00 | |
| E. coli | -0.07 | -0.05 | -0.07 | 0.16 | 0.14 | 0.06 | 0.17 | -0.10 | -0.21 | -0.06 | 0.19 | 0.01 | 1.00 |

Table 4 – PC, λ_i , % VCP e accumulated VCP%

| PC | Dry season | | | Rainy season | | |
|----|-------------|-------|-------------------|--------------|-------|-------------------|
| | λ_i | % VCP | Accumulated % VCP | λ_i | % VCP | Accumulated % VCP |
| 1 | 3.38 | 25.98 | 25.98 | 3.28 | 25.22 | 25.22 |
| 2 | 1.87 | 14.41 | 40.38 | 1.94 | 14.92 | 40.14 |
| 3 | 1.47 | 11.32 | 51.70 | 1.46 | 11.26 | 51.40 |
| 4 | 1.14 | 8.77 | 60.48 | 1.38 | 10.58 | 61.98 |
| 5 | 0.92 | 7.08 | 67.55 | 1.10 | 8.44 | 70.42 |
| 6 | 0.88 | 6.81 | 74.36 | 0.88 | 6.76 | 77.18 |
| 7 | 0.73 | 5.61 | 79.96 | 0.72 | 5.56 | 82.73 |
| 8 | 0.64 | 4.91 | 84.88 | 0.64 | 4.92 | 87.65 |
| 9 | 0.61 | 4.66 | 89.53 | 0.57 | 4.40 | 92.05 |
| 10 | 0.47 | 3.61 | 93.14 | 0.34 | 2.65 | 94.70 |
| 11 | 0.42 | 3.20 | 96.34 | 0.31 | 2.38 | 97.09 |
| 12 | 0.38 | 2.90 | 99.24 | 0.23 | 1.79 | 98.88 |
| 13 | 0.10 | 0.76 | 100.00 | 0.15 | 1.12 | 100.00 |

Table 5 – Weighting coefficient of each PC

| | Dry season | | Rainy season | |
|--------------------|------------|-------|--------------|-------|
| | PC1 | PC2 | PC1 | PC2 |
| EC | 0.49 | 0.12 | 0.50 | 0.02 |
| Cl ⁻ | 0.48 | 0.04 | 0.48 | 0.09 |
| TDS | 0.10 | 0.29 | 0.01 | 0.45 |
| pH | -0.14 | 0.41 | 0.00 | 0.01 |
| BOD | 0.13 | 0.20 | 0.20 | 0.54 |
| COD | 0.03 | 0.40 | -0.08 | 0.57 |
| DO | -0.39 | -0.17 | -0.17 | 0.18 |
| N _{total} | 0.18 | -0.30 | 0.47 | 0.05 |
| P _{total} | 0.40 | 0.06 | 0.21 | 0.18 |
| Turbidity | -0.20 | 0.39 | -0.30 | 0.23 |
| Precipitation | -0.24 | -0.09 | -0.24 | 0.19 |
| Temperature | 0.05 | -0.40 | 0.17 | -0.15 |
| <i>E.coli</i> | -0.15 | 0.29 | -0.08 | 0.09 |

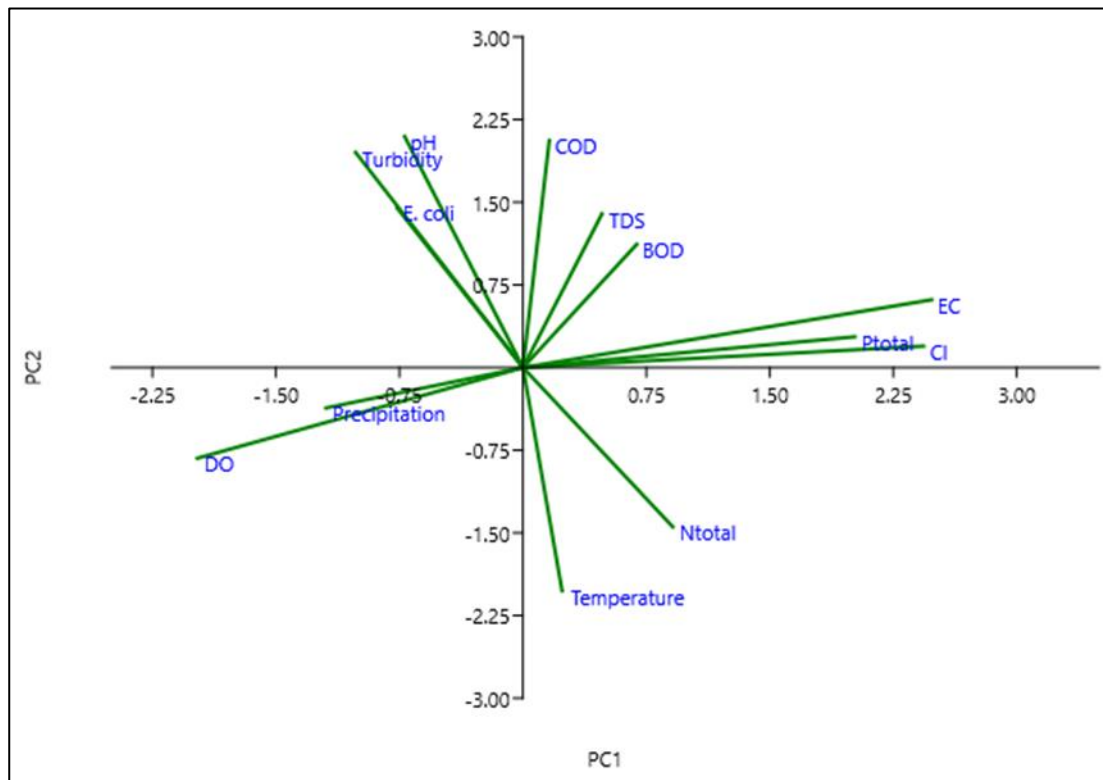
Table 6 – Variables with greater weight in the definition of PCs

| | PC | Variables Dry season | Variables Rainy season |
|----------|----|-------------------------------------------------------------|-----------------------------------------------------|
| PC with | 1 | EC (+), Cl ⁻ (+), DO (-), P _{total} (+) | EC (+), Cl ⁻ (+), N _{total} (+) |
| high | 2 | pH (+), COD (+), turbidity (+), | BOD (+), COD (+), TDS (+) |
| variance | | temperatura (-) | |

The information obtained for PC 1 and 2 is presented graphically taking into account the weights of the variables in these components. Figures 2 and 3 show the PCA graph via biplot with the formation of the mentioned groups of variables for the dry and rainy seasons, respectively.

According to Figure 2, dry season, in PC1, it is noted that the variables EC, Cl⁻ and P_{total} are positively correlated with each other, while DO is negatively correlated with these variables. In component 2, COD, turbidity, and pH are the most positively correlated; temperature is negatively correlated with pH and turbidity.

Figure 2 – PCA chart via biplot - dry season



Source: Authors (2020)

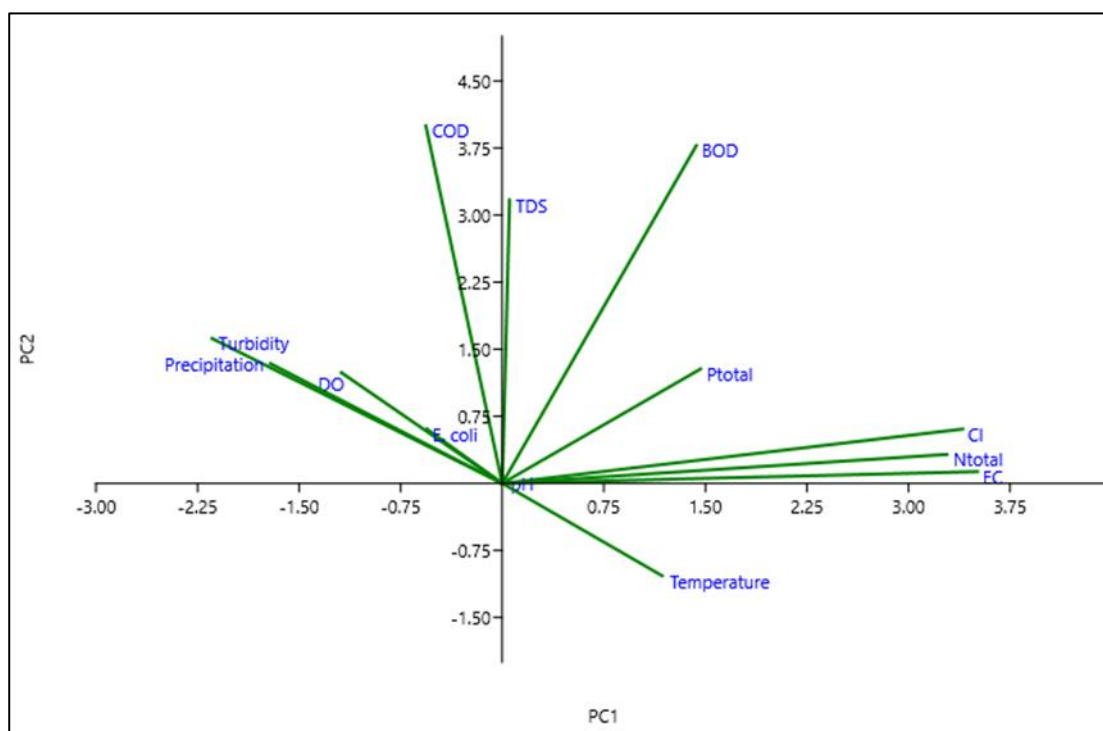
In PC1, the rainy season (Figure 3), it is noted that the variables EC, Cl^- and N_{total} are positively correlated with each other. In component 2, the variables positively correlated with each other are COD, BOD, and TDS. The other variables did not present a significant factor load.

The selected variables, EC, Cl^- , P_{total} , DO, pH, COD, turbidity and temperature in the dry season, and EC, Cl^- , N_{total} , BOD, COD, and TDS in the rainy season, represent contributions from different sources of pollution such as organic pollution and nutrients, industrial and/or domestic effluents, as well as climatic conditions.

For PC1 there was a positive correlation for EC, Cl^- and P_{total} , in the dry season, and EC, Cl^- and N_{total} , in the rainy season. These parameters are related, as these variables influence each other. EC can be altered by the presence of inorganic solids dissolved in water such as chloride, nitrate, and phosphate anions (GASPAROTTO, 2011; KIMURA, 2014; EPA, 2017).

According to Piratoba *et al.* (2017), there is a direct relationship between EC and ions, as high ion concentrations indicate high EC values, indicating the presence of salts in the water body (VASCONCELOS SEGUNDO *et al.*, 2016).

Figure 3 – PCA graph via biplot - rainy season



Source: Authors (2020)

The negative correlation of DO, in the dry season, concerning EC, Cl^- and P_{total} may indicate eutrophication since excess phosphorus provides such a scenario and oxygen depletion (LEITE *et al.*, 2013; EPA, 2017).

According to Vasconcelos Segundo *et al.* (2016), the inverse correlation between DO and EC occurs due to the use of DO in the decomposition of organic matter present in the water body, leading to an increase in ions and, consequently, an increase in EC values.

For PC2, pH, COD, turbidity and temperature, in the dry season, and BOD, COD, and TDS, in the rainy season, showed a significant correlation between them.

It is observed that in periods of low temperature, due to the dry season being present in the coldest months of the year, there is a high pH due to the increased solubility of gases in water (MARCONE, 2006).

The increase in pH can be caused by the intense rate of photosynthesis, characteristic of the eutrophication process, promoting an increase in turbidity and COD (MARCONE, 2006; KIMURA, 2014; OLIVEIRA, 2016).

In times of lower precipitation, the highest ion concentrations are observed, including Cl^- (RIBEIRO *et al.*, 2005; PIRATOBA *et al.*, 2017).

In the rainy season, it is observed that the variables COD, BOD, and TDS have a positive correlation and a high weighting coefficient. The existing correlation between BOD and COD, parameters that point to the degradation of organic matter, indicates a eutrophic environment caused by dumping of domestic and/or industrial organic origin interfering in aquatic life (FRANCE, 2009; GARDIMAN JUNIOR, 2015).

The climatic conditions of the rainy season influence the TDS parameter. This parameter indicates recent organic contamination in rivers by domestic and/or industrial effluents, which affects the organoleptic quality of the water (FRANCE, 2009; GASPAROTTO, 2011; LEITE *et al.*, 2013).

Even with factorial load with low significance and weak correlation, it is observed that, in the rainy season, occurring in the hottest months of the year, the

temperature is opposite to the DO, due to a negative correlation between these variables since the warmer water retains less oxygen (TAOUFIK *et al.*, 2017).

The correlation between TDS and P_{total} also presents factor load with low significance and weak correlation in the rainy season, however, TDS is associated with phosphorus transport (LEITE *et al.*, 2013)

The study shows that in both periods there are parameters in common, such as EC, Cl^- and COD, among the variables surveyed, being necessary to consider the variation of the studied period, rainy and dry, to determine the water quality, its monitoring and management.

4 CONCLUSION

The analysis of the data performed indicates the water quality of the Atibaia river, in the stretch of the municipality of Paulínia/SP, a populous area and of considerable economic relevance in the state of São Paulo. According to the results, subdivided into dry and rainy periods, the surface freshwaters of this water body suffer from the various impacts of anthropic origin, due to the contribution of domestic and/or industrial effluents that cause the degradation of the environment.

Among the thirteen parameters evaluated, only Cl^- , pH, and temperature were fully present, within the maximum limits established by the resolutions CONAMA nº 357/2005 and CONAMA nº 430/2011.

The parameters EC, TDS, BOD, DO, N_{total} , P_{total} , turbidity, and *E. coli* presented average concentrations higher than those recommended by CONAMA Resolution nº 357/2005, in both dry and rainy seasons, in the mentioned period, however, not all configure the water quality index of Brazilian water bodies.

In the dry season, electrical conductivity was (strongly) positively correlated with chlorides and total phosphorus, and negatively correlated with dissolved oxygen. In the rainy season, electrical conductivity was (highly) positively correlated

with chlorides and with total nitrogen. Chlorides and total nitrogen were also highly positively correlated.

According to the analysis of the main components, the most relevant parameters that influenced the water quality of the Atibaia river in the dry periods were: electrical conductivity, chlorides, total phosphorus, dissolved oxygen, pH, chemical oxygen demand, turbidity, and temperature. In the rainy periods, the most influential were electrical conductivity, chlorides, total nitrogen, biochemical oxygen demand, chemical oxygen demand, and total dissolved solids.

The quality characteristics related to water mineralization that most influenced the results obtained, both in the dry season and in the rainy season, were EC, Cl^- , P_{total} , and N_{total} , with emphasis on the high levels of P_{total} and N_{total} that accentuate the problems of eutrophication of a water body.

Thus, given the results achieved, it is considered that the variables EC and Cl^- should continue to be monitored, since they are variables of remarkable relevance for the detection of contaminants from domestic and/or industrial effluents, and in this study they were the most representative the variability of water quality and can be used as a tool for the management and monitoring of surface water quality.

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