Spatial and temporal variation of water quality in a watershed in center-west Paraná, Brazil

Rodrigo Felipe Bedim Godoy, Enzo Luigi Crisiogiovanni, Elias Trevisan and Fernando Aparecido Dias Ramdoski

ABSTRACT

Water quality monitoring is an essential strategy for water resources management. Physicochemical and microbiological parameters play an important role in the characterization of water quality. They are helpful tools for the identification of pollution in aquatic ecosystems, being of natural sources or because of anthropogenic actions, and contribute to making decisions as well as sustainable development in a hydrographic basin. This study analyzed the water quality variation in a period of 20 years in Piquiri River Watershed. Also, TP concentration was estimated using linear regression model from affluent rivers. The Relationship between TN and TP presented a Person’s linear correlation of 0.80, while turbidity and TSS presented correlation of 0.79. The relationship between the predicted and observed values for Turbidity and TP presented $r^2$ higher than 0.60. Spatial-temporal variation of water quality in Piquiri River Watershed has showed good quality over the years, although, unacceptable values of *Escherichia coli*, BOD, COD and Total Phosphorus appeared. Most unacceptable values were identified in affluent rivers, suggesting the improvement in the water quality closer to downstream of the Piquiri River. WQI also showed good quality water for all stations. Key words | aquatic ecosystem, Linear Regression Model, organic pollution, temporal analysis, total phosphorus

HIGHLIGHTS

- Piquiri River watershed presented frequently to have water quality of Class 1.
- Unacceptable values of *E. coli*, BOD, TP were seen mainly on affluent.
- Water Quality Index presented values between 58 and 78.
- Strong Pearson’s correlations between TP and TN, and, between Turbidity and TSS.
- IDW interpolation show higher values of TN in agricultural area.

Rodrigo Felipe Bedim Godoy (corresponding author)
Elias Trevisan
Department of Environment, State University of Maringá, Umuarama, Paraná 87506-370, Brazil
E-mail: rodrigofelipe7@hotmail.com

Enzo Luigi Crisiogiovanni
Postgraduate Program in Forest Sciences, Midwestern State University, Irati, Paraná 84500-131, Brazil

Fernando Aparecido Dias Ramdoski
Post-graduation Program in Science and Materials Engineering, Federal University of Paraná, Curitiba, Paraná 81530-000, Brazil

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The importance of water resources for the maintenance of life, through water consumption for living organism’s regulation and functioning, food production, electricity generation and industrial processes is unquestionable (Muniz et al. 2011). Thus, adequate quantities of water of good quality are essential for economic development and ecological integrity (Wu et al. 2018). However, over the years, changes have affected the amount, distribution and quality of water resources (Benvenutti et al. 2015). These changes might severely impact the water volume and quality of surface waters in rivers, which are the main source of water for domestic, agricultural and industrial purposes (Shil et al. 2019). Thereby, there is a need to assess surface water quality (Şener et al. 2017).

An important strategy for water resources management is to monitor frequently the surface water, to characterize spatial and temporal variation of water quality (Stachelek & Madden 2015). Also, this monitoring plays important roles in the possible identification of sources of pollution. This pollution could be associated with the discharge of industrial sewage, domestic wastewater and agricultural drainage water, and, also coming from natural phenomena driven by hydrological processes (Bortoletto et al. 2015; Shil et al. 2019). According to Fathi et al. (2018), monitoring and controlling surface waters are of vital importance to ensure the availability of water of good quality for its several uses.

As water quality monitoring is of extreme importance, it is necessary to plan and to define parameters and variables to indicate the quality of an aquatic environment. Thereby, physicochemical and microbiological variables are of great importance to estimate environmental quality of a small region or larger areas, such as hydrographic basins (Oliveira et al. 2018b). Through water quality monitoring, important information might be provided, to help river basin management, predict future environmental outcomes and to contribute to a sustainable development of a region (Benvenutti et al. 2015).

Long-term monitoring programs produce a large dataset of several water quality parameters, in which it sometimes becomes difficult to interpret (Bortoletto et al. 2015). Thus, Water Quality Index (WQI) could be an interesting tool for the evaluation of water quality, seeing that it transforms a large amount of water quality parameters data into a single number that describes the water quality qualitatively (e.g., poor, moderate, good) (Benvenutti et al. 2015; Wu et al. 2018). Thereby, understanding the importance of water quality for all living organisms, it is essential and it imposes the need to share the water quality monitoring data to take advantage of and to facilitate in the conservation of natural resources with objectives of sustainable development (Benvenutti et al. 2015).

Complementarily, spatial analyses are also of great importance for water quality studies. However, there are some difficulties in, for instance, collecting many water samples in a watershed. Thus, inverse distance weighted (IDW) is a deterministic method used to interpolate spatial data with the objective of estimating unknown values.
between points with values known (Stachelek & Madden 2015; Pande & Moharir 2018). This technique has been applied for estimations in spatial analysis of groundwater quality and depth (Seyedmohammadi et al. 2016; Adhikary & Dash 2017; Pande & Moharir 2018), spatial interpolation for bathymetry mapping of river, and river channel topography (Zhang et al. 2016; Wu et al. 2019), mapping and estimation of water quality spatial variation, methane flux and rainfall intensity (Yang et al. 2020).

Therefore, this study aimed at evaluating the water quality of Piquiri River Watershed from a dataset of 20 years (2000–2019), comparing the variation of water quality between stations located in the watershed, classifying the water bodies according to Brazilian law through their qualities, identifying possible unacceptable values of water quality parameters, and at evaluating TP and turbidity concentrations in Piquiri River from affluent data. Also, the IDW interpolation method was used to verify the variation of some water quality parameters along Piquiri River and its affluent.

**MATERIALS AND METHODS**

**Study area**

Piquiri River Watershed is located from center south to west of Paraná state, being the third largest watershed of Paraná (Brazil). Its delimitation represents 12% of the total area of Parana, with approximately 660 km of extension (Pires 2018). In addition, the watershed comprises in total 36 municipalities and 32 partially (Araújo et al. 2018; Pires 2018). Piquiri River Watershed possesses a total drainage area of 24,700 km² (Araújo et al. 2015; Correa & Galvani 2017a). Average annual precipitation in the watershed is approximately 1,762.5 mm (Correa & Galvani 2017b). Pires (2018) found the highest precipitation averages in October (198.74 mm), January (185.70 mm) and December (182.93 mm) for a temporal series from 1979 to 2012. Thus, the rainiest season is spring (517.37 mm), followed by summer (483.55 mm) and fall (428.58 mm), while winter (326.04 mm) is the dry season.

Eight stations were selected in the watershed, where the data were obtained from Paraná Waters Institute Website/Land and Water Institute (Public data) and Water National Agency (ANA). Figure 1 shows the elevation in the Piquiri River Watershed varying from lower than 400 meters above sea level (west) to approximately 1,200 meters above sea level (east) (Figure 1(a)). In addition, Figure 1(b) shows the land use and land cover in the watershed (IBGE 2020). Land use in the watershed comprises 53.18% of agricultural area, 23.58% Forest Occupation, 17.31% of Pasture, 3.78% of Forest, 1.11% of silviculture and 1.04% other land uses. Figure 1(c) presents the stations location, being three stations located in affluent of Piquiri River (64785000, 64775000, 64790000) and five stations located in Piquiri River (64771500, 64830000, 64820000, 64799500, 64795000). Information about each station is included in supplementary material.

**Water quality parameters**

Eighteen water quality parameters were chosen for analysis of spatial-temporal variation of water quality in Piquiri river watershed. The period from 2000 to 2019 was chosen to analyze changes occurred in the water quality in Piquiri Watershed. About the observations, 30.4% were collected in the winter, 26.3% in the fall, 32.6% in the spring, and 10.7% in the summer. Complementarily, information about the water quality parameters with the quantity of analyses performed for each variable in each station are in the supplementary material.

**Brazilian law of freshwater bodies classification**

Brazilian law number 357/2005 by CONAMA (CONAMA 2005) establishes guidelines for the classification of freshwater bodies, thus, indicating the maximum allowed value for some variables in each one of the four classes of classification. Through this classification, the use of a water body could vary according to its quality. Table 1 shows the maximum allowed value for some water quality parameters and the type of water treatment for possible human consumption for each class. The parameters analyzed in this study were classified according to this classification.

**Water quality index (WQI)**

Nine of the 18 physical, chemical and microbiological parameters were subjected to the water quality index WQI.
This index was proposed in 2008 by the Sanitation Company of São Paulo CETESB (Companhia de Tecnologia de Saneamento Ambiental, São Paulo, Brazil) with some adaptations for the U.S.EPA. This index uses measures of standardized parameters and weighted by importance. WQI values vary from 0 to 100 and depending on the stream classified according to quality (for example <19 very bad; from 19 to 36 bad; from 36 to 51 regular;
WQI = \prod_{i=1}^{n} q_i^W_i \quad \text{(1)}

where, $q_i$ represents the quality of the $i$–th parameter, a number also between 0 and 100, obtained by the normalization equations (Table 2), depending on its concentration or measure. $W_i$ is the weight corresponding to the $i$–th parameter, a number between 0 and 1, assigned according to its importance for the global conformation of quality. For this case, the following weights were used: Temperature ($W_{\text{Temp}} = 0.10$); Turbidity ($W_{\text{T}} = 0.08$); pH ($W_{\text{pH}} = 0.12$); Dissolved Oxygen ($W_{\text{DO}} = 0.17$); BOD$_{5,20}$ ($W_{\text{BOD}} = 0.10$); Total nitrogen ($W_{\text{TN}} = 0.10$); Total Phosphate ($W_{\text{TP}} = 0.10$); Total Suspended Solids ($W_{\text{TSS}} = 0.08$); and Fecal Coliforms ($W_{i} = 0.15$). And $n$ number of variables included in the calculation of the WQI. Thus, average WQI values were calculated for each season: Summer, Winter, Fall and Spring.

### Linear Regression Model

Linear Regression Model was used to predict values of Total Phosphorus and Turbidity after affluent input into the Piquiri River. Thus, variable values of stations 64771500, 64775000, 64785000 and 64790000 were used to create a linear equation model, and values of Total Nitrogen (prediction of TP) and Total Suspended Solids (prediction of Turbidity) of stations 64795000, 64799500, 64820000 and 64830000 were used for prediction. Thus, the predicted values were compared to observed values. Data for the estimation of turbidity through concentration of TSS, had to be handled. Eight outliers were removed, representing approximately 9% of total data from Piquiri River stations. Shen et al. (2015) also removed extreme values through data trimming using certain limits. According to Oliveira et al. (2018a), environmental data might present censored, lost values and outliers, which implicates in problems in statistical analysis. For the estimation of TP, no value was removed. Pearson’s linear correlation ($r$) and $R^2$-value were calculated. Pearson’s correlation analysis is an interesting

### Table 1: Water body classification according to resolution 357/2005 by CONAMA

| Parameter       | Unity/Use          | 1       | 2       | 3       | 4       |
|-----------------|--------------------|---------|---------|---------|---------|
| Turbidity       | NTU                | ≤40     | 100     | 100     | –       |
| BOD             | mgL$^{-1}$         | ≤3      | ≤5      | ≤10     | –       |
| DO              | mgL$^{-1}$         | ≥6      | ≥5      | ≥4      | ≥2      |
| E.coli          | (UFC/100 ml)       | ≤200    | ≤1000   | ≤2,500  | (recreation); ≤1000(animal consumption); ≤4,000 (other uses) |

Ammoniacal-N: mgL$^{-1}$

| Parameter       | Unity/Use          | 1       | 2       | 3       | 4       |
|-----------------|--------------------|---------|---------|---------|---------|
| Total Nitrogen  | mgL$^{-1}$         | ≤2.18   | ≤2.18   | –       | –       |
| Nitrate         | mgL$^{-1}$         | ≤10     | ≤10     | ≤10     | –       |
| Total Phosphorus| mgL$^{-1}$         | ≤0.1    | ≤0.1    | ≤0.15   | –       |

Human Consumption Use

- After Simplified Treatment
- After Conventional Treatment
- After Conventional or Advanced Treatment
- Use for Navigation and Landscaping

< without limit defined. Source: CONAMA (2005).
statistical tool to understand and to visualize the degree of dependency of one variable in relation to others. Also, this analysis measures interrelation and association among the variables (Shil et al. 2019). And, $r^2$ measures the proportion of variation in the dependent parameter, which can be attributed to the independent parameter. Estimations of total phosphorus (Shen et al. 2020) and use of turbidity to predict total suspended solids concentrations (Oliveira et al. 2020a) using linear regression and machine learning have shown good results.

Inverse distance weighted

IDW interpolation is a deterministic and common technique of interpolation in spatial analysis (Adhikary & Dash 2017; Yang et al. 2020). This method gives weight to data points according to their influence on the prediction is decreased as distance from the points expands (Adhikary & Dash 2017). Thus, close points have more weights than distant points (Seyedmohammadi et al. 2016). The IDW Equation (11) can be described by considering $z(x_0)$ being the interpolated value, $n$ the total number of sample data values, $x_i$ the $i$th element of data value, $d_i$ the horizontal distance between the interpolation points and the sample data value and $k$ is the weighting power.

$$z(x_0) = \frac{\sum_{i=1}^{n} \frac{x_i}{d_i^k}}{\sum_{i=1}^{n} \frac{1}{d_i^k}}$$ (11)

All eight measured stations for TN, TP and DO data were used in the calculation of each interpolation cell (water quality parameter grid). It was created a buffer in the region around the river network to be used for mask. The values predicted using IDW interpolation were calculated in R Software.

RESULTS AND DISCUSSION

Variation of water quality

Figure 2 shows a boxplot of water quality parameters for stations located in Piquiri river and its affluent. Ammoniacal Nitrogen presented to have a low concentration, less than 0.2 mgL$^{-1}$ in almost all campaigns ($n = 118$). The highest concentration was seen in an affluent of Piquiri river (64785000) with concentration of 0.36 mgL$^{-1}$. This parameter is an important indicator of water quality, seen that it could lead water bodies to eutrophication, being toxic for aquatic organisms, and a hazard for public health (Chen et al. 2018). In addition, this variable affects the dissolved oxygen concentration when oxidized to nitrate form (Nuruzzaman et al. 2017). In this collect, the dissolved oxygen concentration was of 6.99 mgL$^{-1}$ below DO mean for this station (8.04 mgL$^{-1}$, $n = 50$). In addition, the boxplot also showed three outliers for station 64785000 and one for station 64830000.

Beyond ammoniacal nitrogen, another crucial parameter to characterization and evaluation of water quality

| Parameter             | Equation                                      |
|-----------------------|-----------------------------------------------|
| BOD$_{5,20}$          | $q_{BOD} = -30 \ln BOD + 103.45$ (2)         |
| Fecal coliforms (E. coli) | $q_{FC} = \log_{10} FC10$ (3)                |
| Total Phosphorus      | $q_{TP} = 99\exp^{-0.91629TP}$ (4)           |
| Total nitrogen        | $q_{TN} = 100 - (9.169TN) + (0.3059TN^2)$ (5) |
| Dissolved Oxygen      | $q_{DO} = 100\exp^{-0.0001DO^2}$ (6)         |
| pH                    | $q_{pH} = -657.2 + (197.38pH) - (12.92(pH)^2)$ (7) |
| Total Suspended Solids| $q_{TSS} = 79.75 + (0.166TSS) - (0.001088(TSS^2))$ (8) |
| Turbidity             | $q_T = 84.76(2.71828^{-0.0162067})$ (9)      |
| Temperature           | $q_{Temp} = 92$ (10)                         |

Table 2 | Empirical equations for obtaining the WQI’s $q_i$
is BOD, in which had the highest concentrations at station 64775000 with values of 15 mgL⁻¹ and 10 mgL⁻¹. The values of BOD for this station could probably indicate contamination for organic pollution at these collects, seen the difference between values found in other periods and in other stations (n = 259). The evaluation of BOD in rivers is of great importance, because it is a parameter for the assessment of biodegradable organic matter concentration in water bodies, in which it could mean input of domestic or industrial wastewater into the water. This fraction of organic matter might be related to microbial growth, the depletion of dissolved oxygen and disturbance in the aquatic ecosystem (Wen et al. 2011). Although, it was seen in some values in higher concentrations, in general the concentrations of BOD stayed below 4 mgL⁻¹ (n = 259).

Electrical conductivity was another water quality parameter that varied between collects and stations. The highest value was also seen at 64775000 with approximately 302 μScm⁻¹ followed by 271 μScm⁻¹ at 64795000 (Piquiri River), 212 μScm⁻¹ at 64771500, and 207 μScm⁻¹ at 64830000 (Piquiri River) (n = 374). This parameter assesses the capacity of water to conduct electrical current, and, it could be influenced by temperature and by presence of inorganic dissolved solids such as nitrate, chloride, sulfate and phosphate anions (EPA 2020). Although Nitrate could influence electrical conductivity in natural waters, the highest nitrate concentration was seen at 64790000 with concentration of 1.23 mgL⁻¹, which presented a low value of conductivity. Generally, concentrations of nitrate stay below 1 mgL⁻¹ (n = 122). In addition, the nitrate concentration is bellow of recommended maximum for health water quality (10 mgL⁻¹) by the World Health Organization (Xue et al. 2009). Also, Xue et al. (2016) affirm that high concentrations of nitrate might result in blooms of toxic algae,
Dissolved Oxygen concentration varied since low concentrations (lower than 6 mgL\(^{-1}\)) to supersaturation (more than 10 mgL\(^{-1}\)) \((n = 308)\), in which it could be associated with the photosynthetic activity (Prasad et al. 2014), and could impact positively in the aquatic organisms such as reduction of stress and diseases in fishes (Edsall & Smith 1990). In relation to lower concentrations, they could be associated with the nitrification process and consumption of aerobic microbes to degrade the organic matter (Prasad et al. 2014). The lowest values were found at 64795000 (5.79 mgL\(^{-1}\), \(n = 43\)), 64771500 (4.82 mgL\(^{-1}\), \(n = 49\)), 64785000 (5.37 mgL\(^{-1}\), \(n = 47\)) and 64775000 (5.63 mgL\(^{-1}\), \(n = 50\)). The highest DO concentrations were found in Piquiri river.

The highest values found of \(E.\ coli\) were seen in Piquiri river affluent: 64785000 (500000 NMP (100 mL\(^{-1}\), \(n = 31\)) and 64775000 (240000 NMP (100 mL\(^{-1}\), \(n = 29\)), and in the initial point in Piquiri river, station 64771500 (280000 NMP (100 mL\(^{-1}\), \(n = 30\)). Another high value found in Piquiri river was at station 64799500 (80000 NMP (100 mL\(^{-1}\), \(n = 28\)). \(E.\ coli\) could be a biological indicator of anthropogenic organic pollution in aquatic ecosystems, where its quantification could be associated with human fecal contamination, differently from fecal coliforms, which present some species that are not necessarily from a fecal contamination (Amirat et al. 2012). Complementarily, fecal and total coliforms were also measured, however in lower quantity compared to \(E.\ coli\) (fecal coliforms: \(n = 30\); total coliforms: \(n = 119\)). The highest quantification of fecal coliforms was seen at 64799500 (50000 NMP (100 mL\(^{-1}\), \(n = 3\)). Generally, fecal coliforms stayed below 10000 NMP (100 mL\(^{-1}\), however, this parameter has a low number of quantifications. In relation to total coliforms, the highest quantification was seen at 64785000 (1600000 NMP (100 mL\(^{-1}\), \(n = 29\)).

Total Nitrogen \((n = 96)\) and Kjedahl Nitrogen \((n = 145)\) were also measured, however Total Nitrogen has highest values (outliers) in Piquiri river, while station 64790000 presented concentration range of values above 1 mgL\(^{-1}\) \((n = 12)\). Total Nitrogen is the sum of organic-N, Ammonium, Ammonia, Nitrate and Nitrite, while Kjedahl Nitrogen involves organic-N, Ammonium and Ammonia (Wall 2015). In relation to Kjedahl Nitrogen, the highest value was found at 64785000 (1.40 mgL\(^{-1}\), \(n = 29\)). Although, there are outliers in stations located in Piquiri river, the boxplot for affluent presented higher concentrations in higher values of Kjedahl Nitrogen.

Phosphorus is another nutrient of great importance to be monitored in aquatic ecosystems. In this study, total phosphorus was higher in stations 64785000 (0.30, 0.23 mgL\(^{-1}\), \(n = 21\)) and 64790000 (0.20 mgL\(^{-1}\), \(n = 12\)). Although, all points in Piquiri river presented outliers, in other words, non-common values for these points seen by temporal analysis. The importance of phosphorus is that this element is an essential and limiting nutrient in aquatic ecosystems, controlling, therefore, primary production. Also, in higher concentrations can affect algae and macrophyte growth (Baldwin 2013). However, the most relevant P-form in aquatic ecosystems is Orthophosphate (Baldwin 2013), in which presented highest value at station 64785000 (0.1 mgL\(^{-1}\), \(n = 6\)). This station also presented highest values of TP, \(E.\ coli\) and total coliforms. It suggests a possible contamination before this station.

pH, another important water quality parameter, varied from acid to alkaline values. The smallest value was of 2.90 \((n = 377)\) at station 64775000 (station with highest Ammonical Nitrogen, BOD and COD concentrations). The highest value was 10.15 \((n = 377)\) at station 64771500. pH out of range of 6–9 could impact the aquatic ecosystem. The effects could include the reduction of biodiversity, disappearance of species sensitive to acidification, modification of trophic status and decrease of fish quantity (Moiseenko 2005). Water temperature presented practically the same range for all points from approximately 10–35 °C \((n = 380)\). However, it is notable that temperatures in the affluent trend to have lower value than in stations located in Piquiri river.

Turbidity usually presented values below 100 NTU \((n = 376)\). However, the boxplot shows several outliers, which means the alteration of natural conditions of turbidity of the rivers. These effects could occur naturally because of precipitation or sewage release into the water. Total Suspended Solids (TSS) also presented some outliers, mainly in Piquiri river, being the highest value of 121 mgL\(^{-1}\) at 64820000 \((n = 137)\). In addition, Total Dissolved Solids (TDS) also presented higher value in Piquiri river with high values in affluent (64775000) too. The highest TDS concentration was of 136 mgL\(^{-1}\) at 64771500. TSS are related to sand, silt, clay, mineral precipitates and biological eutrophication of lakes and reservoirs and impacts on aquatic ecosystems.
matter particles in the water, where the concentration could increase after physical processes driven by hydrological phenomena (Butler & Ford 2018).

**Classification of water quality according to the Brazilian law and water quality index**

Figure 3 shows the variation of nine water quality parameters for each station according to the Brazilian classification of water bodies over twenty years. Ammoniacal Nitrogen stayed below 0.5 mg·L\(^{-1}\) for all stations, in which it indicates class 1 for each station, for both in Piquiri river and in its affluent. It is also notable the higher concentrations of ammoniacal nitrogen after July. Concentrations of nitrate were also classified in class 1, which indicates water of good quality for this parameter, where the concentrations stayed below 1.25 mg·L\(^{-1}\) for all stations. The highest concentrations were seen in the affluent, and the most higher values were also seen after July. Total Nitrogen was classified in class 1 and 2, seen that the maximum concentration for this parameter is 2.18 mg·L\(^{-1}\) (both classes) for lotic environment. In this study, all values were lower than 2 mg·L\(^{-1}\). Differently from Nitrate and Ammoniacal Nitrogen, the highest value was found on Piquiri river.

Another important nutrient to assess water quality, phosphorus presented to have some values of inferior water quality evaluation compared to the analysis of nitrogen forms. The results show classification for class 1 and 2 (≤0.1 mg·L\(^{-1}\), 94%), class 3 (≤0.15 mg·L\(^{-1}\), 3%) and class 4 (>0.15 mg·L\(^{-1}\), 3%). The stations that presented higher concentration of total phosphorus were 64785000 (85% Class 1 and 2, 10% Class 4 and 5% Class 3), 64830000 (91% Class 1, 9% Class 4), 647599500 (96% Class 1, 4% Class 4) and 64795000 (91% Class 1, 9% Class 3).

BOD concentration varied from Class 1 (≤3 mgL\(^{-1}\)) to Class 4 (>10 mgL\(^{-1}\)). For Class 4, just two observations were found, both at station 64775000. Values at class 3 were observed four times at stations 64799500, 64795000 and 64771500 (twice). Although, COD has not upper and lower limit in the water body classification. This variable also indicates the concentration of organic matter in aquatic ecosystems, and presented higher values in Piquiri river affluent. In addition, the DO concentration presented acceptable values most all times, with exception of four values, in which

![Figure 3](http://iwaponline.com/ws/article-pdf/doi/10.2166/ws.2021.026/837653/ws2021026.pdf)

*Figure 3 | Water quality variation and classification from 2000 to 2019.*
they were classified into Class 2, 3 and 4. The lower DO concentration was also seen in a Piquiri river affluent.

E. coli presented several unacceptable values, varying from 20 NMP (100 mL)\(^{-1}\) at station 64771500 to 500000 NMP (100 mL)\(^{-1}\) at station 64785000. The most unacceptable values were seen in Piquiri river affluent, thus indicating a possible contamination in these regions of the watershed. Another parameter that showed several values in Class 4 was Turbidity, which had higher values in campaigns between January and July. Probably, the occurrence of high values of this variable was due to physical processes driven by hydrological phenomena.

Therefore, the results show good water quality in the locations of stations inside of Piquiri river watershed, although some parameters still present inadequate values for Class 1. Thus, for the water treatment station the most values showed that there is no need for a complex system with advanced treatment. However, there is still a necessity of constant water quality monitoring for future improvement.

Figure 4 shows the mean variation of BOD and COD concentration in the stations located in Piquiri river watershed (Figure 4(a)), WQI mean for each season (Figure 4(b)) and WQI boxplot for each water quality station (Figure 4(c)). It is possible to note the low concentration of BOD and COD, in which indicates low organic content in Piquiri river and in its affluent over time. The highest BOD and DOC mean concentrations were of 2.62 mg L\(^{-1}\) and 9.56 mg L\(^{-1}\) respectively at station 64775000. According to Fathi et al. (2018), BOD concentrations varying between 0 and 2 mg L\(^{-1}\) shows a very clean water, while range from 2 to 5 mg L\(^{-1}\) relatively polluted and more than 5 mg L\(^{-1}\) severely polluted.

Complementarily, the Water Quality Index varied from 58.96 at station 64790000 in the summer to 78.62 at station 64795000 in the winter, both values indicate water of good quality. A possible explanation for higher WQI values during the winter is the lower quantity of precipitation during this season of the year (Pires 2018). Beyond that, station 64790000 presented smaller boxplot, although, also presents the water of good quality. The WQI method has been used in assessments of water quality in surface waters of rivers, being an important strategy for water resources management (Wu et al. 2018). Although, there are different adapted WQI methods, this important index is an important methodology for water quality evaluation. Wu et al. (2018) found values of WQI in Lake Taihu varying from 40 to 90, although, the water quality in Lake Taihu basin was classified as moderate (51–70). Fathi et al. (2018) also used WQI, where the authors found values above 60, also classified as moderate. Shil et al. (2019) also used WQI to analyze water quality in a river. The authors found values between 17 and more than 90. Oliveira et al. (2018a), used WQI in their study, to analyze the land use and its impacts on water quality in a watershed. In this watershed, the authors found values varying from 13 to approximately 70. Therefore, WQI has shown to be an interesting tool for the description of water quality in an aquatic environment, however, it is necessary to have low quantity of missing values in the dataset for better characterization.

**Prediction of TP and turbidity in Piquiri river**

Figure 5 shows the relationship between Total Phosphorus and Total Nitrogen, and, between Turbidity and Total Suspended Solids with values of stations located at Piquiri river. In addition, there is a correlation line and prediction limits predicted from affluents and station 64771500 data (Figure 5(a) and 5(c)). Also, there is a comparison between the parameter values predicted and observed in Piquiri river stations (Figure 5(b) and 5(d)). It is notable some values out of prediction region (lines), being two values for TP prediction and nine values for Turbidity prediction. Thus, the graphs show higher concentrations of values between prediction line. For both analyses, \( r^2 \) stayed above 0.60. Values of Pearson’s correlation (r) of 0.80 between TN and TP, and of 0.79 between TSS and Turbidity. Both values are considered strong correlation between the variables (Shil et al. 2019). Another interesting point, is that the best results between predicted and observed data were seen in lower values. Thus, the linear equation model presented to have interesting results in the prediction of TP concentration, and turbidity in Piquiri river.

**IDW interpolation of water quality parameters**

Figure 6 shows the IDW interpolation graphs for spatial variation of TN concentration in the Piquiri river watershed for each season of the year. The lowest concentrations were
Figure 4 | BOD and COD mean concentrations in the stations in Piquiri river watershed. Timescale from 2000 to 2019.
seen in the upper part of Piquiri river, where the percentage of land use is higher for Pasture, Forest and Forest Occupation compared to Agricultural area, where it is most intense in the middle to downstream of the watershed, which presented higher concentrations of TN along with station 64790000 located in one of the affluent of Piquiri river. The highest concentration of TN was seen during the fall at station 64790000. The same station with smaller values in the WQI boxplot. However, during the winter, driest season, stations 64820000 and 64830000 presented higher concentrations than station 64790000. Therefore, the interpolation shows the variation of TN concentrations over seasons, with different hydrological scenarios, and land use and land cover, with higher concentrations seen in agricultural areas.

Figure 7 shows the IDW interpolation graphs for spatial variation of TP concentration in the Piquiri river watershed for each season of the year. During winter, with lower precipitation amounts, higher concentrations of TP were seen in the downstream points (64820000 and 64830000), with a predominance of agricultural area. In the spring, rainiest season, the values of TP in the downstream decreased, with higher values being observed in affluent. A possible explanation for that is the difference between precipitation amount in the watershed. According to Pires (2018), annual precipitation means in affluent of Piquiri river could vary from 1,650 to 1,900, while in the downstream of Piquiri river from 1,450 to 1,550. High concentration of precipitation could bring agricultural drainage water, and, dilute organic components of domestic sewage. During fall and summer, higher concentrations were seen in the Piquiri river affluent.

Figure 8 shows the IDW interpolation graphs for spatial variation of DO concentration in the Piquiri river watershed for each season of the year. The highest DO mean concentrations were seen during winter, the season with a smaller value of temperature. Lower values were seen in the affluent of Piquiri river during summer and Spring, with approximately 8.0 mgL$^{-1}$. A smaller mean DO concentration along the watershed was seen in the fall. Thus, during all seasons dissolved oxygen stayed in great concentrations for aquatic organisms.
CONCLUSION

Spatial-temporal variation of water quality in Piquiri river watershed have over the years showed good quality, although, unacceptable values of *E. coli*, BOD, COD and total phosphorus appeared. Most unacceptable values were identified in affluent rivers, suggesting the improvement in the water quality closer to downstream of the Piquiri river. Use of Water Quality Index confirmed the good quality for all stations, although, there are many missing values, which, it could represent more accurately the variation. In addition, smaller WQI values were observed in summer and fall, while the higher values were seen in the winter, season with a smaller precipitation amount. Generally, all stations were classified into Class 1 or Class 2, according to the Brazilian Law, with exceptions seen for some values of the following parameters: BOD, Total Phosphorus, DO, *E. coli* and turbidity, in which they also presented values referred to Classes 3 and 4. Also, it was found a moderate value of $R^2$ for estimation of Turbidity and Total Phosphorus.
in Piquiri river through a linear regression model using values of affluent stations and station 64771500. IDW interpolation has also showed higher values of TN in agricultural area predominance in the watershed, a lower concentration of TP in winter and fall and higher DO concentration in winter. Still, the work reinforces the necessity of frequent water quality monitoring avoiding missing data in different locations of a watershed to identify possible pollution sources and for better improvement in water resources management and making decisions. Therefore, the techniques applied and methodology used in this study are novelty in the study of water quality in this watershed, and, with the results obtained these methods could also be applied in studies of other watersheds for evaluation of spatial and temporal variation of water quality. Finally, we can conclude that the work has practical applicability, both in general and specific contexts, contributing to the monitoring of basins.
DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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