Climatic seasonality and water quality in watersheds: a study case in Limoeiro River watershed in the western region of São Paulo State, Brazil

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Abstract

Applying the climatological water balance (WB) concept to describe the relationship between climatic seasonality and surface water quality according to different forms of land use and land cover (LULC) is an important issue, but little explored in the literature. In this paper, we evaluate the influence of WB on surface water quality and its impacts when interacting with LULC. We monitored 11 sampling points during the four seasons of the year, from which we estimate WQI (water quality index) and TSI (trophic state index). We found an effect of the seasonality factor on both WQI values ($F(3,30) = 12.472$; $p < 0.01$) and in TSI values ($F(3,30) = 6.967$; $p < 0.01$). We noticed that LULC interferes in the way that the water balance influences the WQI and TSI values since in sampling points closest to higher urban density, with little or no riparian protection, the correlation between water balance and water quality was lower. In the stations that had the lowest water surplus and deficit, there was positive linearity between water balance and WQI. However, in the seasons when the surplus and water deficit recorded were extreme, there was no linearity. We conclude that water deficiency impairs the quality of surface water. In the extreme surplus water season, the homogeneity of WQI samples was lower, suggesting a higher interaction between rainwater and LULC. This study contributes to design management strategies of water resources, considering the climatic seasonality for optimization.

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Introduction

Water quality protection is a global topic concern (Zhang et al. 2018) because water plays a vital role in the industry, agriculture, public health, and environmental conservation (Shi et al. 2017; Zhang et al. 2019). A key parameter that has been adopted to monitoring water quality is the evaluation of land use and land cover (LULC) dynamics. While LULC modifications provide social and economic benefits, they may generate serious impacts on water balance components (Birhanu et al. 2019).

Intense agricultural activities associated with accelerating urbanization have resulted in tremendous pressure on water quality (Shi et al. 2017). There is a significant impairment of water quality in densely anthropomorphized areas intended for agricultural use (Darwiche-Criado et al. 2015). Inadequate land use may provoke the transference of nutrients to water bodies (Pacheco and Fernandes 2016). In this manner, evaluating the relationship between water quality and LULC changes is a worldwide interest (Liu et al. 2014; Ren et al. 2014; Ding et al. 2015; Yu et al. 2016; Ding et al. 2016;

Giri and Qiu 2016; Huang et al. 2016; Pacheco and Fernandes 2016; Tanaka et al. 2016; Lenart-Boroń et al. 2017; Shi et al. 2017; de Mello et al. 2018; Zhang et al. 2018; Birhanu et al. 2019; Woldeab et al. 2019; Zhang et al. 2019).

Water quality is also affected by climatic changes, influencing the hydrological processes (Arnell et al. 2015; Hosseini et al. 2017). The climatic seasonality, caused by the difference in the rainfall pattern, represents a disturbance in the watercourses and has affected water quality (Li et al. 2015). Several studies pointed the influence of climatic seasonality on surface water quality parameters (Park et al. 2011; Pantoja et al. 2016; Puig et al. 2016; Zhang et al. 2015; Liu et al. 2017; Ojok et al. 2017; Shi et al. 2017; Zhang et al. 2017; Yevenes et al. 2018; Bhatti et al. 2018; Mohseni-Bandpei et al. 2018; Wei et al. 2018; Xu et al. 2019; Zhang et al. 2019). One research (Zhong et al. 2018) also argued that surface water quality is affected by factors which depend on each season of the year.

Several studies (Kaseamsawat et al. 2015, Damasceno et al. 2015, Şener et al. 2017, Wang and Zhang 2018, Amâncio et al. 2018, and so on) adopted indices to evaluate water quality. These studies generally consider the volume of precipitation as a seasonal factor. However, the hydrological cycle is a system composed of interaction among several factors, such as evaporation, condensation, precipitation, detention and runoff, infiltration, water percolation in the soil, and the aquifers and fluvial flows (Righetto 1998). In small watersheds, evapotranspiration plays an essential role in water balance (entrance and exit) alongside with precipitation, which is the variable responsible for the flow of the drainage system (Pereira et al. 2007).

It is well established that water quality is related to the hydrological and limnological properties of ground and surface water (Simedo et al. 2018). It is also known that LULC changes are generally linked to water quality within a watershed, and landscape configurations may be used as sensitive predictors of water quality (Shi et al. 2017). However, up to the time of writing, few studies have applied an approach that considers the concept of climatological water balance to characterize the relationship between climatic seasonality, and surface water quality within watersheds, considering different forms of LULC. This strategy of investigation is fundamental to delineate actions for water resources management and to identify threats of contamination in these resources, seeking to mitigate diffuse pollutants. The present study was conducted to evaluate the influence of WB on surface water quality and its impacts when interacting with LULC. The hypothesis raised here is that climatic seasonality, represented by estimation of the climatological water balance, influences the water quality indexes (WQIs) and TSI (trophic state index). We also verified whether the LULC interfered in the way water balance influences these variables. The rest of this paper is organized as follows: the "Study area" section details the study area and the data collection; the "Methodology" section describes the conducted

methods performed in this study; the "Results and discussion" section presents and discusses the results; and the "Conclusion" section concludes the present research.

Study area

We adopted the Limoeiro River watershed as a study case. This area is located in the western region of São Paulo State, Brazil. The Limoeiro River watershed has an area of 92 km^2 and 124.95 km of river extension. This watershed represents one of the most important watersheds included in the 22nd Water Resources Management Unit in the São Paulo state because it crosses the most populous municipality (Presidente Prudente) of the region (Fig. 1). The estimated population for this watershed is 251,902 inhabitants (IBGE 2018). The large part of the Limoeiro River watershed belongs to the urban area of the Presidente Prudente municipality (Fig. 2), while a small part in the Álvares Machado municipality.

We plotted (Fig. 3) both mean temperature (°C) and mean precipitation (mm) from 1969 to 2015, and 2018, using data from a meteorological station located in the Presidente Prudente city. We verified that the study area is characterized by periods with higher rainfall in the spring and summer season (October to March). Moreover, the average of monthly temperatures behaves according to the climatic season; i.e., temperatures are higher in the summer and spring, and they are milder in the autumn and winter. Additionally, when we analyzed the meteorological dynamics over 2018, concerning 1969 until 2015, we observed that in January, February, and August the average temperature was milder, while it was higher in the other months. Regarding the precipitation data, we observed (Fig. 3) an increase in the rainfall volume in January, August, September, October, and November months and a decrease volume in the other months (April, May, June, and July). This decrease in precipitation volume corresponds to the autumn season and the initial period of the winter season, where the reduction in rainfall exceeds 60%.

Methodology

The methodological procedures were composed of four steps (Fig. 4): (1) sampling point selection; (2) surface water quality evaluation; (3) LULC changes mapping; and (4) determination of the climatological water balance.

Sampling points selection

Eleven sampling points were carefully selected to represent the main course and tributaries of the Limoeiro River. We used three materials for selecting these points: the urban

GEOGRAPHIC LOCALIZATION OF THE LIMOEIRO STREAM WATERSHED, SP - BRAZIL
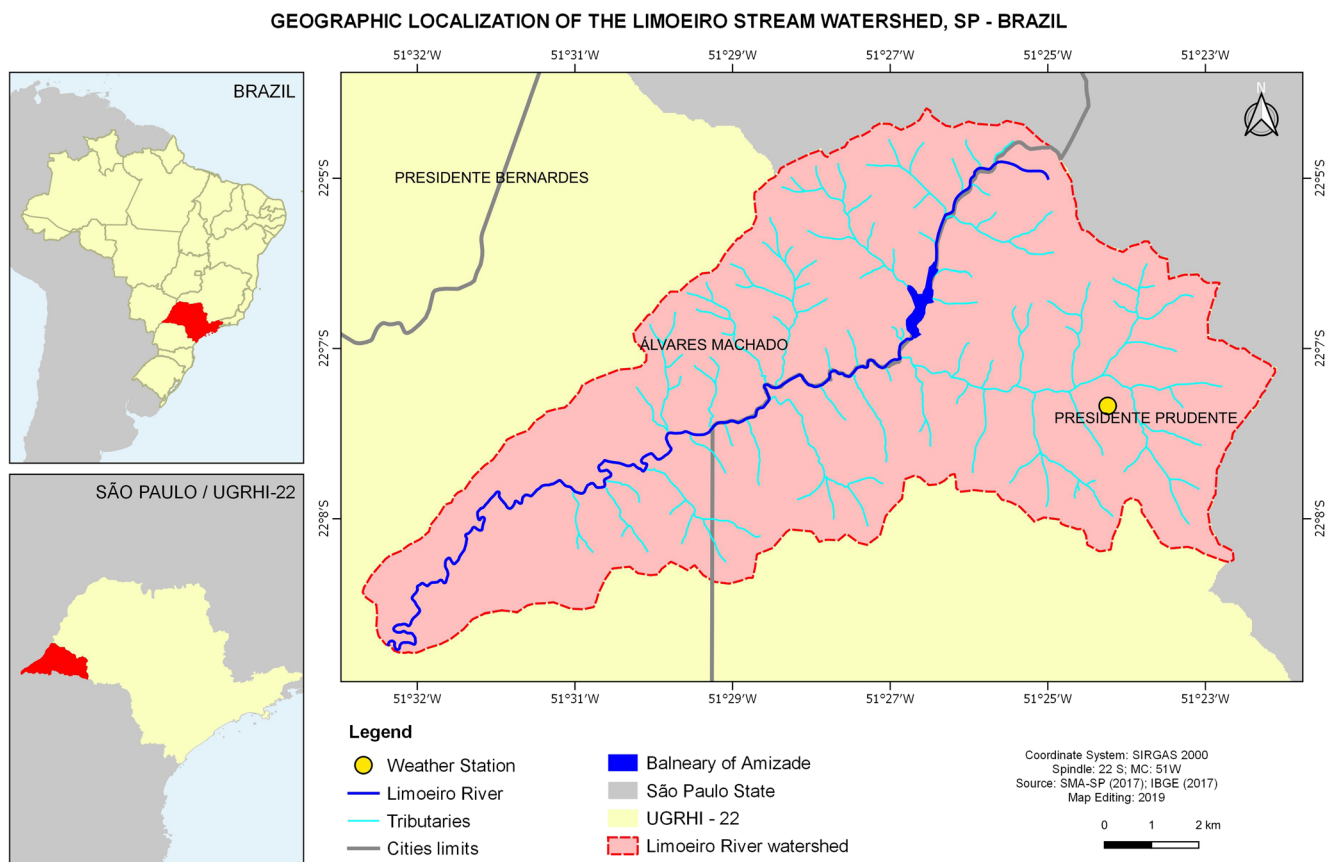
Fig. 1 Study area

zoning map of the Presidente Prudente city (Fig. 2); a multi-spectral image composition of 2017; and visits in the study area to visually the access to candidate points. Part of our study area is located in the Álvares Machado city; however, there is no urban zoning map for this city, which is composed of 24,830 inhabitants (IBGE 2018). The multispectral image composition of 2017 was produced from the 10-m resolution bands 8 (near-infrared), 4 (red), and 3 (green) of the MSI sensor onboard the Sentinel-2B satellite. This scene was provided by the United States Geological Survey (UNITED States Geological Survey - USGS n.d.) (https://espa.cr.usgs.gov/ordering/new/).

Surface water quality characterization

For the characterization the surface water quality of the Limoeiro River, we used 10 physicochemical parameters analyses: dissolved oxygen (DO), hydrogen ionic potential (pH), biochemical oxygen demand (BOD), water temperature (T), total nitrogen (TN), total phosphorus (TP), turbidity (Turb), chlorophyll a (Chl a), and total solids (TS). The microbiological parameter used was *Escherichia coli* (*E. coli*). We characterized surface water quality during four field campaigns: summer (February 26, 2018), autumn (June 18, 2018),

winter (September 10, 2018), and spring (November 26, 2018).

We measured in loco the DO, T, and pH parameters for each of the campaigns. DO and T were measured by using a portable dissolved oxygen meter (Hanna Mark, model HI 9146–04), and pH was measured using a pH indicator paper (Merck Mark). We confirmed the pH value in the laboratory with the bench pH meter (Brand Quimis). For the analysis of the other physicochemical and microbiological parameters, we manually collected (in previously prepared amber glass bottles) water samples in the cross-section of the Limoeiro River and its tributaries. We conditioned the samples in a thermal box with negative temperature for preservation until arrival in the laboratory.

We performed the analysis of the physicochemical and microbiological parameters according to the Standard Methods for the Examination of Water and Wastewater (APHA 2017). We compared the results with values presented by the Resolution of the National Environmental Council, No. 357/05 (CONAMA 2005) and the standards established for rivers of class 2 (Table 1—Supplementary material). The class 2 rivers are characterized by CONAMA (No. 357/05) as those whose waters can be used to supply human consumption after conventional treatment. They are used for protection of aquatic communities, such as recreation activities like swimming,

PRESIDENTE PRUDENTE URBAN ZONING AND ALVARES MACHADO URBAN DENSITY, SP - BRAZIL
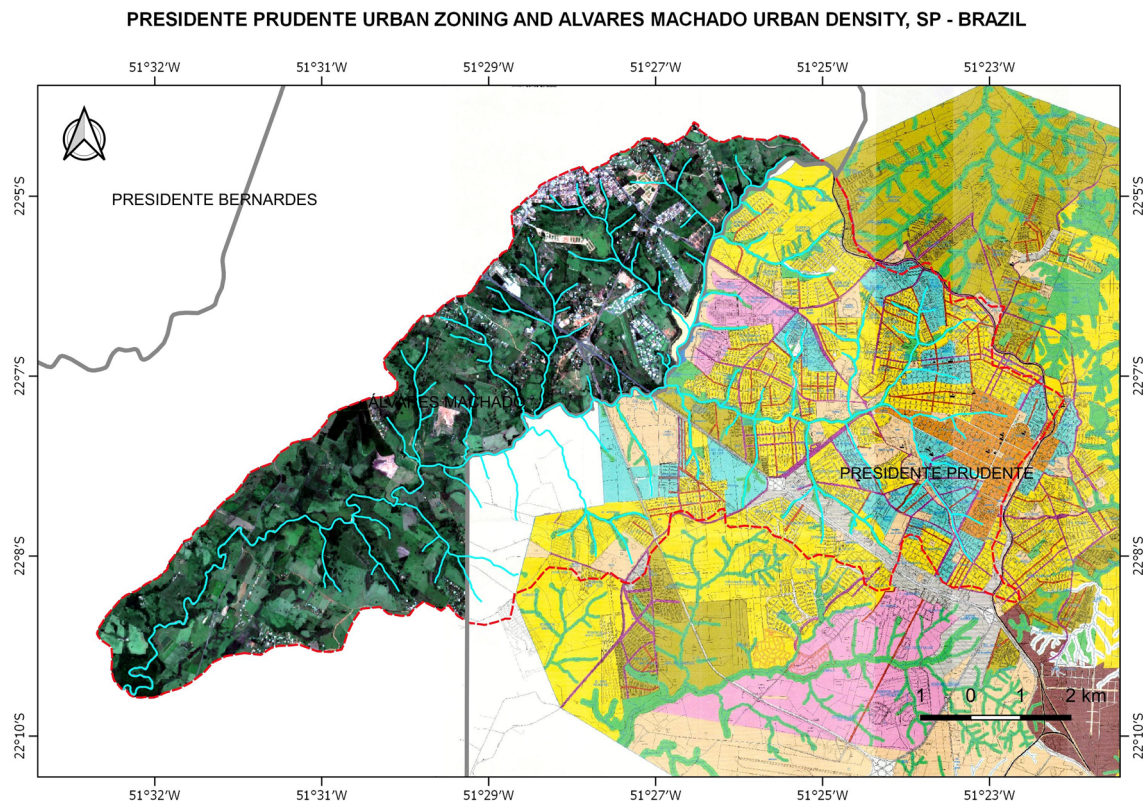
Coordinate system: SIRGAS 2000 / Spindle: 22S; MC: 51W
Source: Presidente Prudente City Hall (2011), adapted by the author/ Multispectral images (bands 4,3 e 2 of the satellite Sentinel 2B at november 24, 2017)
Map editing: 2018

Legend

- ZR1 - Residential zone of low population density, with horizontal occupation;

- ZR2 - Residential zone of medium population density, with horizontal and vertical occupation up to 2 floors;

- ZR3 - Residential zone of high population density of social interest, with horizontal and vertical occupation;

- ZR4 - Residential zone of medium population density of social interest, horizontal and vertical occupation with up to 2 floors

- ZCS1 - Central trade and service zone, of vertical occupation;

- ZCS2 - Trade and service zone of road axles, of vertical occupation;

- ZCS3 - Trade and service zone of neighborhood and region principal and secondary roads;

- ZI1 - Non-polutive industries zone;

- ZI2 - Potentially pollutant industries zone;

- ZPPA - Preservation and environmental protection zone;

- ZE - Special zone:
  1) Zone of special urbanist interest;
  2) Aeroportuary special zone;
  3) Teaching and research special zone;
  4) Exhibition special zone;
  5) Special zone of botherous current use, noxious and dangerous
  6) Electricity lowering substation special zone;
  7) Sports special zone;
  8) Recreational clubs special zone;
  9) Municipal cemetery special zone;
  10) Intercity road transport special zone;
  11) Intercity rail transport special zone;
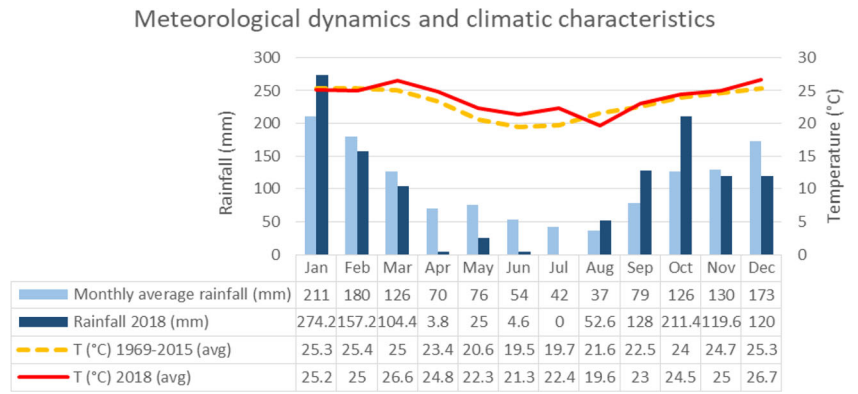 12) Recreation special zone;
  13) Military special zone.

Fig. 2 Urban zoning map

water skiing, and diving; irrigation of vegetables, fruit plants and parks, gardens, sports, and leisure fields, with which the public may come into direct contact; and also for aquaculture and fishing.

For each field campaign, we determined the water quality index (WQI) and the trophic state index (TSI). The WQI is an index created in 1970 by the National Sanitation Foundation and adapted by the Environmental Sanitation Technology Company of São Paulo State (CETESB) for studies of water quality analysis in Brazil. This index represents a weighted average, which is calculated using the following parameters: DO, thermotolerant coliforms, pH, BOD, T, TN, TP, Turb, and TS. We calculated TSI based on CETESB (2018) equation, which refers to the arithmetic mean between

Fig. 3 Multitemporal meteorological data for the study area

Meteorological dynamics and climatic characteristics

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Monthly average rainfall (mm)	211	180	126	70	76	54	42	37	79	126	130	173
Rainfall 2018 (mm)	274.2	157.2	104.4	3.8	25	4.6	0	52.6	128	211.4	119.6	120
T (°C) 1969-2015 (avg)	25.3	25.4	25	23.4	20.6	19.5	19.7	21.6	22.5	24	24.7	25.3
T (°C) 2018 (avg)	25.2	25	26.6	24.8	22.3	21.3	22.4	19.6	23	24.5	25	26.7

the phosphorus trophic state indices (TSI (TP)) and chlorophyll *a* (TSI (Clh *a*)). TSI encompasses the cause and effect of the water eutrophication process, assessing water quality for nutrient enrichment and its effect related to the excessive growth of algae and cyanobacteria (Companhia Ambiental do Estado de São Paulo – CETESB 2018). The range of classes adopted to WQI and TSI has followed the São Paulo state criteria, as shown in the supplementary material (Table 3 and Table 4—Supplementary material, respectively).
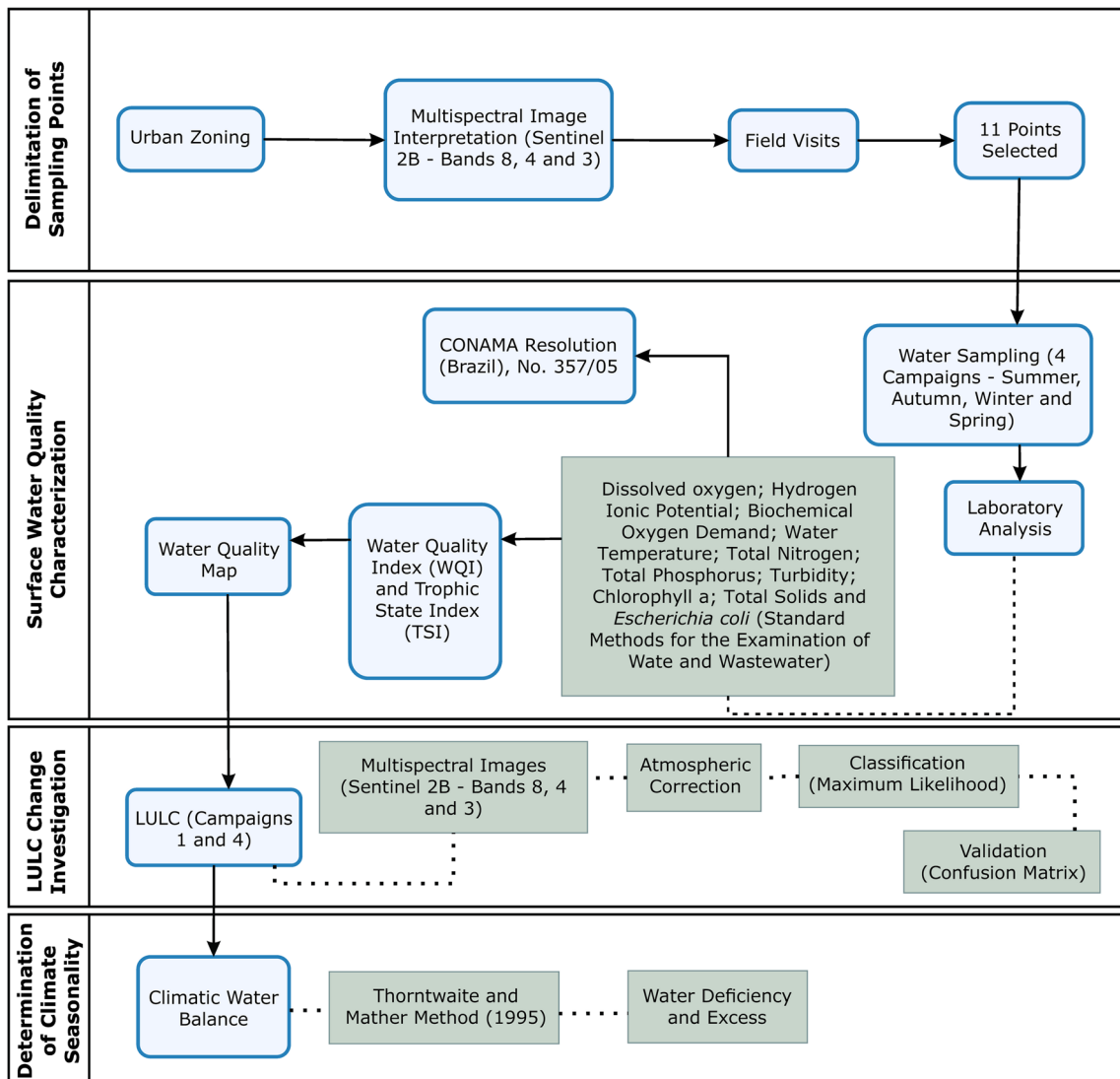
Fig. 4 Workflow

Both WQI and TSI were determined for each of the 11 sampling points. We produced the water quality map for the Limoeiro River watershed, considering each field campaign individually. The water quality maps were marked considering the WQIs of the 11 collection points and attributed these values to the cross-sections of the rivers that connect one collection point to the other. The value of the respective index of a point was attributed to the river extension that goes to the subsequent point, according to their respective flow.

LULC changes mapping

We created the LULC map for the first field campaign (summer, data February 22, 2018) and final field campaign (spring, data October 20, 2018). The LULC map for 2017 was produced with a supervised classification (by using the maximum likelihood algorithm) on multispectral image composition. The composition was generated from the 10-m bands 8, 4, and 3 of the MSI sensor, Sentinel-2B satellite. We identified six LULC classes in the study area: pond/reservoir, tree vegetation, herbaceous vegetation, agriculture, exposed soil, and urban area. We performed the classification process using the Semi-Automatic Classification Plugin (SCP) of QGIS 2.18. To validate the classification, we calculated the confusion matrix (Cohen 1960), using 20 randomly distributed points over the area. We adopted as reference data Planet satellite images, which have a spatial resolution of 03 m, and were acquired on February 25 and October 22, both in 2018. The LULC map resulted in a Kappa index of 88% and 92% representing a very good classification according to Monserud and Leemans (1992).

Determination of climatological water balance

We used precipitation and temperature data of 2018 to investigate the association between water quality and climatic seasonality. The data was provided by the National Institute of Meteorology (http://www.inmet.gov.br/portal/index.php?r=home2/index) from the local meteorological station (Fig. 2) inside the study area. In this website, the National Institute of Meteorology provides data from weather stations distributed throughout the Brazilian territory. Based on the methodology of Thornthwaite and Mather (1955), we estimated the daily sequential climatological water balance for the Limoeiro River watershed in the year of 2018. The changes in the hydrographic volume of a river watershed are directly linked to climatic events occurring near the monitoring date. We chose to consider the sum of water deficit and water surplus of 30 days before each data collection. This method considers the input of water into the system represented by the precipitation and the atmospheric demand (water withdrawal) represented by potential evapotranspiration.

Based on the mean temperature and photoperiod, we estimated the potential evapotranspiration (ETP) by Thornthwaite's method (1948). We then subtracted the estimated values from the recorded values of precipitation (P). For the next step, we considered the available water capacity of 100 mm. The accumulated negative (AcN) and soil water storage (SWS) values were simultaneously calculated, considering the criteria presented by Thornthwaite's method (Thornthwaite 1948). Additionally, we identified the soil moisture variation (CHG) by subtracting from the CHG of the day the CHG from the previous day. We calculated the actual evapotranspiration using ETP, CHG, and P. Finally, we estimated the deficiency and water surplus. The steps to estimate the climatological water balance is detailed better in the supplementary material.

Statistical analysis

Statistical analyses of the data were processed with the free software Past 326 to meet the assumptions of the applied tests. The effects between the climatic seasonality variables and the results from water quality of the sampling points were tested by the one-way ANOVA and Fisher's least significant difference (LSD) methods. For all analyses, we adopted a significance level of 5%. To verify possible LULC influences on the water quality indices (WQI), Pearson's correlation was also performed between the WQI and state trophic index (STI) of each sample and water balance.

Results and discussion

Water quality monitoring points

The spatial distribution of the 11 points used to monitor water quality in the Limoeiro River watershed, associated with the multispectral image composition of 2017, is represented in Fig. 5. There is a homogeneous distribution of the 11 points in the watershed. Samples were collected on stretches of watercourses with and without canalization, in areas with and without vegetation, in a rural area surrounded by riparian forest in good condition or degraded condition, and on areas with herbaceous vegetation, where the watercourse is a water source for animals, is used for primary recreation, or receives residues of the sewage treatment plant. The specific conditions of each sampling point are described in Frame 1.

LULC changes in watershed

LULC maps for both summer (February 2018) and spring periods (October 2018) are illustrated in Fig. 6a, b, respectively. We identified that 28% of the watershed is covered by urban area, being concentrated in the urban perimeter of

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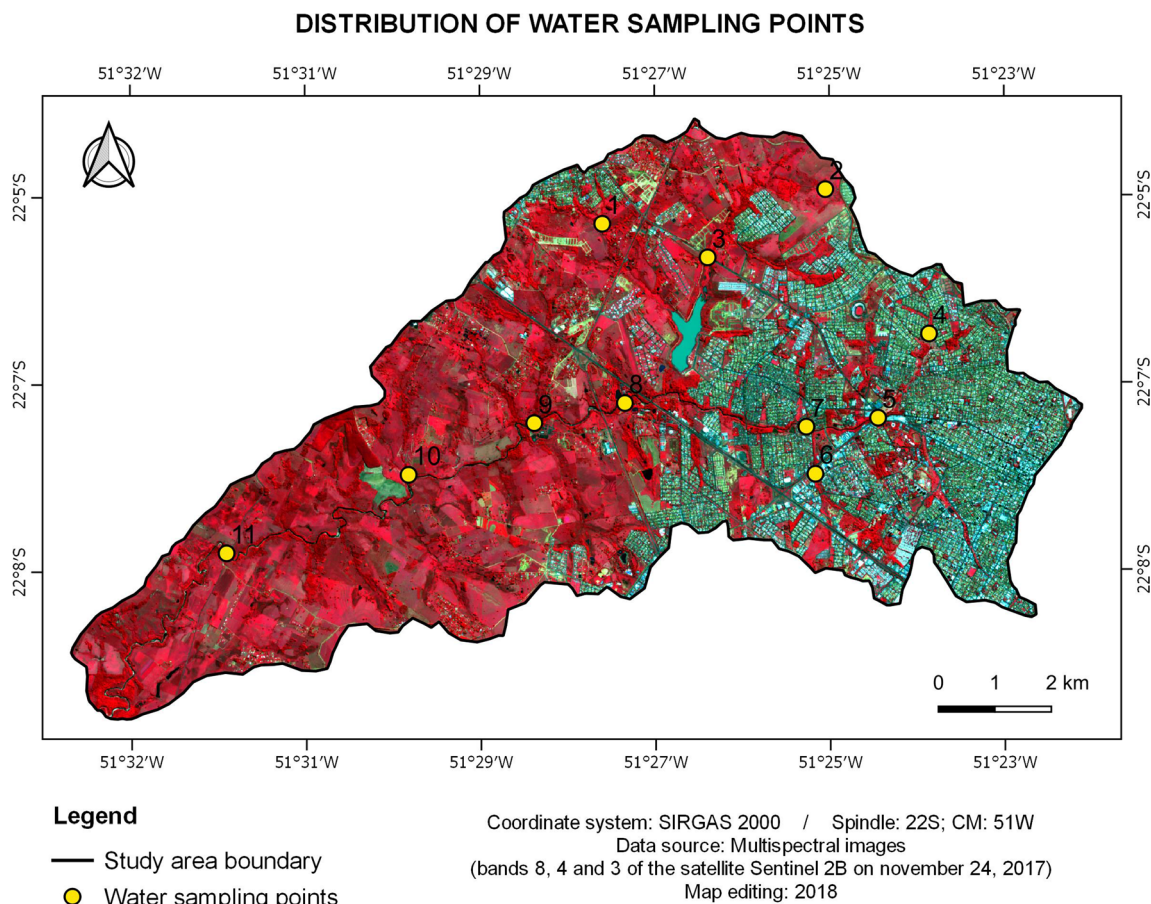
Fig. 5 Distribution of water quality monitoring points

Presidente Prudente, SP, and Álvares Machado, SP. We verified that a few changes in LULC units occurred during the period of analysis. The highest variation was identified to arboreous vegetation class and herbaceous vegetation, corresponding to 5% and 4%, respectively. This difference can be explained by the alteration of the atmospheric parameters. Considering that the more moisture an object has, the higher its emissivity (Jensen 2009), the changes caused by an increase of rainfall patterns interfere with the density of the vegetation, resulting in denser vegetation mass (Kazmierczak 1996; Eastman et al. 2013; Piao et al. 2003). In the summer period, there was a higher water surplus and this fact explained the increase in tree vegetation (Fig. 6a), while for the spring period, the surplus was lower and influenced the vegetation class growth (Fig. 6b). This factor, associated with field crop rotation activities, may still be responsible for the increase of bare soil areas (Fig. 6b) in the spring period.

Seasonality of the climatic water balance of the Limoeiro River watershed

We estimated water balance for all the four field campaigns performed into the Limoeiro River watershed (Fig. 7). We identified a water surplus of 50.7 mm, referring to the 30 days

before the collection samples related to the first campaign, which occurred in February 2018 (the summer season). To the second campaign (June 2018, corresponding to the autumn season), there was a water deficit equivalent to − 34.2 mm. In the third field campaign, September 2018 (the winter season), the water deficit reached − 43.3 mm. In the last campaign, representing the spring period, there was a water surplus of 18.8 mm. We found that the water balance of the spring campaign was at an intermediate level between the summer and winter campaigns.

Water surpluses and deficiencies depend on the amount of precipitation and evapotranspiration process, influencing the water volume of the hydrosphere (Pereira et al. 2007). When precipitation occurs and water balance presents a deficit, soil particles absorb a higher amount of water, completing the available water capacity (Teixeira et al. 2009). When water balance has excess water, the soil is with pores filled, and rainwater is drained down or laterally, increasing the volume of water from groundwater and surface water tables (Lepsch 2002).

Water quality index

The laboratory results related to physicochemical and microbiological parameters determined for the 11 points, for each

Point	Photo of the sampling site	Sample points location in Google Earth Image	Sampling point description
1			This point is located in the municipality of Álvares Machado and is influenced by the municipal urban area. It is possible to see a large amount of waste within and around the watercourse, such as tires, plastic bags, household items, among others. This point has dense vegetation in its surroundings; however, it presented erosive processes and fallen trees. In this area, the river is a tributary of the second order.
2			Corresponds to the mainspring of the Limoeiro River. This point is influenced by the city's residential area with a medium population density. The margin areas are degraded, with intense erosion processes. There are also animals trampling around the watercourse and the spring surrounded by various types of solid waste. In this area, the river is a tributary of the first order.
3			This point is about 3 km away from the mainspring of the Limoeiro River. The river passes under the highway Arthur Boigues Filho, which connects the municipalities of Presidente Prudente and Álvares Machado. This point is influenced by urban areas destined for medium and low population density and areas destined for the special zone (Figure 2). Its riparian forests are partially degraded and are sandbanks within the river extension. This point is before the Balneário da Amizade, a place for recreation of the population. In this area, the river is a tributary of the third order.
4			This point is a direct tributary of the Veado River and has a channeled bed. It is located within the Nelson Bugalho Ecological Park, in an area of medium and high population density. On the day of the visit, a large amount of suspended waste was observed, as well as the dead domestic animal within the river canal. In this area, the river is a tributary of the second order.
5			This point is located in the Veado River, a tributary of the Limoeiro River. The riverbed is channeled. Next to it, there are areas for trade and central services and a residential area with medium population density. It is located next to supermarkets and a mall. On the left bank, a preservation area is covered by vegetation, however, it is possible to observe large amounts of solid waste in its surroundings and within the watercourse. On the right bank of the river, the vegetation is degraded. In this area, the river is a tributary of the third order.
6			This point is in a tributary of the Limoeiro River, which also is channeled. It is located between areas intended for non-pollutant industrial activities, residential of medium population density, and special zone areas. The industries near the area are marble, cement, lime and mortar industry, packaging industry, and the furniture industry. Around the river canalization, there is a large vegetated area with some trees. In this area, the river is a tributary of the third order.

Frame 1 Images, location, and sampling points description
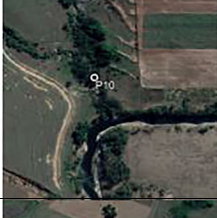
field collection in 2018, are presented in the section "Parameters for the quality of surface water in the catchment area" made available in the supplementary material (Fig. 1—Supplementary material) and technically discussed. We identified that, in general, the results of each analyzed parameter are indicative of the influence of LULC on surface water quality.

Figure 8 shows the values of the water quality index for the 11 monitoring points in the Limoeiro River watershed,

considering the climatic seasonal variation. The one-way repeated measures ANOVA determined that there is an effect of the seasonality factor on the WQI values ($F(3,30) = 12.472$; $p < 0.01$). We verified (Table 1), using the pairwise comparison, that the mean difference was significant between summer and autumn, autumn and winter, autumn and spring, winter, and spring, at a level of significance of 5%.

For comparisons between the summer and autumn WQI values, we found that in the period with a water deficit

7		This point is under the influence of areas destined to the residential area of medium population density and the special zone. In terms of the special zone, its margins have a slaughtering house and a tannery. This point is in a channeled section and on the visit date during the first campaign, the water had an unpleasant odor. In this area, the river is tributary of the fourth-order.
8		This point is located on the Limoeiro River, within the campus of a university, placed before wastewater disposal from a sewage treatment plant. Its riparian forests are in a good state of conservation, but erosive processes were observed on the banks. In this area, the river is tributary of the fourth-order.
9		This point is situated in a rural area within a private property. It has preserved riparian forests and the sampled section is after the effluent disposal of the sewage treatment plant of the municipalities of Presidente Prudente and Álvares Machado. In this area, the river is a tributary of the third order.
10		Selected for allowing a characterization of how exclusively rural areas affect the quality of the Limoeiro River. This point is privately owned, with cattle raised in its adjacencies. The riparian forests are partially degraded, with erosive processes around its margin, cattle trampling around the watercourse, and crops in the surroundings. In this area, the river is tributary of the fourth-order.
11		This point is located downriver of the Limoeiro River, next to the Vereador José Molina vicinal road bridge. Here the riparian forests are degraded and animal trampling was observed, indicating that cattle use such waters. In this area, the river is tributary of the fourth-order.

Frame 1 (continued)

(autumn), in all of the collected points (except for point 7), had a water quality index worse than the period with water surplus (summer). In summer, point 7 has the worst WQI recorded as shown in Table 1. This may be indicative of the influence by the slaughtering house and tannery presences near the area, with their respective effluents' disposal. Associated with the strong odor and visual alteration at this part of the river, during the summer campaign, it is important to consider that this low WQI value is the result of a possible discharge of effluents from these industrial sectors.

Concerning autumn and winter, the best WQI values were recorded during the winter period, when the largest water deficit calculated. This situation highlights the influence of other factors on water quality, for example, the interaction between climatic seasonality and human activities. With a deficit water balance, the volume of precipitation, although with greater infiltration and less runoff, resulted in less entry of possible diffuse contaminants through runoff.

In the autumn and spring campaigns, we noticed that the excess of water volume possibly contributed to the dilution of the contaminants and consequently improve the quality in the analyzed parameters. When comparing the other two periods, which differ in terms of water deficit (winter) and water surplus (spring), we noticed that, except for point 10, the other samplings had a better-quality index during spring.

When comparing climatic seasonality and WQI in a general way, it is noticeable that the spring season with most of the sampling points (1, 2, 3, 4, 5, 6, 7, 8, and 11) had the highest index between the four analysis campaigns. This improvement demonstrates that although the surplus water balance reflects the increase of fluvial volume and groundwater, the lower amount of precipitation in this period in comparison with the summer campaign causes a decrease in surface runoff and, consequently, less diffuse pollutants reach surface water. In point 10, agricultural machinery movement near the area could offer a possible

LAND USE AND LAND COVER OF LIMOEIRO RIVER IN 2018 FOR SUMMER (A) AND SPRING (B)
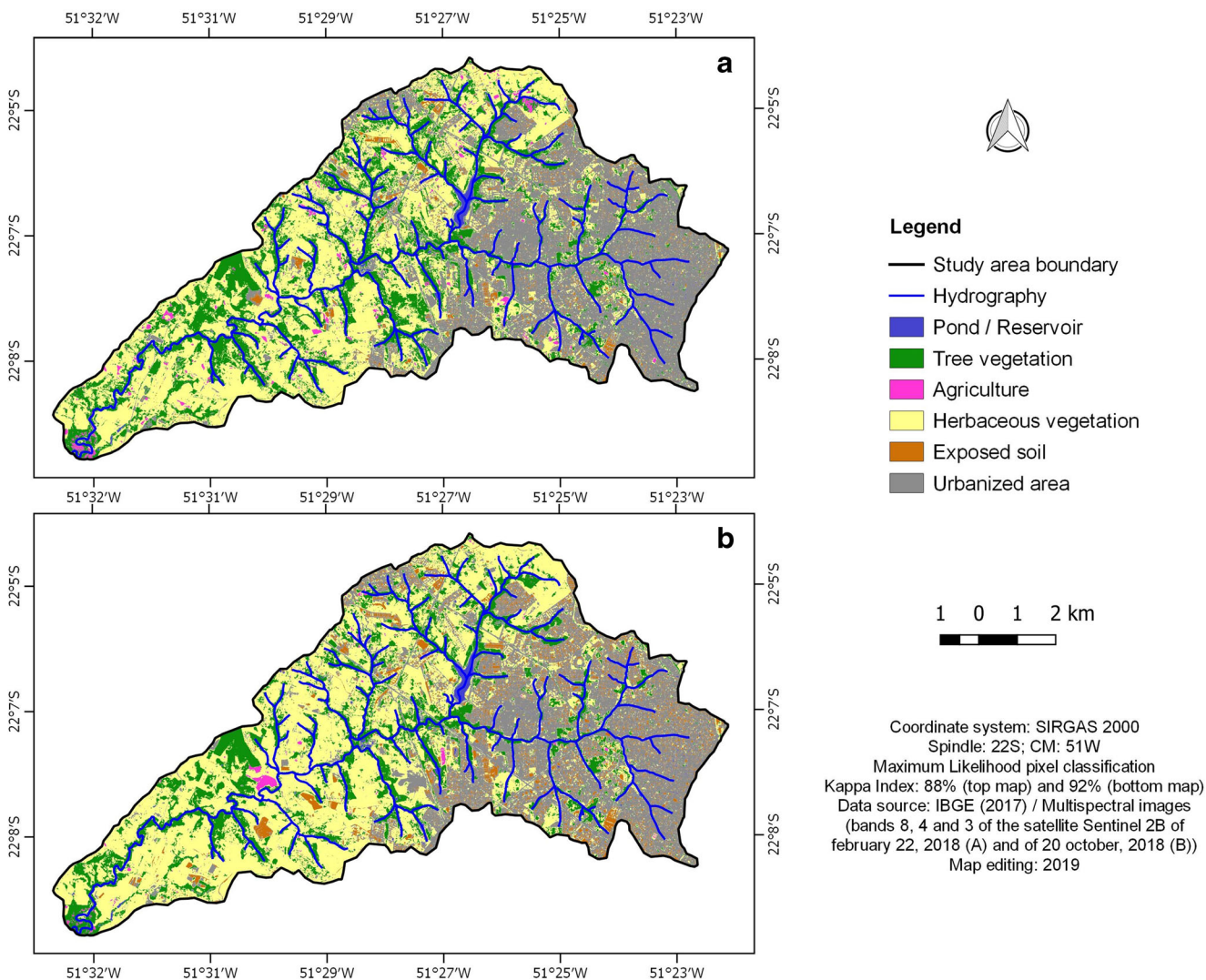
Fig. 6 Land use and land cover of the study area in 2018

explanation to the reason for the WQI is below rates recorded in winter and summer seasons. Additionally, in agricultural areas, Poudel (2016) points out that the use of agronomic defensives increases the organic and chemical loads in water. In point 9, the best index for the summer campaign can be explained by the greater dissolution of domestic sewage due to the higher volume of water. At this point, it is still had high forest cover (Fig. 6), reducing diffuse contaminant pollution, which contributes to improving the water quality.

Fig. 7 Water balance extract of the Limoeiro River
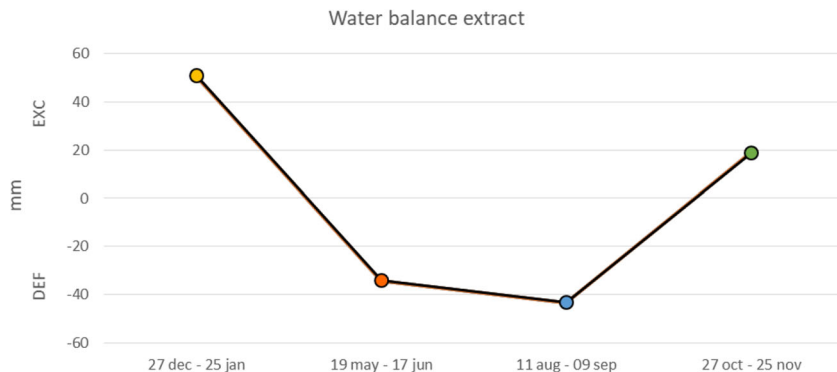
Fig. 8 Water quality index at 11 monitoring points per climate station

	1	2	3	4	5	6	7	8	9	10	11
Summer	68	77	69	44	53	62	14	55	64	76	49
Autumn	46	59	53	31	33	26	43	28	20	49	41
Winter	66	78	77	55	60	45	47	44	28	63	42
Spring	77	83	78	72	61	64	68	64	44	58	54

········ Linear (Summer) ········ Linear (Autumn) ········ Linear (Winter) ········ Linear (Spring)
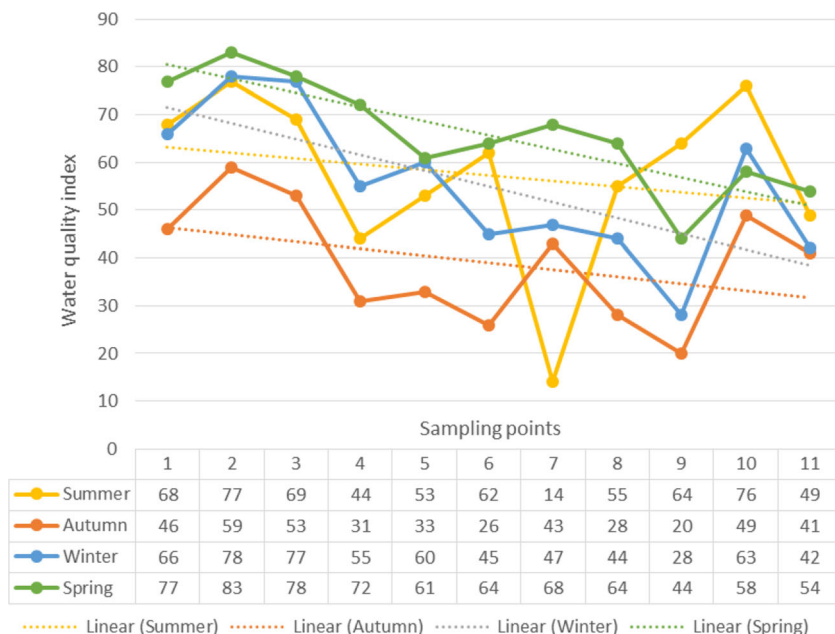
For the WQI of autumn, winter, and spring campaigns, the climatic periods returned a higher correlation with each other. This can confirm that an improvement of water quality has occurred for the seasons in which the water deficit was highest and had water surplus. In WQI values between each sampling point, it is possible to note a better homogeneity for each period. However, when we look at the summer season (the period with the highest water surplus), it is possible to observe that there is a more discrepancy between values obtained at each sampling point.

In the period of highest water surplus (the summer season), we observed that in some sampling points (2, 3, 4, and 5) the WQI values (Fig. 8) were below the values obtained for the winter and spring seasons. For other sampling points (1, 6, 8, and 11), the WQI value presented a smaller quality than the spring WQI value. In the sampling points 9 and 10, the WQI values presented the better indexes calculated. Moreover, we noted for point number 7 a worsening of WQI value, representing the lowest value of all field campaign. When comparing the two periods of water surplus and WQI values

Table 1 Pairwise comparisons of the seasonality

(I) Seasonality	(J) Seasonality	Mean difference (I-J)	Std. error	Sig.[b]	95% confidence interval for difference[b]	
					Lower bound	Upper bound
Summer (50.7)	Autumn	18.364*	5.656	0.009	5.762	30.965
	Winter	2.364	5.386	0.670	− 9.636	14.364
	Spring	− 8.364	6.050	0.197	− 21.844	5.117
Autumn (− 34.2)	Summer	− 18.364*	5.656	0.009	− 30.965	− 5.762
	Winter	− 16.000*	2.558	0.000	− 21.700	− 10.300
	Spring	− 26.727*	2.954	0.000	− 33.310	− 20.144
Winter (− 43.3)	Summer	− 2.364	5.386	0.670	− 14.364	9.636
	Autumn	16.000*	2.558	0.000	10.300	21.700
	Spring	− 10.727*	2.694	0.003	− 16.729	− 4.725
Spring (18.8)	Summer	8.364	6.050	0.197	− 5.117	21.844
	Autumn	26.727*	2.954	0.000	20.144	33.310
	Winter	10.727*	2.694	0.003	4.725	16.729

Based on estimated marginal means

*The mean difference is significant at the 0.05

[b] Adjustment for multiple comparisons: Fisher's least significant difference (LSD)

(Figs. 7 and 8), we may infer that the more surplus in the water balance, resulting in a higher rainfall amount, the greater the LULC influence in water quality by runoff diffuse pollution.

We verified (Fig. 8) that the sampling points that presented the best WQI during the four field campaigns are located far from high-density urban areas (1,2, 3, and 10 for example). They are surrounded by vegetation (1, 3, and 10) or, in case of point 2, by a water source. Vegetation cover is essential for rainfall interception, acting as a barrier to contaminants (Tucci 2012). It also acts as a filter, which controls and decreases the sediments and pollutants that are transported by the surface run-off (Ding et al. 2013). The United Nations Food and Agriculture Organization (FAO 2008) and literature review (Wang et al. 2014; Ding et al. 2015; Zhang et al. 2018) show that the arboreal vegetation cover is related to the excellent quality of water. The arboreal vegetation plays an important role in the improvement of water quality in watersheds since vegetated areas act as a nutrient holding zone (Ding et al. 2015).

We demonstrated that urban areas negatively affected water quality mainly in the period with the highest water surplus (summer). However, pasture areas and riparian forests control the adverse effects brought about by the volume of precipitation. Similarly, Ding et al. (2016), and Huang et al. (2016) concluded that both urban and agricultural areas negatively affect water quality. The pasture class has a positive effect, enabling improvement in surface water quality (Ding et al. 2013).

Our study case and the results pointed by Park et al. (2011), Liu et al. (2017), Ojok et al. (2017), and Mohseni-Bandpei et al. (2018) confirm the influence of climatic seasonality in the surface water quality. Moreover, Li et al. (2015) verified that variations in precipitation patterns negatively affect the water of a reservoir. Damasceno et al. (2015), Medeiros et al. (2017), and Amâncio et al. (2018) confirmed a variation in WQI when comparing rainy/dry periods. Damasceno et al. (2015) showed an improvement in WQI values in the rainy season. Here, we found that surplus water periods contributed to the large part improvement of the water quality indexes, possibly by diluting the water contaminant concentration. However, we emphasize that the presence of extreme situations concerning climatic seasonality recorded in the study (summer and winter) shows the interference of anthropic factors in water quality.

In Table 2, the Pearson's correlation between the water balance and each sampling point varied between high, moderate, and low correlation. In sampling points 6, 8, 9, and 11, there was a positive and high correlation, while a positive and moderate correlation was found for sampling points 1, 2, 5, and 10 and a low correlation was calculated for points 3, 4, and 7. Observing the sampling points with low linear dependence concerning water balance, it is possible to infer the sampling points closest to urban density and with little to no riparian protection (2, 3, 4, 5, and 7) with more significant influences from other factors.

Table 2 Pearson's correlation between water balance and sampling points

| Sampling points	Correlation	Sig. (1-tailed)
1	0.560	0.220
2	0.473	0.264
3	0.241	0.380
4	0.236	0.382
5	0.300	0.350
6	0.805	0.098
7	−0.395	0.302
8	0.729	0.135
9	0.958	0.021
10	0.685	0.157
11	0.793	0.103

The WQI maps for each field campaign are illustrated in Fig. 9. In the summer season, the monitoring points were classified with a good WQI (total of 73% points), regular (18%), and bad (9%). In the autumn season, WQI values were worse. The following distribution can highlight 55% of the points with bad WQI, 27% with regular WQI, and 18% with good WQI. The results for the winter campaign were as follows: 55% of the points had a good WQI; 36% presented regular WQI; and 9% a bad WQI. In the spring season, we recorded the following distribution: 73% of the points with good WQI; 18% with regular WQI; and 9% with optimum WQI. When we interpret the WQI values as a function of climatic seasonality, it is evident that the number of points classified with good WQI is higher in periods of water surplus.

Surface water trophic status index

We determined the trophic state index of the Limoeiro River watershed as a function of climatic seasonality (Table 3). Eutrophication is responsible for an unpleasant taste and odor in water. It also alters other physicochemical and microbiological parameters and may cause the proliferation of algae that release toxins and make it impossible to use water as a resource (Smith and Schindler 2009, Matthewsi & Bernard, 2015). These toxins bring a high-risk threat to human health (Le Moal et al. 2019) and are responsible for fatal, acute, and chronic poisoning of wild/domestic animals in different watercourses around the world (Carmichael 2001; Matthews and Bernard 2015).

In most sampling points (1, 2, 4, 6, 7, 8, 10, and 11), the better TSI results were obtained in the summer or spring season. The better water quality relative to TSI is expressed by lower indexes. It is due to the increase in water flow to these seasons and the reduction of nutrient contents available in watercourses. We observed by the Pearson correlation between each TSI and the averages {(TSI (Chl a) × Average,

WATER QUALITY INDEX ACCORDING TO WEATHER SEASONS
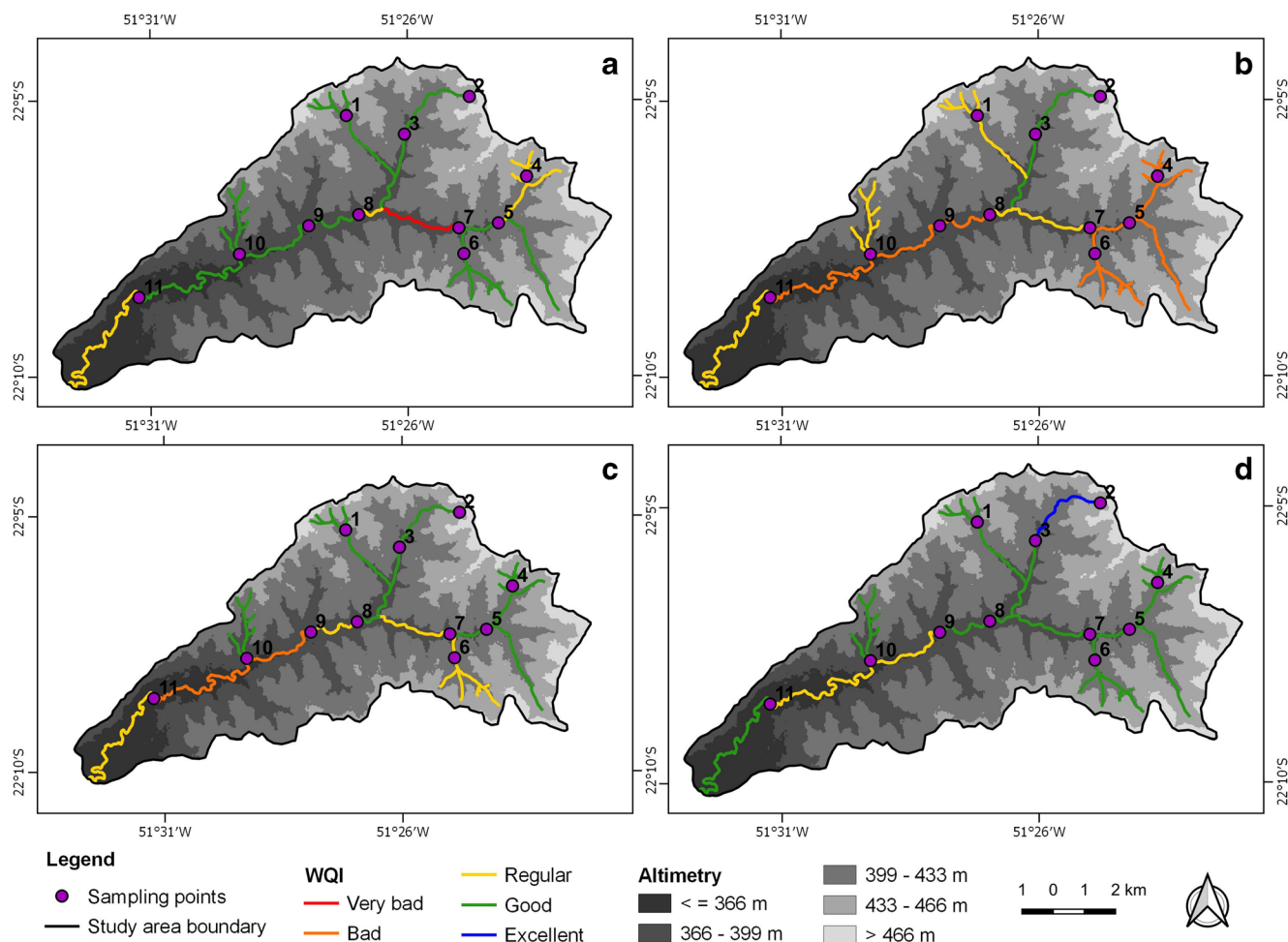
Fig. 9 Water quality index for summer (**a**), autumn (**b**), winter (**c**), and spring (**d**)

$\rho = 0.918$, $p < 0.01$); (TSI (PT) × Average, $\rho = 0.703$, $p < 0.01$)} that TSI used for analyzing the trophic state follows the standard of the TSI (Chl a). In other words, the TSI (Chl a) values influence the trophic state of the sampling points.

The one-way repeated measures ANOVA determined there is an effect of the seasonality factor on the STI values ($F(3,30) = 6.967$; $p < 0.01$). When analyzing the relationship between TSI values and seasonality, we verify by Fisher's least significant difference (LSD) through pairwise comparisons that the mean difference is significant between autumn and the other seasons ($p < 0.05$). Among the periods of surplus water (summer and spring) and the autumn (water deficit), we noted that in autumn the points 1, 2, 6, 7, 8, and 10 had higher values, therefore a worse water quality.

When comparing the TSI between autumn and winter, during the autumn season, only points 2 and 3 had higher values. It is possible to observe in this analysis period the influence of variation of the environmental processes characteristics in chlorophyll a (Companhia Ambiental do Estado de São Paulo – CETESB 2018). Some of these processes are as follows:

increase in water temperature; greater availability of nutrients; and conditions of light penetration into the water. The average temperature (Fig. 3) in the winter season (September) was higher than in the autumn (June). This indicates a higher solar incidence to watercourses in the winter season. In this season, TSI (Chl a) values estimated for points 4, 6, 7, 8, and 11 had higher values. It is noteworthy to emphasize that the TSI (Chl a) values of these sampling points were classified as hypereutrophic (7) and mesotrophic (4, 6, 8, and 11). However, we verified that all values (Fig. 1J—supplementary material) are below the maximum limit established by the Brazilian law (Table 1—supplementary material), which is 30 μg/L. The amounts of chlorophyll a during these three seasons varied from 0.06 to 7.93 μg/L, indicating divergences between current legislation [Resolution of the National Environmental Council, No. 357/05 (CONAMA 2005)].

The correlation between the average of TSI (Chl a and TP) and seasonality demonstrates that sampling points with lower value correlation are the points closest to urban density with little or no riparian protection (3 ($\rho = 0.469, p = 0.27$), 4 ($\rho = -$

Table 3 Trophic state index of surface water

	Points										
	1	2	3	4	5	6	7	8	9	10	11
Summer (WB= 50.7mm)											
TSI (Chl a)	25	29	35	31	29	29	26	22	28	19	54
TSI (PT)	28	22	23	38	35	29	48	33	37	26	39
Average	27	25	29	35	32	29	37	27	32	23	47
Autumn (WB= -34.2mm)											
TSI (Chl a)	26	38	26	32	26	53	54	41	32	25	26
TSI (PT)	31	26	32	38	36	36	34	41	42	28	43
Average	28	32	29	35	31	44	44	41	37	27	35
Winter (WB= -43.3mm)											
TSI (Chl a)	36	29	29	54	41	57	68	59	49	33	53
TSI (PT)	29	27	25	39	36	36	38	40	42	25	43
Average	33	28	27	46	38	47	53	49	46	29	48
Spring (WB=18.8mm)											
TSI (Chl a)	28	27	45	40	51	35	33	44	46	22	48
TSI (PT)	26	22	22	31	32	30	29	28	36	25	34
Average	27	24	34	35	41	32	31	36	41	23	41

■ Ultraoligotrophic   ■ Oligotrophic   ■ Mesotrophic   ■ Hypereutrophic

0.631, $p = 0.18$), and 5 ($\rho = -0.058$, $p = 0.47$)) suggesting an influence of others factors, for example, LULC. In a comparison between the periods, we observed that in the autumn campaign solar radiation was lower than the summer, winter, and spring campaigns. This phenomenon is also noticeable by the temperature's monthly average as shown in Fig. 3. We noted that in the periods when the solar incidence was higher, the downstream point of the sewage treatment plant disposal (point 11) had the highest TSI values. This is because of the large number of nutrients present in the effluents, causing the growth of algae (Mota and Von Sperling 2009; Le Moal et al. 2019) and favorable conditions of light penetration into the water.

Conclusion

Surface water quality of watersheds is influenced by the seasonality of the hydrological cycle process synthesized trough climatic water balance. We demonstrated that in the stations that had the lowest water surplus and deficit, there was positive linearity between the water balance and the quality indices. That is, the water deficit season (autumn) had the worst water quality index and the water surplus season (spring) the best water quality index. However, in the seasons when the

surplus and water deficit recorded were extreme concerning the others, there was no linearity. In this way, the importance of a macro-view of the factors that relate to water quality is emphasized.

In the summer season (extreme surplus water), the homogeneity between the quality indexes of each sampling point was lower, suggesting a greater interaction between the rainwater volume and the forms of land use and land cover. The urban areas affect water quality by sources of diffuse pollution. We confirmed the importance of vegetation in the control of pollutants arrival up to the watercourses because areas with pasture and tree vegetation presented better values for the water quality indexes.

We verified that increasing water volume in watercourses results in improving the trophic state index in the period of water surplus. However, in dry periods (the autumn and winter), we found that the trophic state index is not influenced only by precipitation, but by all characteristics of environmental processes. This work contributes to design management strategies of water resources, considering the climatic seasonality variable for optimization. A strategy may ensure the availability of good quality of water regularly. We recommend water quality analysis based on persistent micropollutants, associated with soil analysis, verifying if some contamination affects the surface water quality of watersheds.

Compliance with ethical standards

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