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Spatiotemporal Effect of Land Use on Water Quality in a Peri-Urban Watershed in a Brazilian Metropolitan Region: An Approach Considering GEP-Based Artificial Intelligence

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Abstract: The suppression of natural spaces due to urban sprawl and increases in built and agricultural environments has affected water resource quality, especially in areas with high population densities. Considering the advances in the Brazilian environmental legal framework, the present study aimed to verify whether land use has still affected water quality through a case study of a peri-urban watershed in a Brazilian metropolitan region. Analyses of physical–chemical indicators, collected at several sample points with various land-use parameters at different seasons of the year, were carried out based on an approach combining variance analysis and genetic programming. As a result, some statistically significant spatiotemporal effects on water quality associated with the land use, such as urban areas and thermotolerant coliform ($\mathbf{R} = -0.82$, p < 0.01), mixed vegetation and dissolved oxygen ($\mathbf{R} = 0.80$, p < 0.001), agriculture/pasture and biochemical oxygen demand ($\mathbf{R} = 0.40$, p < 0.001), and sugarcane and turbidity ($\mathbf{R} = 0.65$, p < 0.001), were verified. In turn, gene expression programming allowed for the computing of the importance of land-use typologies based on their capability to explain the variances of the water quality parameter. In conclusion, in spite of the advances in the Brazilian law, land use has still significantly affected water quality. Public policies and decisions are required to ensure effective compliance with legal guidelines.

Keywords: anthropization; environmental impact; water resource; land use

1. Introduction

In Brazil, agriculture and urbanization are among the major sources of water resource degradation [1]. In turn, forested areas are the most important land cover associated with protecting the water resource quality. Thus, the distribution of agricultural land has been an important factor in the dispersion of nutrients in watersheds, and areas with higher percentages of this typology of land use are more susceptible to turbidity and an elevation of total dissolved solids. Brontowiyono et al. [2] assessed water-quality patterns related to land use change, both seasonally and spatially. Their study concluded that land use has affected water quality, especially in built-up areas with higher population densities and potentially polluting anthropic activities. In line with this, Ullah et al. [3] verified that the suppression of natural areas for their conversion to other land uses, such as urbanization, has significantly affected the protection previously provided by forests. Thus, in the absence



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of vegetation in riparian zones, pollutants and sediments find conditions to reach water bodies, compromising their quality and quantity due to contamination and siltation.

Discussing such issues, Mirzaei et al. [4] argued that understanding the relationship between water quality and land use is valuable for the sustainable management of watersheds and the mitigation of environmental risk, as it helps identify pollution sources and effective solutions in the study area. According to Xu et al. [5], the factors that influence water quality need to be investigated to enable better environmental management. For this purpose, the authors evaluated the impacts of land use on ammoniacal nitrogen and dissolved oxygen concentrations in different seasons and at different spatial scales. Their study concluded that land use and sewage outfalls had the most effects on water quality.

The planning and monitoring of watersheds can help to control potentially polluting land uses, but science-based policies and decisions are essential for the effective protection of water quality in Brazil [6]. The conservation of natural spaces, such as riparian forests and other vegetal coverage, plays a key role in the urban landscape, as these spaces act as contaminant filters, provide ecological habitats in riparian zones, improve the stability of the riverbanks, and reduce surface runoff [7].

Based on a review of Brazilian legislation, Bressane et al. [8] found that environmental protection is widely regulated and represents one of the main public policy strategies adopted in the country. Despite this, the effectiveness of the legal rules applied to land-use control depends on compliance with them, especially in areas with high population densities, such as the metropolitan regions. In the absence of conservation practices and control of anthropogenic activities, there is a concern that land use has still degraded the water quality, affecting the watersheds more due to the effects of polluting loads, which in turn affect their capacity for self-purification [1].

It is worth mentioning that several environmental problems have been aggravated in recent years due to setbacks in the area/environmental legislation during the 2019–2022 federal government, including legal flexibility for the use of pesticides that contribute to water pollution. As a consequence, the scarcity of water for human supply is becoming greater in Brazil, as in several other regions of the world, due to the poor quality of the surface resources available in urban areas and the high costs of their treatment [6].

Considering the advance in the Brazilian legal framework, the present study aimed to verify whether land use has still significantly affected water quality through a case study of a Brazilian metropolitan region. The results of the present study are here discussed in comparison with the findings from the studies carried out in the same region approximately 10 years ago [9–13]. Furthermore, an artificial intelligence based on gene expression programming was applied to assess the importance of land use typologies based on their ability to explain variations in the water quality parameter.

2. Materials and Method

2.1. Study Area

The study area corresponded to the peri-urban watershed of Stones River in the Brazilian southwest, a metropolitan region of São Paulo State (Figure 1). This region has a subtropical climate, with hot and rainy periods in the months of October to April alternating with cold and dry intervals in the months of May to September. Taking into account the hypothetical seasonal effect, the sampling for water quality analysis was carried out at four moments, in October (T01), January (T02), April (T03), and July (T04). Considering the possible spatial effects, the data were collected at six survey points (P01–P06), five of which were distributed along the main riverbed and one of which was located in a lagoon, a tributary of the main watercourse, all of them belonging to class II.

The first point (P01: $22^{\circ}51'45.84''$ S, $47^{\circ}3'24.64''$ W), further upstream, corresponded to the main source of Stones River. The second (P02: $22^{\circ}51'2.57''$ S, $47^{\circ}3'56.48''$ W) was in the riverbed, approximately 1.8 km downstream, adjacent to a large commercial enterprise. The third (P03: $22^{\circ}49'38.54''$ S, $47^{\circ}4'24.73''$ W) was at the midpoint of the micro-basin, which receives sediments from agricultural soil, as well as effluent from a large enterprise.

The fourth (P04: $22^{\circ}48'37.05''$ S, $47^{\circ}04'26.11''$ W) was in a public park adjacent to the main bed of the lotic body. The fifth was at the junction of the watercourse with the Rhodia highway (P05: $22^{\circ}48'12.73''$ S, $47^{\circ}4'37.25''$ W), where flooding is observed during periods of intense rainfall. Finally, the sixth point (P06: $22^{\circ}47'20.42''$ S, $47^{\circ}4'47.09''$ W), further downstream, was collected approximately 50 m from the mouth of the Anhumas river, an important contributor to the Atibaia river, which is used to supply adjacent cities.

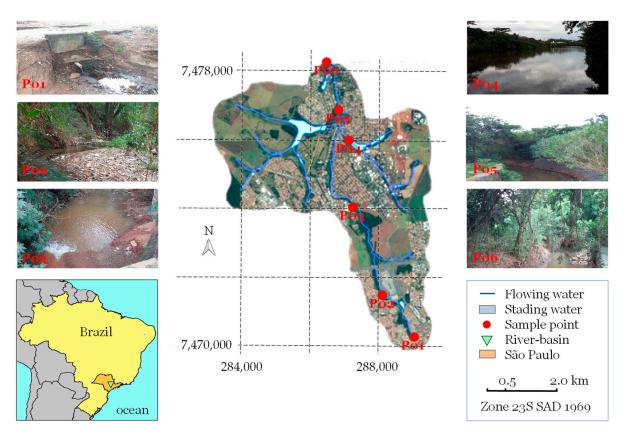


Figure 1. Sampling points in the study area.

2.2. Sampling and Experimental Analysis

The samples were collected according to the Standard Methods for the Examination of Water and Wastewater of the American Public Health Association (APHA). They were always collected under equivalent conditions—at similar times, for example. A total of 12 sample repetitions were collected at each point and, while we were still in the field, the dissolved oxygen (DO) and temperature (T) were measured following the guidelines of the APHA [14–16]. The turbidity (TU), potential of hydrogen (pH), biochemical oxygen demand (BOD_{5,20}), total nitrogen (TN), total phosphorus (TP), thermotolerant colliforms (TtC), and total dissolved solids (TDS) were analyzed in the laboratory, following the procedures shown in Table 1.

Table 1. Analysis procedures for the indicator parameters.

Parameter	Procedure	Guideline
TU (NTU)	2130-В	APHA [14]
TtC (CFUg-1)	9222-G	APHA [15]
TN (mg· L^{-1})	4500-N	APHA [16]
$BOD_{5,20} (mg \cdot L^{-1})$	5220-В	APHA [15]
TDS (mg·L ^{-1})	2540-В	APHA [14]
pH (mg·L ^{-1})	4500-H ⁺	APHA [14]
TP (mg·L ^{-1})	4500-P	APHA [15]

To verify if the land use had affected the water quality, a two-way (seasonal and spatial) analysis of variance, followed by a multiple paired comparison with a Tukey test, was carried out [17]. The Pearson's correlation and a hierarchical clustering based on the Ward's linkage method were also established. All of these analyses were performed considering a significance (α) of 0.05 and a test power (1- β) equal to 0.82 for a sensitivity (ρ) of 50% (detectable effect size) using Jamovi version 2.3, a statistical computer software [18]. The QGis version 3.28.1 software was used to create the maps [19].

Considering the complex interdependencies of the various influencing factors, Xu et al. [5] proposed the use of artificial intelligence based on Bayesian networks to recognize patterns of the association between land uses and water quality. In the present study, in addition to the classical methods, we also evaluated the use of gene expression programming (GEP)-based artificial intelligence as an alternative to identify the land uses with the greatest effect on water quality. This analysis was conducted using a data-mining tool available in the DTreg demo version software [20]. The GEP fitness function was based on the explained variance, using a population size equal to 50, eight genes per chromosome, and 2×10^3 generations, which provided the best fit of the model to the data ($R^2 = 0.78$).

3. Results

The land uses in the micro-basins of each sample point are shown in Table 2 and Figure 2. It can be seen that the micro-basin areas at P01 and P02 are predominantly urbanized (100 and 89.4%, respectively), with few or no riparian forests or with mixed vegetation. Land use has impacted the Stones river basin for almost a decade, generating fragile ecosystems characterized by deforestation due to urbanization, agriculture, and industry [9–11]. At P03, the sugarcane plantation occupies around 25% of the micro-basin. In addition to sugarcane (16.1%), pasture represents 28.6% of the land use in the P04 area. Together, the diversified agriculture, sugarcane, and pasture add up to 43.5 and 40.3% of micro-basins at P05 and P06, respectively.

	Sample Point (%)						
	P01	P02	P03	P04	P05	P06	
Hydrography	-	1.03	0.32	2.16	1.51	1.53	
Urban areas	100	89.38	54.88	42.74	42.86	45.47	
Commercial forestry	-	-	-	1.20	0.30	0.28	
Riparian forest	-	2.50	6.90	0.07	3.90	4.52	
Mixed vegetation	-	7.09	9.91	9.15	7.07	6.55	
Sugarcane	-	-	24.94	16.08	18.05	16.73	
Diversified agriculture	-	-	-	-	4.77	4.42	
Pasture	-	-	-	28.60	20.07	19.15	

Table 2. Land uses in the micro-basin areas.

In general, there is a predominant occupation by urbanized areas, followed by agricultural uses, which have affected these micro-basins, mainly from 1990 [9,12]. The physical– chemical indicators of water quality at the sampling points are summarized in Figure 3.

A significant variation of indicator parameters can be seen in Figure 3, indicating possible effects caused by the different land uses predominant in each micro-basin. Table 3 and Figure 4 present the association between land uses and water quality indicators. A two-way analysis of variance (spatiotemporal) is shown in Table 4.

Considering the possible interdependence relationships between the influencing factors, Table 5 presents the importance of each land-use typology in terms of its contribution to the explained variance of the water quality parameter, as determined by GEP-based artificial intelligence.

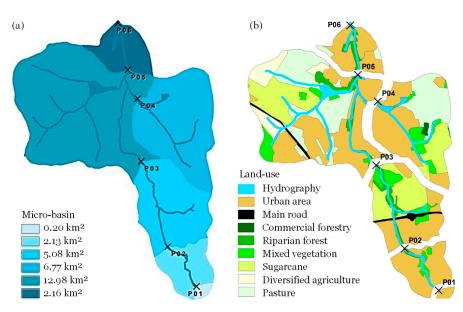


Figure 2. Micro-basin areas (a) and land uses (b) at sampling points.

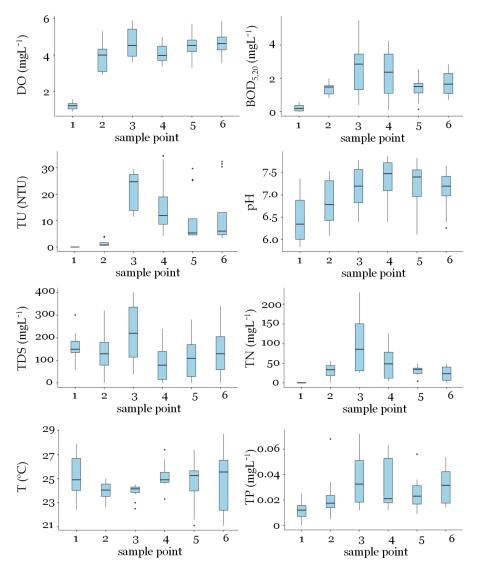


Figure 3. Physical-chemical indicators of water quality at sampling points.

	TtC(CFU.g ⁻¹)	DO(mg·L ⁻¹)	$BOD(_{5,20})(mg\cdot L^{-1})$	T(°C)	TU(NTU)	pH	TP(mg·L ⁻¹)	TDS(mg·L ⁻¹)	$TN(mg \cdot L^{-1})$
Urban areas	0.816 **	-0.718 ***	-0.734 ***	-0.029	-0.547 ***	-0.448 ***	-0.377 **	0.091	-0.289 *
Com. forestry	0.204	0.215	0.237 *	0.190	0.259 *	0.304 **	0.164	-0.266 *	0.025
Rip. forestry	0.294 *	0.611 ***	0.600 ***	-0.235 *	0.394 ***	0.186	0.294 *	0.240 *	0.448 ***
Mix. vegetation	0.416 ***	0.799 ***	0.800 ***	-0.140	0.536 ***	0.422 ***	0.416 ***	-0.004	0.529 ***
Sugarcane	0.395 ***	0.667 ***	0.675 ***	-0.046	0.646 ***	0.389 ***	0.395 ***	0.092	0.490 ***
Div. agriculture	0.138	0.387 ***	0.398 ***	0.030	0.068	0.156	0 0.094	-0.101	-0.178
Pasture	0.246 *	0.384 ***	0.410 ***	0.179	0.259 *	0.343 **	0.191	-0.281 *	-0.071

Table 3. Correlation between land uses and water quality (Pearson's R).

* p < 0.05, ** p < 0.01, *** p < 0.001.

Table 4. Spatiotemporal effects on the water quality parameters.

		Sampling Points					
		P01	P02	P03	P04	P05	P06
	T01	23.07 ^{bC}	23.83 ^{aBC}	24.30 aBC	24.70 aBC	25.57 ^{aB}	27.50 ^{aA}
Û.	T02	26.20 aA	23.30 ^{aB}	23.33 ^{aB}	25.10 aAB	25.97 ^{aA}	24.13 bB
T (°C)	T03	26.53 ^{aA}	24.10 ^{aB}	24.23 ^{aB}	26.33 ^{aA}	25.10 aAB	26.20 ^{aA}
	T04	24.73 abA	24.63 aA	23.83 aA	24.73 ^{aA}	21.50 bB	21.27 ^{cB}
<u>_</u>	T01	1.44 ^{aC}	3.42 bcB	4.54 ^{bA}	4.42 ^{abA}	4.65 cAB	3.93 bAB
DO (mg·L ⁻¹)	T02	1.05 ^{aC}	4.79 ^{aA}	4.53 ^{bAB}	3.78 bcB	4.57 bab	4.52 bab
DO B.L.	T03	1.07 ^{aD}	3.00 cC	3.98 bAB	3.51 ^{cBC}	4.42 cbAB	4.62 bA
لل ل	T04	1.39 ^{aD}	4.15 abC	5.68 ^{aA}	4.68 aBC	5.47 ^{aAB}	5.55 ^{aAB}
	T01	0.50 ^{aC}	1.49 aBC	4.40 ^{aA}	3.95 ^{aA}	2.17 ^{aB}	2.25 abB
	T02	0.21 ^{aB}	1.52 ^{aA}	1.65 cA	1.59 ^{bA}	1.37 ^{abA}	2.49 aA
BOD (mg·L ⁻	T03	0.15 ^{aD}	1.54 ^{aB}	3.32 ^{bA}	3.11 aA	1.31 abB	1.33 bcB
j T	T04	0.02 ^{aA}	0.97 ^{aA}	0.94 cA	0.65 bA	0.73 ^{bA}	0.88 cA
	T01	133.33 ^{aC}	180.00 aC	386.67 ^{aA}	206.67 ^{aBC}	233.33 aBC	313.33 aAI
ω ^Γ ,	T02	226.27 aAB	151.33 aAB	266.67 ^{bA}	126.67 abB	126.67 abB	166.67 ^{bAE}
TDS (mg·L ⁻¹)	T03	133.33 aA	120.00 aA	153.33 cA	26.67 bcA	86.67 bcA	100.00 bcA
j j	T04	146.67 ^{aA}	73.33 ^{aAB}	66.67 cAB	6.67 ^{cB}	0.00 ^{cB}	0.00 ^{cB}
	T01	0.02 ^{aC}	0.66 ^{aC}	11.64 cA	13.77 ^{bA}	4.77 bB	4.86 aBC
UTU) (UTU)	T02	0.02 ^{aD}	3.91 ^{aC}	24.35 abB	34.40 aA	26.80 aB	31.37 ^{aA}
ΕĘ	T03	0.02 ^{aD}	0.66 ^{aD}	26.83 ^{aA}	10.49 ^{bB}	5.76 ^{bC}	6.83 bBC
Ð	T04	0.02 aB	0.93 ^{aB}	21.66 bA	4.22 cB	4.43 bB	4.53 bB
	T01	6.04 ^{bC}	6.86 bB	7.51 ^{aA}	7.71 ^{aA}	7.61 ^{aA}	7.27 ^{aAB}
Ŧ	T02	6.09 ^{bB}	6.82 bcA	7.08 ^{aA}	7.37 ^{aA}	7.26 ^{aA}	7.19 ^{aA}
Г. T03		6.72 ^{aA}	6.30 cA	6.41 ^{bA}	6.19 ^{bA}	6.23 ^{bA}	6.35 ^{bA}
	T04	7.11 ^{aA}	7.42 ^{aA}	7.58 ^{aA}	7.71 ^{aA}	7.59 ^{aA}	7.65 ^{aA}
<u> </u>	T01	0.54 ^{aB}	15.62 ^{aB}	89.22 bA	11.45 ^{bB}	22.71 ^{aB}	24.93 abB
TN (mg·L ⁻¹)	T02	0.43 aA	17.32 ^{aA}	30.17 cA	15.09 bA	30.49 aA	19.75 ^{abA}
	T03	0.27 ^{aD}	44.13 ^{aC}	227.95 ^{aA}	91.76 ^{aB}	39.06 ^{aC}	7.95 ^{bCD}
	T04	0.00 ^{aC}	49.33 ^{aAB}	82.71 ^{bA}	79.86 ^{aA}	36.52 ^{aBC}	44.94 aAB

Averages followed by the same lowercase and capital letter do not differ significantly, respectively, regarding seasonal and spatial effect ($\alpha = 5\%$). The other parameters were not analyzed because the interaction F was not significant.

Table 5. Im	portance of land	l-use typologies	for water c	quality (%).

	TtC	DO	BOD _{5,20}	TDS	TU	TN
Urban areas	82.1	52.2	_	4.2		—
Commercial forestry	8.6	3.33	—	_	_	13.4
Riparian forest	50.4	62.49	50.7	69.0	82.2	60.2
Mixed vegetation	41.0	34.19	49.3	31.0	17.8	26.4
Sugarcane	17.9	15.6	75.3	95.8	90.9	60.1
Diversified agriculture	_	17.2	12.3	—	7.9	39.9
Pasture		14.9	12.4	_	1.2	

Cells highlighted in blue and red represent positive and negative effects, respectively; non-highlighted cells represent non-effects computed by the GEP-based artificial intelligence. The other parameters were not analyzed because there were no good fits of the model to the data.

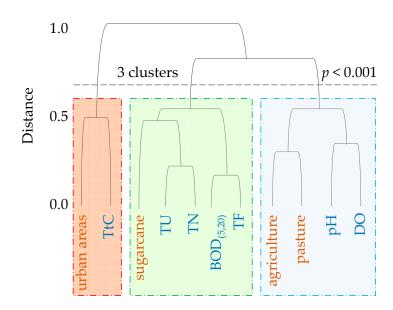


Figure 4. Association between land uses and water quality (Ward's method).

4. Discussion

Considering the advancement of Brazilian legislation as a public-policy strategy for environmental recovery and protection in the country, this study sought to analyze whether land use has still significantly affected water quality in a peri-urban watershed in a Brazilian metropolitan region. To determine this, an analytical approach based on classical and artificial-intelligence methods was used. It can be seen in Table 3 that there are extremely (p < 0.001) or very significant (p < 0.01), moderate (|R| > 0.5) to strong (|R| > 0.75) correlations between most of the land uses and the physical–chemical indicators of water quality.

Thermotolerant coliforms (TtC) are microorganisms (bacteria) that occur in the intestinal tracts of warm-blooded animals and, therefore, are indicators of pollution by domestic sewage. A very significant association was verified between urban areas and TtC (R = -0.82, p < 0.01) in the study area, which points to the possibility of dumping untreated domestic effluents and/or clandestine connections with the city's storm sewers [21].

The vegetation cover acts as an important filter of contaminants, including organic waste transported by rainwater. By verifying that mixed vegetation and dissolved oxygen have a direct, strong (R = 0.80), and extremely significant (p < 0.001) association, the results indicate that the occurrence of vegetation has prevented the degradation of organic matter from consuming the dissolved oxygen [22–24].

In contrast, agricultural activities and pasture have moderately (R = 0.4), but significantly (<0.001), increased biochemical oxygen demand. This indicates that animals' feces, as well as the nutrients applied for soil correction, have represented a risk of eutrophication in the study area [25,26].

In turn, sugarcane showed a moderately strong and extremely significant association with turbidity (R = 0.65, p < 0.001). During the period between harvests, the exposed soil is vulnerable to the weathering of rain, which causes the detachment and dragging of sediments to the valley bottoms, causing an increase in turbidity and the respective silting of water courses [27,28].

In line with this, the hierarchical clustering also revealed an association between urban areas and thermotolerant coliform, as well as ones between sugarcane and turbidity, nitrogen, biochemical oxygen demand, and phosphorus, and between agriculture and pastures with pH and dissolved oxygen (Figure 4).

Table 4 shows that only the temperature of the samples in P01 and P06 showed significant seasonal effects, as was also found years ago in the study by Göransson et al. [29]. In the main headwater, the concentrations of dissolved oxygen were significantly lower in comparison with the other points, indicating a possible effect of land uses downstream.

The concentrations obtained at T04 (July) were higher, indicating an improvement in the oxygenation of the water associated with the absence of precipitation and the presence of permeable areas, except for the headwater (P01) and P02, in which practically the entire drainage area had been waterproofed.

In the sampling at T04, the points P03, P05, and P06 presented the concentrations of 5.68, 5.47, and 5.55 mg·L⁻¹, respectively. These higher concentrations of dissolved oxygen may be associated with the presence of riptides and waterfalls, which cause greater turbulence in the waters in the stretches immediately upstream of these points. According to Nozaki et al. [30], dissolved oxygen levels can increase due to this turbulence, which causes greater reaeration; that is, an increase in oxygen exchange between the atmosphere and water body. It is worth highlighting that P04 was not located in the main riverbed, as the others were.

Regarding the biochemical oxygen demand (BOD), it can be observed that July (T04) showed a significant decrease in the concentrations, which may be related to the fall in the monthly precipitation as well as to the absence of precipitation 24 days prior to the data collection. The drop in BOD associated with the absence of precipitation allowed us to conclude that there was no particle transport to the bed of the water course. According to Basso et al. [31], the particles carried by the surface runoff are composed of organic materials, which can increase the BOD values, especially in the rainy periods. As verified by Souza and Gastaldini [13], the influence of domestic effluents has also been a source of water contamination for about 10 years, with high contributions of organic matter, pathogenic agents, and nutrients. Aside from the seasonality, there was an effect related to the land uses in the drainage areas, as P01 and P02 presented lower BODs than the concentrations found in P03 and P04. There has been a change of land use in the aforementioned areas that promotes the waterproofing of the soil, such as agricultural and pasture areas, which makes them vulnerable to weathering processes and to the respective particle transport to the riverbed in rainy periods. Despite the observed facts, the degree of particle transport was in compliance with the current legislation, which defines the maximum as $5.0 \text{ mg} \cdot \text{L}^{-1}$.

An analysis of the total dissolved solids showed that there are statistically significant effects promoted by both seasonality and land use. This finding is in agreement with studies that have indicated the influence of the infiltration rates on the quality of the water coming from surface runoff [10]. The finding corroborates the higher concentration of total solids in the headwater area, as the infiltration of the precipitated water is lower due to the high resistance to penetration, promoting a higher solids drift through the runoff. The precipitation observed at T03 (April) was not enough to promote the transport of particles to the stream bed. The increase in concentrations at P03 (from T01 to T03) may have been due to the increase of 41.8% in permeable areas without adequate protection of the watercourse, as well as to the launching of effluent of the commercial venture in the vicinity.

Souza and Gastaldini [13] found that river basins with predominant agricultural areas and with low incidences of native forests are more susceptible to changes in total solids concentrations and turbidity. In the current study, it was observed that at P01 and P02, there was no significant change in turbidity as a function of seasonality. This was in contrast with P03 onwards, with the highest concentration at T02. Thus, seasonality has a significant effect on the turbidity values, as previously indicated by observations from Göransson et al. [29]. Von Sperling [32] related the increase in turbidity to the discarding of domestic and industrial effluents, which corroborates the increase observed at P03 in the months of October (T01), April (T02), and July (T04), as P03 receives the effluent from a large shopping mall located in its drainage area. However, all samples complied with the applicable law, which determines a maximum value of 100 NTU to maintain good quality in class-II water bodies.

It was verified that in July (T04), all of the points sampled were significantly higher in pH, indicating that in the absence of precipitation, the water presents more basic characteristics. No significant changes were observed in terms of spatial distribution, except for in October (T01) and January (T02), in which there were lower values in P01, which has a 100% urbanized drainage area. This was not the same relation seen by Lima [33], who found that in basins with drainage areas occupied by agriculture, the pHs of the water are slightly more acidic. Nevertheless, Longo et al. [11,12] indicated that changes in the physical and chemical parameters of the soil were anthropic effects in the micro-basin under analysis. In this study, the values found at P01 and P02 were slightly lower, indicating that between the subsequent points (P02 and P03), there was an effect of land use raising the pH, which may have been related to the presence of a large commercial enterprise (which discharges its treated effluent into the waters of the stream). Soon afterward, an agricultural area was observed in which fertilizers and pH-correcting substances are commonly applied, corroborating the variation observed. All points presented values between six and nine, which were within the limit established by the law.

The increase in nitrogen concentrations may be associated with the occurrences of agricultural areas, as well as the precipitation that generates surface runoff and, consequently, favors the transport of particles to the riverbed. Among the evaluated points, P03 presented significant alteration of this parameter. It receives a contribution from an area lacking forest vegetation and with larger proportions devoted to agricultural crops. The total nitrogen was high in the samples from April (T03) and July (T04) at P04. This result was related to the fact that it is a lentic environment. As it is a lagoon, when there is an absence or reduction of precipitation, the circulation of water is also smaller, favoring the high concentration of this nutrient. The legislation defines the boundary concentrations according to the pH ranges. Samples with a pH \leq 7.5 must comply with a maximum of 3.7 mg·L⁻¹, while for those at 7.5 < pH \leq 8.0, the established maximum is 2.0 mg·L⁻¹, so that only the main headwater of Stones River meets the established limits.

For the concentrations of total phosphorus, there was no statistically significant difference between the mean values established by the Tukey test, but there was evidence of seasonal interference, as in July (T04) the concentrations remained below those at the other analyzed dates. There was an increase in the concentrations between P01 and P03 (P01 < P02 < P03), indicating spatial interference with water quality. At point one, where the area is completely urbanized, the phosphorus concentration was low (river headwater). At point two, where a little vegetation (less than 10%) has been inserted, there was an increase. At point three, an even-more-evident increase was noticed, which may affect bigger vegetation areas (approximately 40%). The legal limit was not met in the January (T02) sample at P03, which may have been be due to the increase in permeable areas without riparian vegetation. At P04, the samples from October (T01) and April (T03) did not present an evident relationship. Only the samples collected in the headwater of Stones River met the requirements.

It can be seen From Table 5 that vegetation cover (commercial forestry, riparian forestry, and mixed vegetation) is the land use with the greatest positive effect on water quality. In turn, the main causes of negative impacts on the occurrence of thermotolerant coliforms, reduced dissolved oxygen, and increased DOB, turbidity, and nitrogen are urban areas and sugarcane. However, the GEP-based approach still allowed us to identify important secondary causes of these impacts (agriculture and pasture), thus contributing to pollution-control actions and sustainable environmental management in the watershed.

5. Conclusions

From the analysis of the physical–chemical parameters using different approaches based on classical methods and artificial intelligence (GEP), it can be concluded that, despite advances in the Brazilian legal framework, land use has still significantly affected water quality in a peri-urban river basin in a metropolitan region of southeastern Brazil. Therefore, the protection of water resource quality requires effective compliance with the rules for controlling land use and occupation, the capable monitoring of this compliance, and the guiding of land use through more sustainable practices. In addition, it is important to apply legal punishment to companies and farmers involved in environmentally irregular activities, to expand the environmental education of the population in general, and to improve urban effluent treatment systems.

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References

- Mello, K.; Valente, R.A.; Randhir, T.O.; dos Santos, A.C.A.; Vettorazzi, C.A. Effects of land use and land cover on water quality of low-order streams in Southeastern Brazil: Watershed versus riparian zone. *Catena* 2018, 167, 130–138. [CrossRef]
- Brontowiyono, W.; Asmara, A.A.; Jana, R.; Yulianto, A.; Rahmawati, S. Land-Use Impact on Water Quality of the Opak Sub-Watershed, Yogyakarta, Indonesia. Sustainability 2022, 14, 4346. [CrossRef]
- Ullah, K.A.; Jiang, J.; Wang, P. Land use impacts on surface water quality by statistical approaches. *Global J. Environ. Sci. Manag.* 2018, 4, 231–250.
- 4. Mirzaei, M.; Jafari, A.; Gholamalifard, M.; Azadi, H.; Shooshtari, S.J.; Moghaddam, S.M.; Witlox, F. Mitigating environmental risks: Modeling the interaction of water quality parameters and land use cover. *Land Use Policy* **2020**, *95*, e103766. [CrossRef]
- 5. Xu, J.; Jin, G.; Tang, H.; Mo, Y.; Wang, Y.-G.; Li, L. Response of water quality to land use and sewage outfalls in different seasons. *Sci. Total Environ.* **2019**, *696*, e134014. [CrossRef]
- Mello, K.; Taniwaki, R.H.; Paula, F.R.; Valente, R.A.; Randhir, T.O.; Macedo, D.R.; Leal, C.G.; Rodrigues, C.B.; Hughes, R.M. Multiscale land-use impacts on water quality: Assessment, planning, and future perspectives in Brazil. *J. Environ. Manag.* 2020, 270, e110879. [CrossRef]
- De-Carli, B.P.; Souza, J.C.; Souza, J.A.P.; Shoegima, T.F.; Barreiro, M.P.R.; Dutra, A.C.; Medeiros, G.A.; Ribeiro, A.I.; Bressane, A. Relationship Between Land Use and Water Quality in a Subtropical River Basin. *J. Soc. Technol. Environ. Sci.* 2019, 7, 245–261. [CrossRef]
- Bressane, A.; Ribeiro, A.I.; Medeiro, G.A. Environmental reclamation as strategy for sustainability. *Veredas* 2016, 13, 109–133. [CrossRef]
- 9. Etto, T.L.; Longo, R.M.; Arruda, D.R.; Invenzioni, R.; Cereda Junior, A. Landscape ecology of the forest fragments of Stones River watershed-Campinas, São Paulo State–Campinas/SP. *Rev. Árvore* 2013, *37*, 1063–1071. [CrossRef]
- 10. Kemerich, P.D.C.; Martins, S.R.; Kobiyama, M.; Santi, A.L.; Flores, E.B.; Borba, W.F.; Fernandes, G.D.; Cherubin, M.R. Water quality originated from the superficial outflow simulated in a hydrographic bay. *Ciência E Nat.* **2013**, *35*, 136–151.
- Longo, R.M.; Reis, M.S.; Yamaguchi, C.S.; Demamboro, A.C.; Bettine, S.C.; Ribeiro, A.I.; Medeiros, G.S. Indicators of soil degradation in urban forests: Physical and chemical parameters. *Trans. Ecol. Environ.* 2012, 162, 497–506.
- Longo, R.M.; Zangirolami, G.F.; Yamaguchi, C.S.; Demamboro, A.C.; Bettine, S.C.; Ribeiro, A.I. Impacts of agricultural activities in remaining forest: Campinas/SP, Brazil. *Trans. Ecol. Environ.* 2013, 170, 15–23.
- 13. Souza, M.M.; GastaldinI, M.C.C. Water quality assessment in watersheds with different anthropogenic impacts. *Eng. Sanit. Ambient.* **2014**, *19*, 263–274. [CrossRef]
- 14. American Public Health Association. *Standard Methods For the Examination of Water and Wastewater*; Lipps, W.C., Baxter, T.E., Braun-Howland, E., Eds.; APHA Press: Washington, DC, USA, 2018.
- 15. American Public Health Association. *Standard Methods For the Examination of Water and Wastewater;* Lipps, W.C., Baxter, T.E., Braun-Howland, E., Eds.; APHA Press: Washington, DC, USA, 2012.
- 16. American Public Health Association. *Standard Methods For the Examination of Water and Wastewater*; Lipps, W.C., Baxter, T.E., Braun-Howland, E., Eds.; APHA Press: Washington, DC, USA, 2021.
- 17. Batista, B.D.D.O.; Ferreira, D.F. Alternative to Tukey test. Sci. Agrotechnol. 2020, 44, 1–55. [CrossRef]
- Jamovi Project. Jamovi Version 2.3 [Computer Software]. 2022. Available online: https://www.jamovi.org (accessed on 1 October 2022).
- 19. QGIS Development Team. QGIS v. 3.28.1 [Computer Software]. 2022. Available online: https://www.qgis.org (accessed on 1 October 2022).
- 20. Sherrod, P.H. DTREG Demo Version [Computer Software]. 2022. Available online: https://www.dtreg.com (accessed on 1 October 2022).

- Garbossa, L.H.; Souza, R.V.; Campos, C.J.; Vanz, A.; Vianna, L.F.; Rupp, G.S. Thermotolerant coliform loadings to coastal areas of Santa Catarina (Brazil) evidence the effect of growing urbanisation and insufficient provision of sewerage infrastructure. *Environ. Monit. Assess.* 2017, 189, 27. [CrossRef] [PubMed]
- Ouma, Y.O.; Okuku, C.O.; Njau, E.N. Use of artificial neural networks and multiple linear regression model for the prediction of dissolved oxygen in rivers: Case study of hydrographic basin of River Nyando, Kenya. Complexity 2020, 2020, 9570789. [CrossRef]
- 23. Ahmed, M.H.; Lin, L.S. Dissolved oxygen concentration predictions for running waters with different land use land cover using a quantile regression forest machine learning technique. *J. Hydrol.* **2021**, 597, 126213. [CrossRef]
- 24. Feng, Z.; Xu, C.; Zuo, Y.; Luo, X.; Wang, L.; Chen, H.; Liang, T. Analysis of water quality indexes and their relationships with vegetation using self-organizing map and geographically and temporally weighted regression. *Environ. Res.* 2023, 216, 114587. [CrossRef]
- Bajard, M.; Etienne, D.; Quinsac, S.; Dambrine, E.; Sabatier, P.; Frossard, V.; Gaillard, J.; Develle, A.L.; Poulenard, J.; Arnaud, F.; et al. Legacy of early anthropogenic effects on recent lake eutrophication (Lake Bénit, northern French Alps). *Anthropocene* 2018, 24, 72–87. [CrossRef]
- Garcia-Hernandez, J.A.; Brouwer, R.; Pinto, R. Estimating the Total Economic Costs of Nutrient Emission Reduction Policies to Halt Eutrophication in the Great Lakes. *Water Resour. Res.* 2022, 58, e2021WR030772. [CrossRef]
- Seidl, C.; Wheeler, S.A.; Zuo, A. High turbidity: Water valuation and accounting in the Murray-Darling Basin. *Agric. Water Manag.* 2020, 230, 105929. [CrossRef]
- Vargas-Lopez, I.A.; Kelso, W.E.; Bonvillain, C.P.; Keim, R.F.; Kaller, M.D. Influence of water quality, local knowledge and river–floodplain connectivity on commercial wild crayfish harvesting in the Atchafalaya River Basin. *Fish. Manag. Ecol.* 2020, 27, 417–428. [CrossRef]
- 29. Göransson, G.; Larson, M.; Bendz, D. Variation in turbidity with precipitation and flow in a regulated river system. *Hydrol. Earth Syst. Sci.* **2013**, *14*, 2529–2542. [CrossRef]
- 30. Nozaki, C.T.; Marcondes, M.A.; Lopes, A.F.; Satos, K.F.; Larizzatti, P.C. Temporal behavior of dissolved oxygen and pH in rivers and urban streams. *Atas Saúde Ambient*. **2014**, *2*, 29–44.
- 31. Basso, l.A.; Moreira, l.G.R.; Pizzato, F. The influence of precipitation on the concentration and load of solids in urban streams: The case of the Dilúvio stream, Porto Alegre-RS. *Geosul* 2012, *26*, 145–163. [CrossRef]
- 32. von Sperling, M. Introduction to Water Quality and Sewage Treatment, 3rd ed.; DESA: Belo Horizonte, Brazil, 2007.
- Lima, E.B.N.R. Integrated Model for the Water Quality Management of Cuiabá River Basin. Ph.D. Thesis, UFRJ, Rio de Janeiro, Brazil, 2001.

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