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Water quality and land use in Ipanema Stream Watershed (Doce River Basin/Brazil): effects of urbanization

Qualidade da água e uso e cobertura do solo na bacia do Ribeirão Ipanema (Bacia do Rio Doce/Brasil): efeitos da urbanização

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ABSTRACT

We evaluated the water quality conditions and their relationships with the land cover/use throughout the entire Ipanema Stream Watershed (ISW), also considering temporal differences. Thirteen water quality variables were evaluated in fourteen sampling stations located in rural, peri-urban, and urban zones in both dry and rainy seasons from 2015 to 2018. A PCA was performed to detect which variables explain most of the data variability and to detect spatial and/or temporal trends in ISW water quality. The four PCs explained 74% of the data variability, but strong relationships with environmental variables were only observed in the two main components. PC1 was related to nutrients, alkalinity, BOD, electrical conductivity, DO, and pH, while PC2 was related to total suspended solids (TSS) and chlorophyll-a. A spatial pattern related to sampling stations and land uses was observed, but no temporal pattern was identified. Ammoniacal-N and TSS were most important variables (loading values > │0.75│), and showed higher values in urban zone probably due to inadequate sewage discharge. Ipanema Stream did not show a self-purification capacity, and the high TSS concentrations in rural mainstream ask for riparian zone restoration. These management actions for water quality improvement would even contribute to the recovery of Doce River.

Keywords: Surface water; Urban expansion; PCA; Ammoniacal-N; Suspended solids.

RESUMO

Avaliou-se as condições de qualidade da água e suas relações com cobertura e uso do solo ao longo de toda a Bacia Hidrográfica do Ribeirão Ipanema (BHRI), considerando também as diferenças espaciais e temporais. Treze variáveis foram avaliadas em quatorze estações amostrais localizadas nas zonas rural, periurbana e urbana nas estações seca e chuvosa, de 2015 a 2018. A Análise de Componentes Principais (ACP) foi aplicada para detectar quais variáveis melhor explicam a variância dos dados e para detectar possíveis tendências espaciais e/ou temporais na qualidade da água da BHRI. Os quatro CPs explicaram 74% da variação dos dados, mas relações fortes com as variáveis ambientais ocorreram apenas nos dois primeiros componentes principais. CP1 foi relacionado com nutrientes, alcalinidade, DBO, condutividade elétrica, OD e pH; e CP2 foi relacionado com sólidos totais suspensos (STS) e clorofila-a. Foi observado um padrão de distribuição espacial com base nas zonas de uso do solo e nas estações amostrais, no entanto nenhum padrão temporal foi identificado. N-amoniacal e STS foram as variáveis mais importantes (valores de *loadings* > │0,75│). Eles apresentaram valores elevados na zona urbana provavelmente devido ao lançamento inadequado de esgoto. O Ribeirão Ipanema não mostrou capacidade de autopurificação e as elevadas concentrações de STS na zona rural do rio principal clamam pela restauração da mata ripária. Essas ações de manejo para a melhoria da qualidade da água podem contribuir na restauração do Rio Doce.

Palavras-chave: Águas superficiais; Expansão urbana; ACP; N-amoniacal; Sólidos suspensos.

INTRODUCTION

The ecological quality of aquatic systems, including those used as water resources, is directly impacted by anthropic activities, mainly due to the replacement of natural vegetation by human occupation (for agriculture, urbanization, etc.), the reduction or alteration of riparian vegetation, and the direct pollution by the sewage discharge. The effects of land cover/use on aquatic ecosystems have been well reported and some patterns were observed, such as the changes in the flux and concentration of suspended solids and nutrients (specially phosphorus and nitrogen) (e.g., Cunha et al., 2019; Pärn et al., 2018), and changes in composition and integrity of the biota (e.g., Krynak & Yates, 2018; Tromboni et al., 2019). Additionally, other forms of matter and energy have been released into water bodies by humans, as toxic metals, thermal energy, pathogens, pesticides, chloride, sulfate, and organic solvents, damaging the ecological integrity of these environments and limiting their potentials for different uses (Akhtar et al., 2021; Chaudhry & Malik, 2017; Khatri & Tyagi, 2015; Le Moal et al., 2019; Walker et al., 2019).

Some patterns related to the land cover/use can be also observed in their influences on aquatic environments, such as the common record that water bodies located in urban areas are more polluted than those found in rural areas. The decrease of the natural vegetation cover and increasing industrialization, soil waterproofing, and sewage discharge are typical from urban areas and contribute to the input of contaminants into the aquatic systems (Chaudhry & Malik, 2017; Khatri & Tyagi, 2015; Richardson & Soloviev, 2021).

A watershed is the most adequate unit for environmental large-scale studies, since it contains all interactions between physical, chemical, and biological elements, including the relationships between terrestrial and aquatic ecosystems (Cheng et al., 2014). Thus, for water quality diagnosis and monitoring programs, the sampling design should cover the entire watershed whenever possible, mainly for management purposes (Wang et al., 2016). However, the large spatial dimensions of the watersheds are frequently a limiting factor for the studies due to human resources, logistics, and financial difficulties.

A diagnosis and monitoring program should be focused on the environmental variables that are more sensitive to potential impacts, and in sampling stations that represent the watershed variations, always considering the watershed as study unit. In this way, multivariate statistical techniques are commonly applied to large databases to optimize future studies/monitoring programs. The PCA (Principal Component Analysis) is one of the most used tools for establishing the sampling design in environmental research (e.g., Bega et al., 2022; Cecconello et al., 2018; Centeno et al., 2023; Passos et al., 2021). Olsen et al. (2012) reinforced that PCA is a suitable method for this purpose in studies of aquatic systems, since it can recognize the major pollutants that cause relevant changes in water quality.

In 2015, Doce River Basin was highlighted internationally due to the worst socioenvironmental disaster occurred in Brazil. The collapse of a mining dam from Samarco released 43 million m^3 of iron ore tailings in the basin, impacting 668 km of watercourses from a tributary of the Doce River to the Atlantic Ocean (Carmo et al., 2017). The water quality in Doce River Basin was impacted by anthropic occupation (erosion, sewage discard, mining, and agriculture) even before the dam rupture (e.g. Fraga et al., 2020), but some studies reported that total suspended solids, turbidity, and toxic metals significatively enhanced after the disaster (Kütter et al., 2023). Although most studies are focused on Doce River, researches focused on the water quality of tributaries are also important, since these systems contribute to the basin recovery.

The Ipanema Stream Watershed (ISW) is a subwatershed of Doce River Basin. It practically drains the entire surface area of Ipatinga city (Est of Minas Gerais State in Brazil), which has the largest population and urban area in the Metropolitan Region of Steel Valley (the second largest metropolitan region in Minas Gerais, with 778,983 habitants, according to Instituto Brasileiro de Geografia e Estatística, 2023). Some studies were already performed in Ipanema Stream, but all of them were based in analyses focused on just one sampling station, generally close to the stream mouth (e.g., Medeiros et al., 2012; Petrucio et al., 2005). The localization of these sampling points represents the entire watershed, but more detailed information based on multiple samplings in spatial and temporal terms is necessary to better understand the functioning of this system, and for adequate management.

Based on three major aspects: (i) land cover/use influences water quality, (ii) PCA is a suitable method to identify the most important variables for ecosystem dynamics, and (iii) no study using broad scales were done in ISW, this study aims to evaluate the surface water quality in ISW and its relationship with different land use/cover types. The PCA method was employed to search for differences/trends on spatial and/or temporal scales. The results will be useful in helping detect the main sites/periods that need management for water quality maintenance/improvement in ISW.

METHODS

Study area, water sampling, and analyses

The Ipanema Stream is the main lotic system of a subwatershed (ISW) from Doce River Basin. The ISW drains 145 km^2, which corresponds to 87.2% from the total area of Ipatinga city (Minas Gerais, Brazil). In 2022, Ipatinga population was estimated in 227,731 people, with a density of 1,381.16 people. km^{-2}, and an urban area covering approximately 33% of the city (Instituto Brasileiro de Geografia e Estatística, 2023). The local climate is hot semihumid tropical (Aw, KÖPPEN), with effectively two typical periods: a rainy (October–April) and a dry (May–September) seasons. The average annual rainfall in the region is 1,208 mm, and the average annual temperature is 24 °C (data from meteorological database by CENIBRA SA in 19°19'09.9"S 42°23'41.4"W, from 1985 to 2015).

To evaluate spatial differences in the ISW, we collected superficial water from 14 sampling stations distributed along the mainstream (Ipanema Stream) and some tributaries to represent up, middle, and downstream regions of the watershed, also aimed to evaluate temporal variations in the water characteristics. Since there was financial restrictions and little funding, the samplings did not cover all sampling stations every year, and temporal analyses were not a primary focus in this study. Thus, every year four or five stations were sampled five or six times, always covering the dry and rainy seasons. To characterize the entire watershed, we changed the set of stations sampled at each year along the sampling period, from 2015 to 2018. Samplings were extended for a longer period (one more year) in MR2 and MP3 stations. The sampling stations were categorized based on land use zones: rural, peri-urban, and urban. A general description of each sampling station is presented in Table 1, codes are used to differ the type of streams (T: tributary; M: mainstream) and land use zone (R: rural; P: peri-urban; U: urban). Figure 1 shows the localization of sampling stations and the land cover in the watershed.

Water temperature, pH, dissolved oxygen (DO), and electrical conductivity (EC) were measured in situ via a multiparameter probe (HI98194, ®Hanna or YSI – Professional Plus, ®Yellow Springs). Water samples were kept refrigerated until laboratory processing (filtration, freezing, and storage) for posteriori analysis.

The water filtration was carried out via GF-3 (Macherey-Nalgen®) glass microfiber filters. The filters were used to quantify total suspended solids (TSS) via gravimetric method. The filtered water was used to analyze dissolved nutrients via spectrophotometric methods, and color via Spectroquant Merck method (NOVA 60 or PHARO 300 spectrophotometers by MERCK®). Ammoniacal-N ($N\text{-}NH_3$ + $N\text{-}NH_4$) was quantified via phenate method, and nitrite ($N\text{-}NO_2$) was quantified via sulfanilamide/N-(naphthyl) method. Nitrate ($N\text{-}NO_3$) was first transformed into nitrite via cadmium reduction, and quantified as the difference between the total nitrite in the reduced sample and the original nitrite concentration in the water. Alkalinity, biochemical oxygen demand (BOD), total phosphorus (TP), and turbidity were analyzed using a fraction of nonfiltered water. They were measured, respectively, via (i) titration with 0.02 M sulfuric acid, (ii) respirometric BOD measuring system Oxitop®, (iii) molybdenum blue spectrophotometric method after sulfuric acid-nitric acid digestion, and (iv) in model bench-top turbidimeter (2100Q HACH®) or by Spectroquant Merck method (NOVA 60 or PHARO 300 spectrophotometers by MERCK®). For chlorophyll-a analysis, the filtration was performed using GF-5 (Macherey-Nalgen®) glass microfiber filters, which were frozen and submitted to the acetone extraction, followed by centrifugation, and quantification via spectrophotometric method. All laboratory analysis were performed according to standardized methods (American Public Health Association, 2012).

Principal Component Analysis and correlation

A Principal Component Analysis (PCA) was performed to identify the main variables that characterize the water quality variations in ISW. The PCA was used because it reduces a set of variables to a smaller group that is more representative of the total variability. This new dataset contains new orthogonal, uncorrelated variables, called principal components (PCs). The PCs are generated via diagonalizing a symmetric correlation or covariance matrix. The variances and coefficients of the PCs are, respectively, eigenvalues and eigenvectors of the sample matrix. They are linear functions of the original variables, and the sum of their variances are equal to that of the original variables. The PCs are obtained in descending order of maximum variance. Thus, PC1 explains the maximum of the total data variability, the PC2 explains the maximum of the remaining total data variability, and is not correlated with the PC1, PC3 explains the maximum of the remaining total data variability, and it must be uncorrelated with the first and second PCs, and so on until the number of PCs is equal to the number of original variables (Jolliffe & Cadima, 2016; Olsen et al., 2012).

The PCA was performed in the free software PAST 4.2 (Hammer et al., 2001). The data was Log_{10}-transformed ($Log_{10}(x+1)$, where x is an individual value for each variable) for standardization of data and based the analysis on the correlation matrix. The PCA matrix corresponded to 88 cases (samples) and 16 variables (water variables plus categoric variables: climate season,

Table 1. Description of sampling stations (identified by codes) in Ipanema Stream Watershed.

Code	Description	Coordinates	Sampling period	Land use zone
MR1	One of the water sources from Ipanema Stream, which has the highest flow.	19°25'00.0"S 42°39'05.0"W	2015	Rural
MR2	Ipanema Stream at the confluence of the creeks Ipanemão, Ipaneminha, and Tribuna.	19°26'12.0"S 42°36'55.0"W	2015 2016 2017	Rural
TR1	Mouth portion from Ipanemão Creek in rural zone.	19°25'42.0"S 42°38'25.0"W	2016	Rural
TR2	Mouth portion from Ipaneminha Creek in rural zone.	19°23'46.98"S 42°38'15.70"W	2016	Rural
TR3	Mouth portion from Tribuna Creek in rural zone.	19°24'32.0"S 42°36'57.0"W	2016	Rural
TR5	Mouth portion from Morro Escuro Creek in rural zone.	19°26'57.0"S 42°36'04.0"W	2017	Rural
TP4	Mouth portion from Barra Alegre Creek in rural zone.	19°25'16.0"S 42°35'30.0"W	2017	Peri-urban
MP3	Ipanema Stream downstream from the confluence of the creeks Limoeiro and Tribuna.	19°27'07.1"S 42°34'47.5"W	2017 2018	Peri-urban
TU6	Mouth portion from Taúbas Creek in urban zone.	19°27'45.0"S 42°33'13.0"W	2018	Urban
TU7	Mouth portion from Forquilha Creek in urban zone.	19°26'35.0"S 42°33'43.0"W	2018	Urban
TU8	Mouth portion from Bom Jardim Creek in urban zone.	19°28'08.0"S 42°33'49.0"W	2018	Urban
MU4	Ipanema Stream upstream from Ipatinga downtown at Iguaçu District in urban zone.	19°28'13.0"S 42°32'57.0"W	2018	Urban
MU5	Ipanema Stream at Ipatinga downtown.	19°28'42.0"S 42°31'16.0"W	2015	Urban
MU6	Mouth portion from Ipanema Stream.	19°29'20.0"S 42°30'20.0"W	2015	Urban

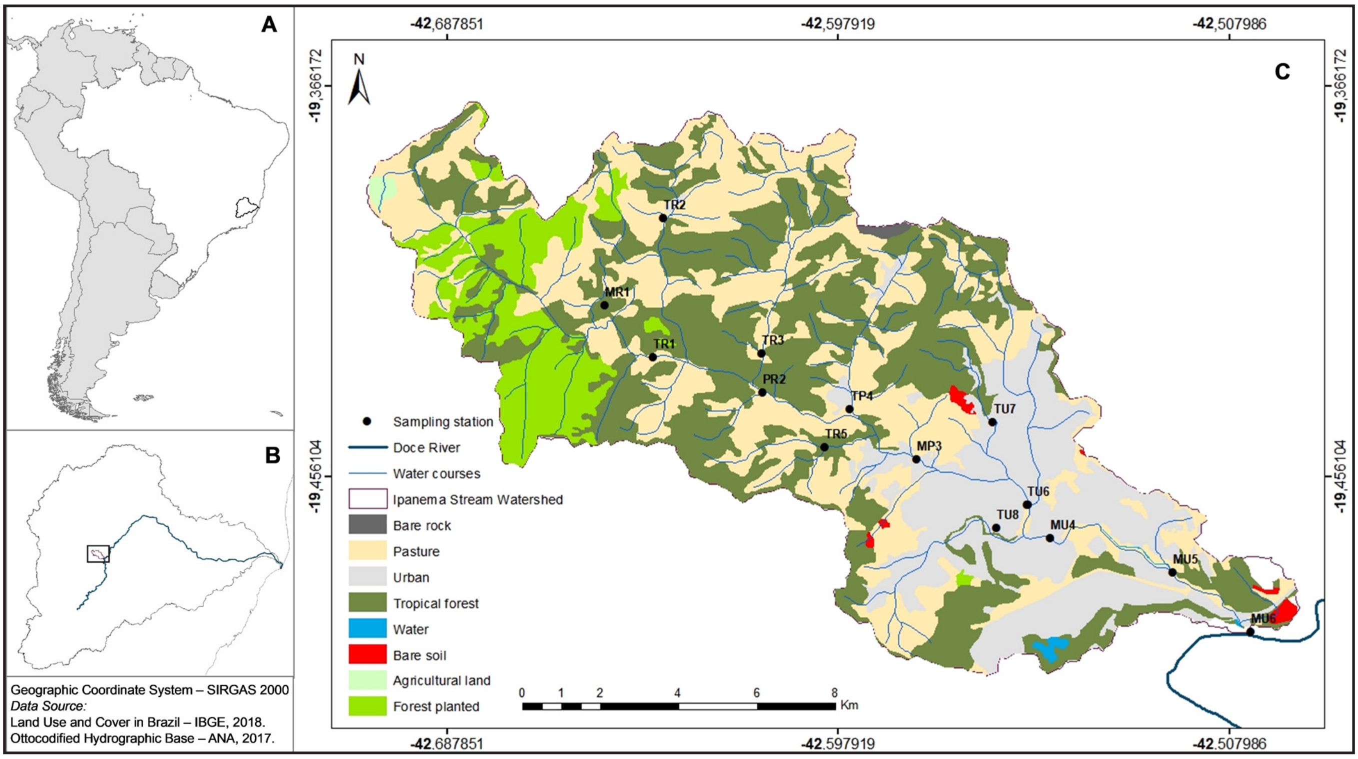

Figure 1. Localization of the Doce River Basin in Brazil (A) and localization of the Ipanema Stream Watershed in Doce River Basin (B). Sampling stations and land cover in Ipanema Stream Watershed (C).

land use zone and sampling station). Nitrite was not used because it presented very low values, frequently lower than the detection limit of the method. Twenty-four cases were excluded from the analysis because some variables were not measured. Thus, the final PCA matrix showed a 66 × 16 form.

Based on the correlation matrix, a Pearson correlation analysis was also carried out to identify the possible significant correlations among the water quality variables. Previously to these analyses, the data normality was verified by Shapiro-Wilk test at a significance level of 5%.

As proposed by Liu et al. (2003), we adopted the terms 'strong' (> 0.75), 'moderate' (< 0.75 – > 0.5), and 'weak' (< 0.5 – > 0.4) for PCA's factor loadings and Pearson's coefficients.

RESULTS AND DISCUSSION

Physical and chemical variables relevance on general conditions of the ISW

Except for nitrate, the availability of nutrients was moderately (< |0.75| and > |0.50|) or strongly correlated (> |0.75|) to some environmental variables (Table 2), which suggest their relevance in determine the water condition. It was observed a strong correlation between ammoniacal-N and TP ($r = 0.839$, $p = 0.000$), and both nutrients were moderately correlated to EC (ammoniacal-N: $r = 0.676$, $p = 0.000$; TP: $r = 0.641$, $p = 0.000$). These significant positive Pearson's correlations reinforced that there is a large amount of sewage discharge in ISW, producing a concomitant increase on the concentrations of the different nutrients and in EC, since these nutrients are present in the water as ions.

Differently from nutrients, the water quality variables related to particulate fraction of solids (TSS, turbidity, and chlorophyll-a) did not show moderately or strongly correlations, exhibiting Pearson correlation coefficients < |0.50| (Table 2).

The water quality variables showed high standard deviation (Table 2), suggesting broad ranges in spatial and/or temporal scales in ISW, and reinforcing the importance of monitoring programs that considering multiples sampling points and sampling periods.

Even only some variables have presented strong to moderate relationships each other, we considered all thirteen water quality variables measured for the PCA analysis, since they can indicate different sources of pollution in water degradation, and exhibit spatial or temporal patterns.

The thresholds of 70% of cumulative explained variance and eigenvalues ≥ 1 are usually predefined to decide how many PCs should be retained and considered meaningful (Jolliffe & Cadima, 2016; Olsen et al., 2012). Using this approach for the PCA applied to ISW data, the four main PCs explained 74% of the total variance of the original dataset, and only the two main components explaining more than 55% and showing eigenvalues ranging from 5.42 to 1.16 (Table 3). These results also agree with the observations obtained by Olsen et al. (2012) in their review about the use of PCA to evaluate water quality in rivers. These authors demonstrated that the "number of meaningful PCs identified" and "the variance explained meaningful PCs by" ranged 2-6 and 48-98%, respectively.

Table 2. Pearson Correlation Matrix, mean, and standard deviation (S.D.) for water quality variables from Ipanema Stream Watershed surface water.

	Variables	1	2	3	4	5	6	7	8	9	10	11	12	13
1	Alk.	1												
2	BOD	**0.548** ***	1											
3	Chl.	0.062	0.004	1										
4	Color	**0.655** ***	0.496 ***	-0.105	1									
5	DO	-0.373 **	-0.296 *	-0.122	-0.383 **	1								
6	EC	**0.772** ***	0.420 ***	0.221	0.375 **	-0.315 **	1							
7	NH_4-N	**0.769** ***	0.440 ***	0.161	0.443 ***	-0.416 ***	**0.676** ***	1						
8	NO_3^-	0.463 ***	0.265 *	0.400 ***	0.292 **	-0.205	0.406 ***	0.368 **	1					
9	pH	**0.580** ***	0.279 *	0.209	0.365 **	-0.183	0.402 ***	0.478 ***	0.383 **	1				
10	Temp.	0.575 ***	0.443 ***	0.028	**0.710** ***	-0.412 ***	0.512 ***	0.365 **	0.429 ***	**0.540** ***	1			
11	TP	**0.706** ***	0.375 **	-0.017	0.324 **	-0.350 **	**0.641** ***	**0.839** ***	0.254 *	0.392 ***	0.232	1		
12	TSS	-0.029	0.023	0.404 ***	-0.028	-0.01	0.114	0.015	0.300 *	-0.227	-0.072	-0.064	1	
13	Turb.	0.380 **	0.353 **	0.138	0.421 ***	-0.151	0.357 **	0.410 ***	0.442 ***	0.078	0.246 *	0.326 **	0.470 ***	1
	Mean	31.52	2.9	2.67	9.58	5.64	73.5	0.260	0.235	7.06	23.1	0.095	13.76	8.8
	S.D.	27.82	6.2	3.66	23.70	2.09	63.2	1,209	0.379	0.81	3.1	0.235	100.88	25.5

Alk.: Alkalinity; BOD: Biochemical Oxygen Demand; Chl.: Chlorophyll-a; DO: Dissolved Oxygen; EC: Electrical conductivity; NH_4-N: Ammnoniacal-N; NO_3^-: Nitrate; Temp.: Temperature; TP: Total Phosphorus; TSS: Total Suspended Solids; Turb.: Turbidity. *p ≤ 0.05; **p ≤ 0.01; and ***p ≤ 0.001. Bold values: r ≥ 0.500.

Table 3. Loadings values of Principal Component Analysis (PCA) for the four main components for Ipanema Stream Watershed surface water.

Variables	PC1	PC2	PC3	PC4
Alkalinity	**-0.911**	0.138	0.089	0.050
Ammnoniacal-N	**-0.833**	0.040	0.362	0.219
Biochemical Oxygen Demand (BOD)	**-0.636**	0.086	-0.279	0.170
Chlorophyll-a	-0.190	**-0.668**	0.309	-0.469
Color	**-0.705**	0.203	**-0.523**	0.012
Dissolved Oxygen (DO)	**0.516**	-0.083	0.094	0.018
Electrical conductivity (EC)	**-0.797**	-0.066	0.247	0.064
Nitrate	**-0.587**	-0.463	-0.055	-0.331
pH	**-0.619**	0.224	0.201	**-0.536**
Temperature	**-0.706**	0.185	-0.428	-0.370
Total Phosphorus (TP)	**-0.730**	0.154	0.459	0.368
Total Suspended Solids (TSS)	-0.076	**-0.866**	-0.152	0.197
Turbidity	**-0.533**	-0.495	-0.286	0.387
Eigenvalue	5.42	1.84	1.21	1.16
% Explained variance	41.66	14.18	9.27	8.95
% Cumulative explained variance	41.66	55.84	65.11	74.06

Bold values are ≥ │0.50│.

Guedes et al. (2012) and Passos et al. (2021) argued that the highest loadings are the most significant variables for each PC. In the studies focused on surface water quality, high loading for a variable indicates that it is an important component to a pollution source or a specific process, the opposite occurs for low loading (Olsen et al., 2012). Based on the two main components, our data showed that all variables were moderately or strongly correlated to at least one of the two main PCs (Table 3). For example, TSS was weakly related to PC1, but showed a correlation of -0.866 with PC2. Liu et al. (2003) emphasized that variables with loading values higher than │0.75│ should have a strong influence on the environmental process indicated by the PC. For the dataset of Ipanema Stream, the PCA showed loading values higher than │0.75│ for alkalinity, ammoniacal-N, and EC in PC1, and TSS in PC2, but no strong correlations occurred in PC3 or PC4 (Table 3).

The results indicated that PC1 is related to nutrient availability, while PC2 is related to suspended solids and chlorophyll-a (Table 3). Therefore, PC1 corresponds to nutrient load from domestic sewage and uses of nitrogenous and phosphate compounds in other activities. The PC1 also showed that the high input of nutrients (TP, ammoniacal-N, and nitrate) results in high biological demand for oxygen (high BOD), and consequently a decrease in dissolved oxygen concentrations (low DO values). These variables and correlations (both in PC1 and PC2) are well documented in the urban stream syndrome (Richardson & Soloviev, 2021; Walsh et al., 2005).

Supporting the urban stream syndrome showed by PC1, ammoniacal-N and TP had a strong and positive Pearson's correlation coefficient (r = 0.839, p = 0.000), which was the highest coefficient observed (Table 2). BOD and DO presented weak correlations (< │0.50│) with these nutrients, but the coefficients were, respectively, positive (ammoniacal-N: r = 0.44, p = 0.000; TP: r = 0.38, p = 0.002) and negative (ammoniacal-N: r = -0.42, p = 0.001; TP: r = -0.35, p = 0.004), as expected. Thus, the higher nutrient concentrations resulted in higher demand for oxygen and, consequently, lower oxygen concentrations in the water.

Nitrogenous fertilizers used in agriculture (as ammonium sulfate, ammonium nitrate, and urea) and sewage discharge are the main sources of ammoniacal-N ($NH_4^+ + NH_3$) in water systems. In domestic sewage, ammoniacal-N has much higher concentrations than nitrate, which is also related to the ammonification process, that it is the first process occurring during the reduction of organic nitrogen (Edwards et al., 2024; Ghaly & Ramakrishnan, 2015). As expected, the ammoniacal-N showed higher concentrations than nitrate in the urban sampling stations, although nitrate was also abundant in some of them (Figure 2A).

The balance between ammonium and ammonia is influenced by pH and temperature. Ammonia is positively correlated to these variables, thus higher ammonia concentrations will occur when pH and temperatures values are higher, which increase the risk of ammonia intoxication by the biota (Edwards et al., 2024; Purwono et al., 2017). This situation may be occurring in the Taúbas (TU6) and Bom Jardim (TU8) creeks since these stations were characterized by higher ammoniacal-N concentrations and higher pH values. Other sampling stations, as TR3 and MU6, showed high pH, but lower concentrations of ammoniacal-N (Figure 2). The Brazilian (Brasil, 2005) and the regional (Minas Gerais, 2022) legal limits for ammoniacal-N concentrations were compared with the values observed in TU6 and TU8. All samples from TU6 and 70% of the samples from TU8 presented concentrations on average three times higher than the legal limit (3.0 $mg.L^{-1}$ for pH ≤ 7.5; 2.0 $mg.L^{-1}$ for 7.5<pH≤8.0; 1.0 $mg.L^{-1}$ for 8.0<pH≤8.5; 0.5 $mg.L^{-1}$ for pH>8.5).

The total suspended solids were negatively related to PC2 (-0.866), and therefore low values in PC2 indicate high mass of suspended solids in the water. PC2 was also negatively related to chlorophyll-a concentration (-0.668), which is an indirect measure of phytoplankton biomass, a component of the suspended particulate matter in surface waters. The TSS concentration in surface waters is related to terrestrial surface runoff and influenced by land use/cover. In the rural zones, the input of solids in surface waters comes from agricultural and livestock activities, whereas the input in urban zones come from domestic sewage, erosion process, solid waste, and non-planned urban occupation (Khatri & Tyagi, 2015; Lollo, 2016).

Spatial characterization of ISW by land use zones and sampling stations

The relationship between water quality and land use/cover was evidenced by PC1 × PC2 score plots (Figure 3). The type of land uses (rural, peri-urban, and urban) was segregated by PC1 (nutrient axis), with positive values for rural and peri-urban zone, and negative values for urban zone.

The PC1 × PC2 scores plotted by land use zone indicated that whereas surface waters in rural zone tend to present lower nutrients availability and electrical conductivity values, and higher DO concentrations, the urban zone waters present opposite trends.

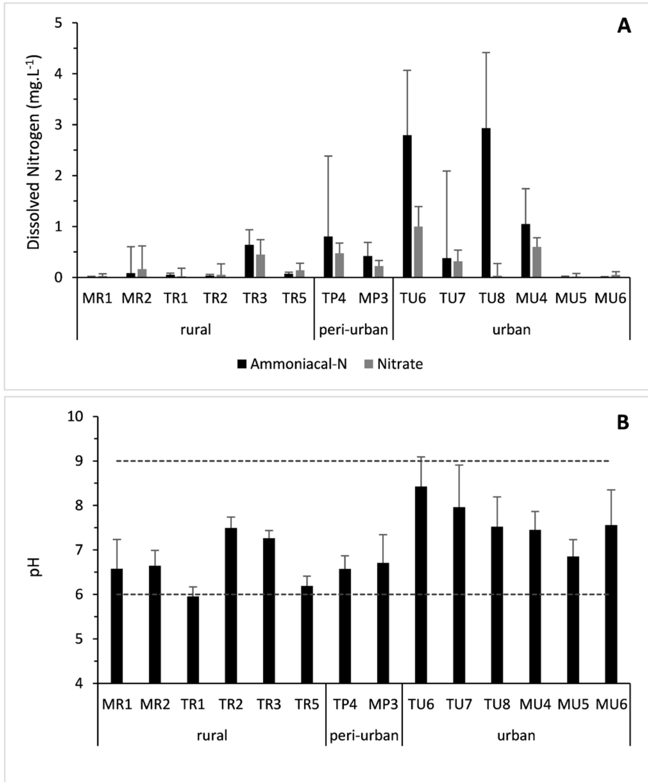

Figure 2. Average concentration and standard deviation of water quality variables in surface water at sampling stations in Ipanema Stream Watershed. (A) Ammoniacal-N and Nitrate, and (B) pH. Dashed lines in (B) represent the legal tolerable range of pH values established for Brazilian (Brasil, 2005) and regional (Minas Gerais, 2022) scales.

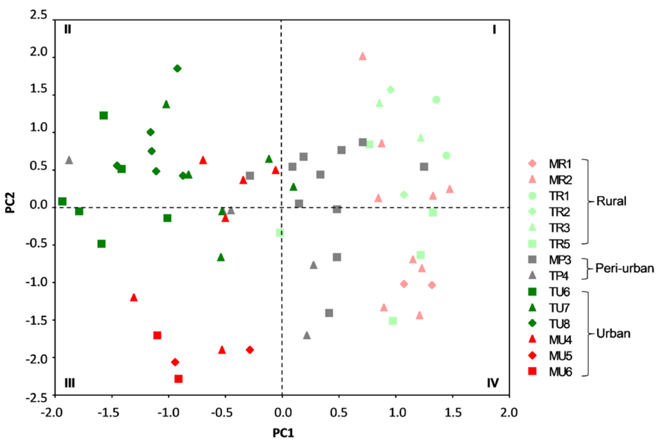

Figure 3. PC1 versus PC2 scores from the PCA performed with the dataset of surface water in Ipanema Stream Watershed. Samples were categorized by sampling stations and by land use zone (color unfilled dots: rural; gray dots: peri-urban; filled dots: urban). Quadrants were identified by the Roman numbers inside plot.

Thus, as discussed above about the urban stream syndrome, the surface waters in urban zone have poor water quality and are vulnerable to eutrophication (Fia et al., 2015; Menezes et al., 2016; Porto et al., 2017). A better water condition in rural zone is also expected, since the rural sampling stations in this study had smaller drainage area, consequently less pollution sources and anthropic interference (lower population density and larger area covered by native vegetation). Conversely, the urban zone had greater population density, and consequently an intensive negative interference on the environment by, for example, sewage discharge, soil compaction, and waterproofing (Lollo, 2016; Souza & Gastaldini, 2014).

The samples segregated by land use zone (PC1) were also segregated by sampling station in PC2, which means that even in the same land use zone (same PC1 range), the sampling points showed particularities, mainly due to different TSS values, related to PC2 (Figure 3). In this approach and analyzing the graph of PC1 × PC2 scores by quadrants (I, II, III and IV), clusters of sampling stations were observed, which allowed us to detect trends, although some stations had their samples distributed between more than one quadrant.

The quadrant I is related to better water quality conditions, characterized by lower availability of nutrients, lower BOD values, and higher DO concentrations (PC1), besides lower values of TSS and chlorophyll concentrations (PC2). The lower availability of nutrients and higher DO concentrations in the rural zone was discussed above, and the lower suspended solid concentrations improved this good water quality condition. All sampling stations in rural zone were dispersed in quadrant I, except by MR1 (water spring) and MR2, which were dispersed in the opposite quadrant (IV) by PC2, due to their higher TSS concentrations (Figure 3). This condition may be a negative consequence of the riparian zone deforestation for pasture and agricultural activities. Since the vegetation at riparian zone acts as a buffer for surface runoff, the deforestation intensifies this process, increasing the input of solid material to aquatic environments, which affects the water quality and accelerate siltation, producing negative ecological impacts (Graziano et al., 2022; Vera Mercado & Engel, 2021).

The urban sampling stations were completely clustered in quadrants II and III (Figure 3), associated to negative values in PC1 and related to poor water quality conditions, as discussed above. MU5 and MU6 were completely clustered in quadrant III, and showed PC2 values lower than -1.5, consequently showing higher TSS concentrations and the worst water quality conditions (Figure 3). Some samples of MU4 were also dispersed in quadrant III, with PC1 values lower than -1.0. This indication of poor water quality is expected since this sampling station covers practically the entire drainage area of the Ipanema Stream and its main tributaries, including those draining urban areas. Thus, the most polluted loads are already influencing MU4, and the sampling stations downstream MU4, including the stream mouth (MU6), still receive meaningful load of TSS. These poor conditions at downstream indicate that Ipanema Stream has low self-purification capacity in relation to the input of pollutants it receives nowadays. For monitoring and management purposes, it is important to consider that the capacity of self-purification is affected by many factors beyond the levels of pollutants, such as hydrological, biological, and other chemicals variables (Šaulys et al., 2020). Further, the problems are not only restricted to Ipanema Stream since these poor water quality conditions probably have negative effects on Doce River. This condition reinforces the necessity of watershed management actions to improve the water quality conditions in ISW, contributing to the effects of programs for the restoration of Doce River.

TP4 scores were more scattered in PC1 × PC2 plot, and the samples were not clustered. The values were generally closer to 0 in relation to PC1, they were similar to the samples from the other peri-urban station (MP3), except by one that exhibited a very low PC1 value, as observed for TU6 samples (Figure 3). This outlier likely resulted from an effluent discharge just upstream of TP4, observed at the time sampling was performed.

Despite TU6 and TU8 samples did not segregate from the other urban stations (except MU5 and MU6), and did not be grouped near the lowest PC2 values, these stations exhibited the lowest PC1 values (Figure 3), i.e. their worst water quality conditions are more related to BOD, nutrients, and DO concentrations. Moreover, as previously discussed, these conditions could be harmful for the biota due to the possibility of intoxication by ammonia. Thus, we suggest that more attention would be paid by the sanitation programs focused on these urban tributaries and reinforce that it is essential to eradicate any domestic sewage discharge without previous treatment.

The relationship between water quality and land use/cover was also evidenced through PCA analysis followed by factor analysis (FA/PCA) by Guedes et al. (2012). The authors evaluated the Middle Pomba River, also located in the State of Minas Gerais/Brazil, but in another large basin – São Francisco Basin. In that study, PCA was explained by 3 PCs (74.4%), and showed that nutrients and suspended solids were the most meaningful variables. The water quality variations were a consequence of contamination by untreated sewage, diffused pollution, and water erosion in the watershed. These results are similar to those described in the present study. Our results are also similar to Fraga et al. (2020), who used a large database from a monitoring program performed by Minas Gerais Government in 64 sampling stations from Doce River Basin, between 2010 to 2017. Since this monitoring program have no sampling point situated in ISW, our results are interesting to contribute to an expansion in the knowledge about Doce River Basin. The most meaningful variables were TSS, EC, ammoniacal-N, BOD and chlorophyll-a, which exhibited strong relation (> 0.70) to FA/PCA components. These variables were associated to erosion, runoff (mainly from agriculture), and domestic sewage discharge. Some toxic metals were also considered important in Fraga et al. (2020) study, but these variables were not measured in our study.

Temporal characterization of ISW by climate seasons

Although spatial differences (land use zones and sampling stations) in ISW were evident and showed strong relationships with land use/cover and their pollution sources, no temporal pattern (climate seasons) was observed. Furthermore, the PC1 × PC2 scores plot by climate seasons did not present any dots clustering, either with PC1 or PC2 (Figure 4).

In a previous study performed in Doce River Basin, Fraga et al. (2020) reported that climate seasonality was important

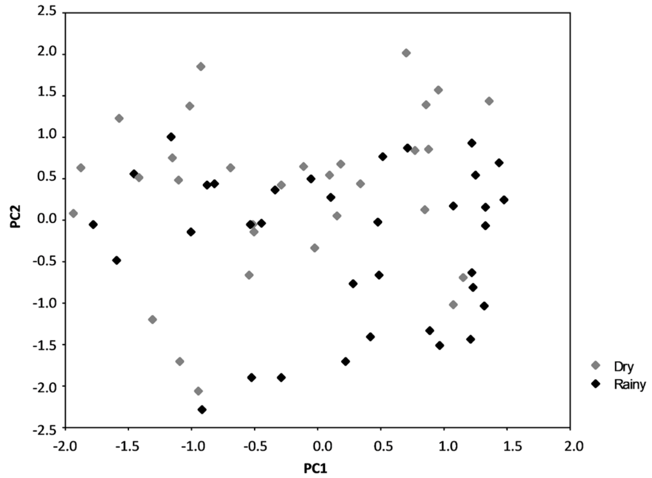

Figure 4. PC1 versus PC2 scores from the PCA performed with the dataset of surface water in Ipanema Stream Watershed. Samples were categorized by climatic seasons.

to determine water quality variations. Likewise, Passos et al. (2021) affirmed that it is expected to observe higher concentrations of solids in suspension during rainy season compared to dry season due to the well-known relationship of solids runoff and rainfall. Even PC2 showed a strong correlation to TSS, we did not observe any seasonal difference on scores scattering for ISW water quality data. Thus, the water quality seems to be more dependent of spatial than temporal differences in ISW.

CONCLUSIONS

The surface water quality of Ipanema Stream Watershed was clearly related to land use/cover in the region. An evident spatial pattern was detected based on land use zones and sampling stations by PCA method. Nevertheless, no temporal pattern was detected. Nutrients, especially ammoniacal-N, and suspended solids were the main variables explaining the spatial variance of the water quality in ISW. The urban waters exhibited the worst water quality conditions, which is in line with the stream river syndrome.

Urban tributaries seem to contribute significantly to the degradation of Ipanema Stream, despite official data indicate that 97.7% of the city's sewage is adequately treated (Instituto Brasileiro de Geografia e Estatística, 2023). Thus, special attention must be paid to disposal of sanitary sewage into the storm drainage network. The eradication of this source of pollution seems promising to water quality improvement in ISW and indirectly in Doce River, since Ipanema Stream did not show significant self-purification capacity for the current input of pollutants.

Although urban zone seems to be more relevant in ISW, more attention must be paid to the rural zone, mainly in mainstream, since showed low nutrients concentration but high total suspended solids. Thereby, preservation and management actions to riparian vegetation restoration seem to be a good choice to improve the water quality, especially in rural zone.

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Gabriela von Rückert: Conceptualization (leader), data curation (leader), formal analysis (supporting), funding acquisition (leader), investigation (equal), methodology (leader), project administration (leader), resources (leader), supervision (leader), validation (supporting), writing – original draft (supporting), writing – review & editing (equal).

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