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EFFECT OF RAINFALL SEASONALITY AND LAND USE ON THE WATER QUALITY OF THE PARAÍBA DO SUL RIVER

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Keywords:
WQI_{NSF}
Rainfall
Water quality parameters

ABSTRACT

Monitoring water quality is important for the suitable management of water resources. Therefore, this study aims to assess the main water quality parameters and the National Sanitation Foundation-Water Quality Index (WQI_{NSF}) of four locations on the Paraíba do Sul River basin, in the state of Rio de Janeiro, influenced by different land use and land cover, and in the dry and rainy seasons. The following quality parameters were evaluated: total phosphorus (TP), nitrate (NO_3^-), dissolved oxygen (DO), potential of hydrogen (pH), turbidity (Turb), thermotolerant coliforms (Col), total dissolved solids (TDS), biochemical oxygen demand (BOD), water temperature (T_{water}) and air temperature (T_{air}). Statistical differences ($p < 0.05$) were observed between the dry and rainy seasons for the parameters: TP, Col, Turb, TDS, T_{water}, T_{air}, NO_3^-, DO, and WQI_{NSF}. The concentration of rainfall was effective in water quality parameters behavior. WQI_{NSF} was lower in the rainy season and possibly the runoff was the major cause of water quality degradation. Land use and land cover influenced the concentration of DO and Col and, consequently, WQI_{NSF}. Despite statistical differences, in most cases, the Paraíba do Sul River basin lies in medium water quality index according to the classification of the National Water and Sanitation Agency (ANA).

Palavras-chave:
WQI_{NSF}
Precipitação pluviométrica
Parâmetros de qualidade da água

EFEITO DA SAZONALIDADE PLUVIOMÉTRICA E DO USO DA TERRA NA QUALIDADE DA ÁGUA DO RIO PARAÍBA DO SUL

RESUMO

O monitoramento da qualidade da água é importante para uma gestão adequada dos recursos hídricos. Diante disso, este estudo teve como objetivo comparar os principais parâmetros de qualidade da água e o Índice de Qualidade das Águas (WQI_{NSF}) de quatro localidades no rio Paraíba do Sul, no estado do Rio de Janeiro, sob diferentes influências de uso da terra e entre os períodos seco e chuvoso. Avaliaram-se os seguintes parâmetros de qualidade: fósforo total (TP), nitrato (NO_3^-), oxigênio dissolvido (DO), potencial hidrogeniônico (pH), turbidez (Turb), coliformes termotolerantes (Col), sólidos totais dissolvidos (TDS), demanda bioquímica de oxigênio (BOD), temperatura da água (T_{water}) e do ar (T_{air}), além do WQI_{NSF}. Diferenças significativas foram observadas entre os períodos seco e chuvoso para os parâmetros: TP, Col, Turb, TDS, T_{water}, T_{air}, NO_3^-, DO e o WQI_{NSF}, sendo a concentração da precipitação pluvial, efetiva no comportamento desses parâmetros. WQI_{NSF} foi menor no período chuvoso e o escoamento superficial foi o principal fator contribuinte para a piora da qualidade da água. O uso da terra influenciou na concentração de DO e Col e, consequentemente, no WQI_{NSF}. Apesar das diferenças estatísticas, para a maioria dos casos o rio Paraíba do Sul se enquadra em classe média de qualidade da água, de acordo com a classificação da Agência Nacional de Águas.

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INTRODUCTION

Water quality analysis is an essential tool to pollution monitoring and control and to support the sustainable management of natural resources (BARAKAT *et al.*, 2018). Moreover, when associated with meteorological and land use and land cover, it helps to identify the main pollutant for different watersheds at seasons (TOMCZYK *et al.*, 2018), thus facilitating mitigation actions.

The stream's water quality is influenced by several factors, such as human activities, climate variability, geology, soil erosion (FRAGA *et al.*, 2020a), and land use and land cover (RODRIGUES *et al.*, 2018). Besides, agricultural expansion, population growth and industrial activities tend to increase the number of effluents discharged into the streams (FRAGA *et al.*, 2019), influencing the water quality. In contrast, rainfall seasonality influences the presence of pollutants in the rivers. In the rainy season more pollutants reach the rivers by the overland flow (runoff). In the dry season, the pollutants concentration rises due the stream's low solubility/purification capacity (FRAGA *et al.*, 2020a).

The Water Quality Index developed by the *National Sanitation Foundation* (WQI_{NSF}) is a dimensionless number (ranging from 0 to 100) that provides the classification of the stream's water quality that is the most disseminated in Brazilian water resources researches (MARMONTEL *et al.*, 2018). The WQI_{NSF} uses nine parameters to assess the water quality: total phosphorus, nitrate, dissolved oxygen, potential of hydrogen, turbidity, thermotolerant coliforms, total dissolved solids, biochemical oxygen demand, and water temperature (OLIVEIRA *et al.*, 2017; OLIVEIRA *et al.*, 2018). The higher values of WQI_{NSF} indicate a better overall water quality status. In addition, it is used as a comparative index of different water bodies (MANDARIC *et al.*, 2018). Thus, it can be assigned to identify priority areas for pollution mitigation.

Water quality assessment requires monitoring on a spatial and temporal scale, coupling this analysis to questions about land use and watershed climate, inasmuch as these factors directly influence the essential components for water quality (WU *et al.*, 2018). Some studies analyzed the influence of land use and land cover and/or climate seasonality on water quality (ZHANG *et al.*, 2011; PONTES *et al.*, 2012; ZHAO *et al.*, 2015; OLIVEIRA *et al.*, 2017; OLIVEIRA *et al.*, 2018; RODRIGUES *et al.*, 2018; TOMCZYK *et al.*, 2018; WU *et al.*, 2018; FRAGA *et al.*, 2020a). However, in Brazil, these studies are scarce due to unavailability and/or difficulty obtaining water quality parameters data set at appropriate temporal and spatial scales.

The Paraíba do Sul River basin drains one of the country's most developed regions with hydroelectric power plants, industries, and a primarily high-density urban population (PAIVA *et al.*, 2020). However, the degradation of water quality in the Paraíba do Sul river occurs due to the discharge of domestic and industrial effluents and agricultural residues in the river and problems of conservation of adjacent areas (PACHECO *et al.*, 2017; LUCHINI, 2020).

In this context, this study was conducted to assess the water quality parameters and the WQI_{NSF} in the rainy and dry periods in four stretches of the Paraíba do Sul River in the north of Rio de Janeiro State, Brazil, under different conditions of land use and land cover. Moreover, it seeks to generate information for support planning and management actions, thus improving the water quality in the Paraíba do Sul River basin.

MATERIAL AND METHODS

Study Area

The Paraíba do Sul River (Figure 1) is located in the southeastern region of Brazil downstream the confluence of the Piratinga and the Paraibuna rivers in the Paraibuna Dam in São Paulo State. It covers about 1,140 km and flows through Vale do Paraíba in Sao Paulo, Zona da Mata in Minas Gerais State (MG) until it reaches the Atlantic Ocean, in the Northern Rio de Janeiro. The Paraíba do Sul River basin (PSRB) drains one of the most economically important regions in Brazil (PAIVA *et al.*, 2020).

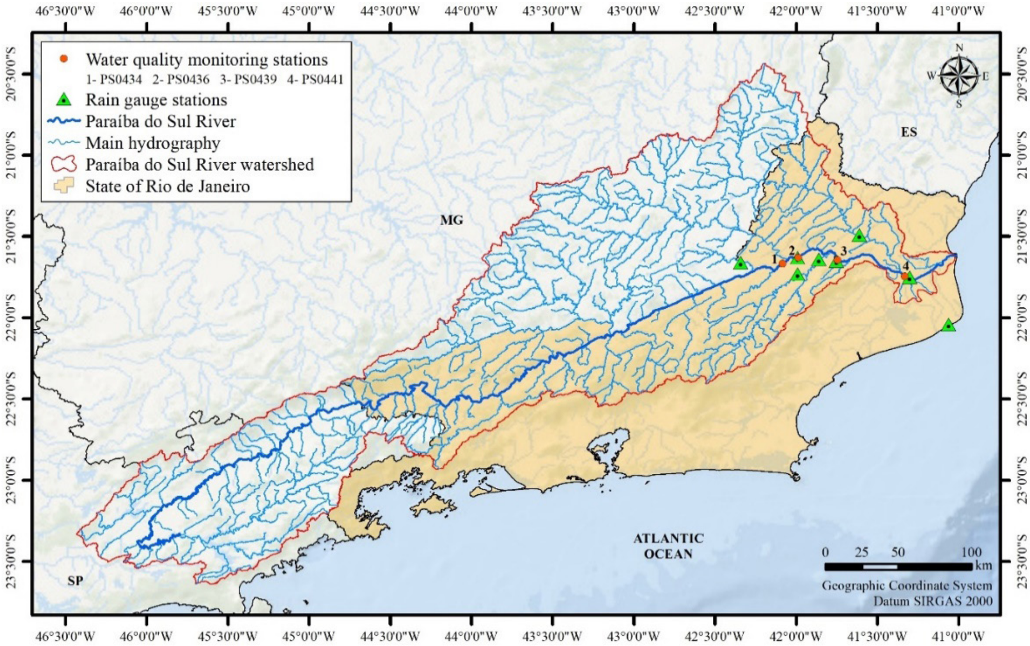

Figure 1. Location of water quality monitoring station, rain gauge station, and Paraíba do Sul river

The PSRB is inserted in the Atlantic Forest biome. However, only a small part of its total area is occupied by forest remnants, generally in the highest regions and most rugged terrain, as integral protection conservation units such as Serra dos Órgãos National Park, Serra da Bocaina National Park, Itatiaia National Park, and Serra da Mantiqueira National Park. Land use in the Paraíba do Sul River basin land use account for 60% of pasture/grassland, approximately 12% of crops, and about 12% of forest fragments, among other less significant uses.

The study area comprises the lower Paraíba do Sul region between -21.5º and -22.0º latitudes and ranging from the longitudes of -42.5º and -41.0º, in the Northern Rio de Janeiro. The monthly rainfall depths range between 10 and 300 mm, with a distinct seasonal pattern (rainy season - summer, dry season - winter) and an annual average depth equals 1082.5 mm (BRITO *et al*., 2017). The region has a predominantly warm and humid tropical climate (Aw and Am, according to the Köppen's classification), with average annual air temperature between 19º and 25ºC and annual rainfall between 700 and 1200 mm (ALVARES *et al*., 2013; BOHN *et al*., 2020). The region climate is conditioned by the Frontal Systems (FS) South Atlantic Convergence Zone (SAZC), South Atlantic Subtropical High (SASH), Instability Lines (IL), Atmospheric Blocking (AB), Mesoscale Convective Systems (MCS), besides physiographic factors, such as orography continentality/maritime (BRITO *et al*., 2017; BOHN *et al*., 2020).

Land Use and Land Cover

The land use and land cover map for the year 2019 (Figure 2) was obtained based on the mapping carried out by the MapBiomas Project, collection 4.1 (MAPBIOMAS, 2019). The MapBiomas Project is an initiative that involves a collaborative network of experts in biomes, land uses, remote sensing, geographic information system (GIS), and computer science. Cloud processing and automated classifiers developed and powered by the Google Earth Engine® platform have been used to make available a historical series of annual land cover and land use maps of Brazil.

For each water quality station, the surrounding land use and land cover classes were considered through Google Earth images (Figure 3) with the assistance of a geographic coordinate system. The influences of land use and land cover in the water quality stations surroundings were considered qualitatively to classify the stations according to the most important land uses and land cover. The stations most influenced by urbanized areas were PS0441, PS0439, PS0434, and PS0436, in order of greatest influence. The stations that suffer the strongest influence from pastures and/or agriculture were PS0436, PS0434, PS0439, and PS0441, in the order of greatest influence.

Rainfall Data

The daily precipitation data of eight rain gauges (Table 1) were obtained from the Hidroweb Platform from the National Water and Sanitation Agency (ANA, 2015) and integrated into accumulated monthly, considering the same base period, from 2014 to 2019. The accumulated monthly rainfall in

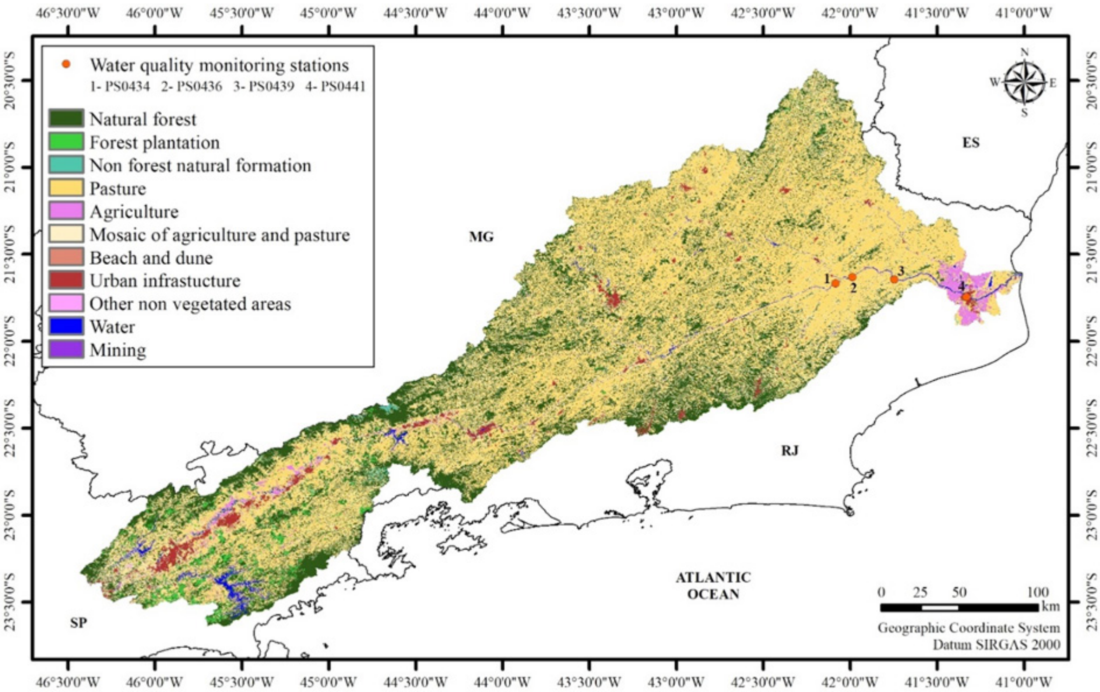

Figure 2. Land use in the Paraíba do Sul River Basin

Figure 3. Land use around water quality monitoring station, PS0434 (panel a), PS0436 (panel b), PS0439 (panel c), PS0441 (panel d), in the Paraíba do Sul River basin

the rainy period (between October and March) and the dry period (between April and September) were measured according to the local hydrological year (BRITO *et al*., 2017).

Water Quality Data

The water quality parameters include physical, chemical and biological parameters, and WQI_{NSF} historical data series. These databases were measured at four water quality monitoring stations (Table 2), available at the State Environmental Institute (INEA, 2019) website (http://www.inea.rj.gov.br/). The water quality parameters includes the following water quality parameters: total phosphorus (TP, in mgL^{-1}), nitrate (NO_3^-, in mgL^{-1}), dissolved oxygen (DO, in mg L^{-1}), hydrogen potential (pH), turbidity (Turb, in NTU), thermotolerant coliforms (Col, in MPN 100 ml^{-1}), total dissolved solids (TDS, in mg L^{-1}), biochemical oxygen demand (BOD, in mg L^{-1}), water temperature (T_{water}, in °C), and air temperature (T_{air}, in °C), and the WQI_{NSF} index. The Table 2 shows the number of available data for each period (rainy and dry periods), in each year.

The WQI_{NSF} was calculated using equation 1. The numerical result indicates the water quality classification; according to Table 3,

$$WQI = \prod_{i=1}^{n} q_i^{\,wi} \tag{1}$$

where:

WQI_{NSF} = National Sanitation Foundation-Water Quality Index;

q_i = quality of the i-th parameter (a number between 0 and 100, obtained from the average curve of quality variation, result of the analysis);

wi = weight corresponding to the i-th parameter (a number between 0 and 1, assigned according to its importance for the global quality configuration).

Table 1. Rain gauge station; respective geographical coordinate, altitude, and municipality

Rain gauge	Localização	Code	Latitude	Longitude	Altitude (m)
Três Irmãos	Cambuci	2141007	-21.63	-41.99	42
Ponto de Pergunta	Itaocara	2141100	21.73	-41.99	61
Fazenda da Barra (Pirapetinga)	Pirapetinga	2142007	-21.66	-42.34	152
São Fidélis	São Fidelis	2141005	-21.65	-41.75	10
Dois Rios	São Fidelis	2141006	-21.64	-41.86	50
Farol São Tomé	Campos dos Goytacazes	2241001	-22.04	-41.06	2.00
Campos - Ponte Municipal	Campos dos Goytacazes	2141002	-21.75	-41.3	14
Cardoso Pereira	Campos dos Goytacazes	2141003	-21.49	-41.61	29.00

Table 2. Water quality monitoring station, respective geographic coordinate, municipality, and the number of observations per season (rainy or dry)

Estação	Latitude	Longitude	Local	2014	2015	2016	2017	2018	2019	Total
Rainy Season										
PS0434	-21.67	-42.08	Itaocara	6	5	5	5	0	4	25
PS0436	-21.64	-41.75	Itaocara	6	5	5	5	5	4	30
PS0439	-21.64	-41.75	São Fidelis	6	5	5	5	5	4	30
PS0441	-21.74	-41.33	Campos dos Goytacazes	6	5	3	5	5	4	28
Dry Season										
PS0434	-21.67	-42.08	Itaocara	6	4	5	2	0	6	23
PS0436	-21.64	-41.75	Itaocara	6	4	5	2	0	6	23
PS0439	-21.64	-41.75	São Fidelis	6	4	5	2	0	6	23
PS0441	-21.74	-41.33	Campos dos Goytacazes	6	4	1	2	0	6	19

Table 3. Classification of the Water Quality Index according to the State Environment Institute of the state of Rio de Janeiro (INEA, 2019) and the National Water and Sanitation Agency (ANA, 2015)

Water Quality Status	INEA	ANA
	Index	Index
Excellent	100 ≥ WQI ≥90	91-100
Good	90 > WQI ≥ 70	71-90
Medium	70 > WQI ≥ 50	51-70
Poor Water	50 > WQI ≥ 25	26-50
Unsuitable	25 > WQI ≥ 0	0-25

Source: Water Quality Index, Rio De Janeiro state, INEA (2019) and ANA (2015)

The weights assigned to each water quality parameter can be found on the INEA (2019), as follow: 0.16 for Col, 0.11 for BOD and pH, 0.10 for TP and NO_3^-, 0.10 for T_{water} and T_{air}, 0.17 for DO, 0.07 for TSD and 0.08 for turb.

Analysis of Water Quality Data

The statistical analysis was performed using the R software, version 3.4.3 (R CORE TEAM, 2020) and a 5% significance level was adopted for all of them. The first step was the linear regression analysis ($Y = \beta_0 + \beta_1 X$) of the water quality parameters and the WQI_{NSF} as a function of the years under analysis for each water quality monitoring station, to check whether there are trends, over time. For that, Student's t-test was carried out in the linear regression parameters, intercept (β_0) and the slope coefficient (β_1), under the null hypothesis (H_0), these parameters are equal to zero. Rejection of the null hypothesis under the slope coefficient indicates a significant trend of water quality parameters and/or WQI_{NSF}. The fit quality was determined by the coefficient of determination (r^2), as described in Abreu *et al.* (2020). The r^2 represents the ratio of the regression sum of squares to the total sum of squares.

After that, the nonparametric Wilcoxon-Mann-Whitney test, which compares outcomes between two independent samples, was performed to check for equality between the water quality monitoring station and the period of the year (rainy and dry period), for each water quality parameters and WQI_{NSF}. The rainy and dry periods were compared to verify the effect of the climate seasonality on the water quality parameters and WQI_{NSF}. The influence of the land use and land cover was verified by comparing the water quality monitoring station in the same period (rainy and dry), i.e, each water quality monitoring station was compared separately for the rainy and dry periods.

The analysis of the Notch box-plot verified the data dispersion of each season in each period and compared the corresponding medians. The Notch box-plot displays an interquartile range (IQR) around the median, which is usually based on the median ± 1.57 · IQR /$\sqrt{n}$, where n is the number of observations, according to Chambers (1983), although it is not a formal test, if the notches on two boxes do not overlap, there is "strong evidence" (95% confidence) their medians differ from each other (ABREU *et al*., 2020).

Spearman (r) rank correlation analysis was used to measure the correlation between water quality parameters. Correlation analysis was made for each water quality season, considering the periods' data and separately for the rainy and dry periods. Correlations above 0.7 and below -0.7 were considered as strong positive and negative correlations, respectively (STEPS *et al*., 2021).

RESULTS AND DISCUSSION

Linear Regression Analysis and Wilcoxon Rank Sum Test

The regression coefficients between the water quality parameters and the WQI_{NSF} as a function of the analyzed years (Figure 4 and Table 4) have demonstrated that, only pH presented trends at all the water quality monitoring station. Moreover, trends were also observed to thermotolerant coliforms at the PS0441 water quality monitoring station. The r^2 was considered low ($r^2 < 0.27$) for all the regressions (Table 4). There has been an increasing pH unit trend in all study water quality stations, although the rate of increase is low (at most 0.1 per year). The thermotolerant coliforms of the PS0441 Station showed a decreasing trend of 325 MPN $100ml^{-1}$ $year^{-1}$. Temporal limitation (number of years in analysis) may have been a factor that influenced the trend of pH units, which is a parameter very sensitive to rainfall (RODRIGUES *et al.*, 2018; VAROL, 2020), land-use and land cover changes (GIRARD *et al.*, 2016), air temperature, and solar radiation (GIRARD *et al.*, 2016). pH affects the metabolism of several aquatic species, in addition to influencing the effect of other substances (GIRARDI *et al.*, 2016), and its ideal value in body of water is between 6 and 9 (OLIVEIRA *et al.*, 2020). That has been observed in this study on average (Table 4), having few non-standard points (Figure 4 and 6). The reduction of thermotolerant coliforms in the PS0441 Station (Campo dos Goytacazes municipality) can be considered small in relation to average values and standard deviations (Figure 4 and Table 5). Cintra *et al.* (2020) also observed a trend of reduction in the Col values in Campos dos Goytacazes and showed that the reason of this reduction was the

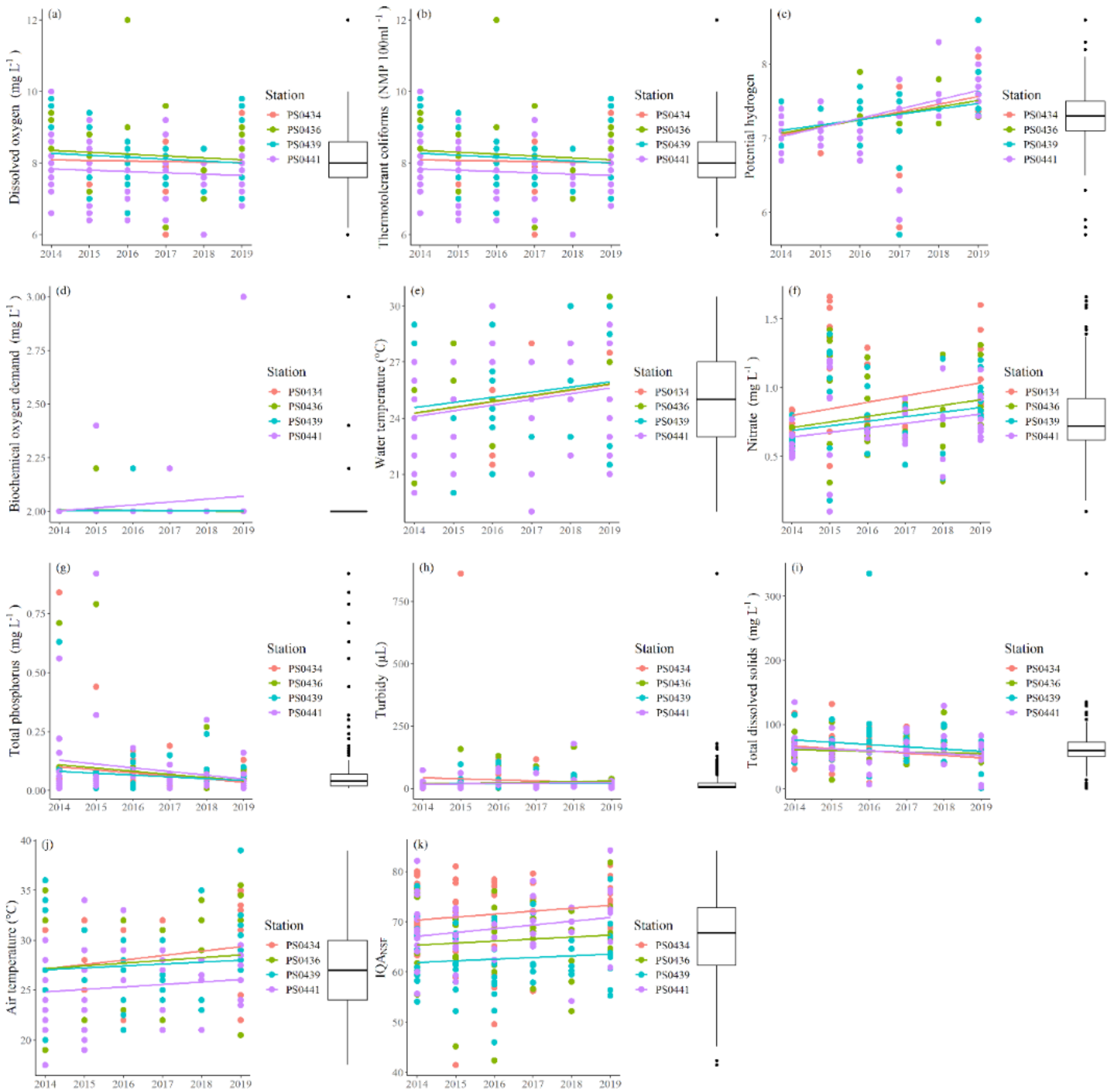

Figure 4. Regression analysis between water quality parameters and water quality index regarding the years of analysis for water quality stations in the Paraíba do Sul River

Table 4. Regression analysis between water quality parameters and water quality index regarding the years of analysis of the water quality stations in the Paraíba do Sul River

Regression analisys	WQI_{NSF}	BOD (mgL^{-1})	TP (mgL^{-1})	NO_3^- (mgL^{-1})	DO (mgL^{-1})	pH	Turb (UNT)	col (NMP $100ml^{-1}$)	TDS (mgL^{-1})	T_{water} (°C)	T_{air} (°C)
						PS0434					
β_0	-1118.618	4.847	26.259	-94.757	38.560	-202.052	8780.609	1177734.551	7327.246	-597.204	-871.749
p-value for β_0	0.420	0.311	0.226	0.088	0.739	0.001*	0.670	0.372	0.080	0.178	0.195
β_1	0.590	-0.001	-0.013	0.047	-0.015	0.104	-4.338	-583.054	-3.605	0.309	0.446
p-value for β_1	0.391	0.551	0.227	0.086	0.792	0.001*	0.672	0.373	0.083	0.161	0.181
r^2	0.016	0.008	0.032	0.063	0.002	0.213	0.004	0.017	0.064	0.042	0.038
						PS0436					
β_0	-743.644	4.997	27.327	-80.758	113.943	-170.820	-4219.809	1132764.578	2407.939	-605.632	-523.194
p-value for β_0	0.522	0.247	0.217	0.079	0.398	0.000*	0.479	0.073	0.522	0.136	0.429
β_1	0.402	-0.001	-0.014	0.040	-0.052	0.088	2.105	-560.279	-1.165	0.313	0.273
p-value for β_1	0.486	0.486	0.218	0.076	0.433	0.000*	0.477	0.074	0.532	0.121	0.405
r^2	0.009	0.000	0.021	0.050	0.015	0.119	0.002	0.018	0.020	0.037	0.007
						PS0439					
β_0	-601.140	2.629	15.844	-66.474	118.413	-139.501	-1207.345	1351916.853	7172.539	-529.586	-361.998
p-value for β_0	0.550	0.542	0.300	0.113	0.344	0.016*	0.773	0.334	0.302	0.187	0.580
β_1	0.329	0.000	-0.008	0.033	-0.055	0.073	0.609	-666.676	-3.524	0.275	0.193
p-value for β_1	0.509	0.885	0.302	0.109	0.378	0.012*	0.770	0.337	0.307	0.168	0.552
r^2	0.010	0.010	0.030	0.060	0.012	0.243	0.010	0.061	0.008	0.046	0.014
						PS0441					
β_0	-1434.142	-25.550	32.145	-66.395	80.706	-244.671	-2854.317	656216.114	4883.809	-592.328	-473.124
p-value for β_0	0.137	0.299	0.195	0.088	0.542	0.000*	0.557	0.019*	0.242	0.157	0.389
β_1	0.745	0.014	-0.016	0.033	-0.036	0.125	1.426	-324.661	-2.393	0.306	0.247
p-value for β_1	0.119	0.263	0.196	0.085	0.581	0.000*	0.554	0.019*	0.247	0.140	0.364
r^2	0.053	0.028	0.037	0.065	0.007	0.268	0.008	0.116	0.030	0.048	0.018

* Significant result by Student's t- test under null hypothesis (H_0) where $\beta_0 = 0$ and $\beta_1 = 0$

increase in municipal wastewater collection and domestic sewage treatment, a fact that had not occurred effectively before the year 2000.

The Table 5 show the water quality parameter variables, the WQI_{NSF}, and the result of the test of Wilcoxon-Mann-Whitney. The lowercase letters compare the water quality monitoring stations in the dry and rainy periods. The capital letters compare the dry and rainy periods in the same water quality monitoring station. Overall, the test showed the water quality parameter and the WQI_{NSF} varied little between the water quality monitoring station, the only observed differences have been in the parameters of DO and Col, $T_{air,}$ and the WQI_{NSF}, for at least one of the periods (dry or rainy). In the rainy period, the DO was higher at the PS0436 Station, although this season did not show a significant difference in PS0439 and PS0434. The PS0441 Station had a lower DO value than the PS0436 Station, and equivalent values to PS0439 and PS0434 Station PS0441 presented lower Col values than PS0439. However, the PS0441 did not differ statistically from PS0434 and PS0436, as PS0434 and PS0436 did not differ from PS0439 in the rainy period. In the dry period, differences in Col were observed between the PS0439 Station (lower value) and other stations (higher values). This was reflected in the WQI_{NSF}, which, in the rainy period, was higher in stations PS0441, PS0434, and PS0436. The lowest values were observed at station PS0439. In the dry period, station PS0434 had the highest WQI_{NSF}, statistically equivalent to the WQI_{NSF} of the PS0441. The WQI_{NSF} of PS0441 did not differ statistically from the observed one at The PS0436 Station. Station PS0439 had the lowest WQI_{NSF} in the dry period. T_{air} was higher at stations PS0434, PS0436, and PS0439 compared to PS0441.

In the dry period, the differences between the water quality monitoring stations were displayed only in Col and $WQI_{NSF.}$ The highest Col values were observed in PS0439, while the PS0434, PS0436 and PS0439 stations were equivalent. The PS0434 and PS0441 obtained higher WQI_{NSF}, while the PS0441 did not differ from station PS0436 in terms of WQI_{NSF}. The lowest values were observed in PS0439, according to the Wilcoxon-Mann-Whitney test, in the dry season.

Differences were observed in almost all water quality parameters between the dry and rainy periods in all water quality monitoring stations. In general, the magnitude of the values was higher for the rainy period for the parameters: Col (except for PS0439 in which they were equivalent in the dry and rainy periods), TDS (except in PS0434 and PS0436 in which they were equivalent in the dry and rainy periods), T_{water} and T_{air} (except for PS0434 in which they were equivalent in the dry and rainy periods); and lower in the rainy season for the parameters: NO_3^- (except in PS0441 in which they were equivalents in the dry and rainy periods), Turb (except for PS0441, in the rainy period Turb was higher) and WQI_{NSF} (except for PS0439 in which they were equivalents in the dry and rainy periods). These results corroborate studies that analyze the effect of seasonality on water quality parameters (FRAGA *et al*., 2020a).

The PS0439 Station, downstream from the municipality of São Fidelis and upstream from Campos dos Goytacazes, in an area influenced by degraded pastures and urbanization (Figure 3), has presented the lowest WQI_{NSF} values in the dry period and one of the smallest in the rainy period (Table 5), classified with the status of medium water quality, both in the dry and rainy periods, according to the classification of INEA (2019) and ANA (2015) (Table 3). The concentration of Col in this region was also one of the highest in the study region, the major pollution problem. The Col significantly influence the WQI_{NSF} due to the

Table 5. Test of the sum of Wilcoxon-Mann-Whitney ranks with continuity correction factor and p-value for water quality variables in the Paraíba do Sul River

Water quality variables	PS0434 Rainy period	PS0434 Dry period	PS0436 Rainy period	PS0436 Dry period	PS0439 Rainy period	PS0439 Dry period	PS0441 Rainy period	PS0441 Dry period
DO (mgL^{-1})	7.69 ± 0.5abA	8.46 ± 0.6aA	8.03 ± 1.0aA	8.50 ± 0.6aA	7.81 ± 0.6abA	8.60 ± 0.8aA	7.48 ± 0.8bA	8.16 ± 0.8aA
col(NMP $100ml^{-1}$)	3691 ± 10812abA	684 ± 2255bB	4143 ± 4970abA	1727 ± 1915.4bB	7702 ± 9241.5aA	7750 ± 8809.5aA	2032 ± 2093.9bA	971 ± 1139.5bB
pH	7.26 ± 0.3aA	7.27 ± 0.5aA	7.27 ± 0.3aA	7.28 ± 0.4aA	7.26 ± 0.3aA	7.30 ± 0.5aA	7.34 ± 0.4aA	7.26 ± 0.5 aA
BOD (mgL^{-1})	2.01 ± 0.0aA	2.00 ± 0.0aA	2.01 ± 0.0aA	2.00 ± 0.0aA	2.01 ± 0.0aA	2.00 ± 0.00aA	2.02 ± 0.1aA	2.05 ± 0.2aA
T_{water} (°C)	26.30 ± 2.1aA	23.37 ± 2.5aB	26.20 ± 2.1aA	23.39 ± 2.4aB	26.48 ± 2.1aA	23.50 ± 2.2aB	25.71 ± 2.3aA	23.42 ± 2.7aB
NO_3^- (mgL^{-1})	0.76 ± 0.3aB	1.04 ± 0.4aA	0.71 ± 0.3aB	0.93 ± 0.3aA	0.68 ± 0.2aB	0.88 ± 0.3aA	0.66 ± 0.2aA	0.81 ± 0.3aA
TP (mgL^{-1})	0.08 ± 0.1aA	0.07 ± 0.2aA	0.09 ± 0.1aA	0.06 ± 0.1aA	0.07 ± 0.1aA	0.05 ± 0.1aA	0.08 ± 0.1aB	0.11 ± 0.2aA
Turb (UNT)	59.98 ± 170.5aB	6.01 ± 6.0aA	37.23 ± 46.2aB	5.71 ± 5.7aA	30.40 ± 31.4aB	5.42 ± 4.5aA	29.91 ± 37.2aA	6.40 ± 4.5aB
TDS (mgL^{-1})	65.52 ± 23.4aA	51.60 ± 26.7aA	64.90 ± 21.0aA	49.37 ± 25.3aA	80.67 ± 51.4aA	51.56 ± 26.7aB	67.93 ± 25.4aA	44.82 ± 22.9aB
T_{air} (°C)	29.18 ± 3.7aA	26.83 ± 4.3aA	28.95 ± 34.0aA	26.26 ± 4.2aB	28.82 ± 4.1aA	25.72 ± 3.7aB	26.20 ± 2.8bA	24.21 ± 4.2aB
WQI_{NSF}	68.46 ± 9.9aB	74.95 ± 4.8aA	63.51 ± 8.0abB	69.84 ± 4.6bA	61.15 ± 6.0bA	64.59 ± 6.6cA	66.81 ± 6.1aB	71.82 ± 5.3abA

The capital letters compare the dry and rainy periods in the same Station.

Lower case letters compare the seasons in the rainy season and the dry season individually.

assigned weight to this parameter in the WQI_{NSF} calculation (equation 1).

PS0434 and PS0436 are water quality monitoring stations located in regions with less urban influence, mainly the PS0434 Station, reflecting in larger values of WQI_{NSF}, DO, and intermediate Col concentration values (Table 5). PS0434 Station has always displayed one of the largest WQI_{NSF} in both the dry and rainy periods. Although being one of the highest WQI_{NSF} of the region, according to the classification of the INEA (2019) and ANA (2015), the water quality is medium and good rainy and dry periods for this water quality monitoring stations, respectively. For station PS0436, water quality was classified as medium in the dry and rainy periods, in accordance with Table 3. The DO values in these two seasons were high in the rainy period, whereas no statistical differences were observed between seasons in the dry season. The Col concentrations in these water quality monitoring stations were intermediate, both in the dry and rainy periods.

The statistical approach aims to find higher or lower values in terms of the quality of water to identify priority points for the improvement of the situation. The classification of the management body of water by the WQI_{NSF} is a classification relates to a specific use of water resources (Table 3). PS0441 Station, for example, despite being located in Campos dos Goytacazes, a large urban region and having a population of approximately 511,168 thousand inhabitants (IBGE, 2020), showed a medium WQI_{NSF} rating in the rainy period and a reasonable rate in the dry period, according to INEA (2019) and ANA (2015), classification (Table 3) and thePS0441 had one of the highest WQI_{NSF} ratings in the dry and rainy periods (Table 5). Despite the slight difference in terms of $WQI_{NSF,}$ the differences in the water quality monitoring stations surroundings indicate that although the PS0441 Station is in an area with substantial urban influence, it is a region with sewage collections, having relatively low values of Coliforms and high values of WQI_{NSF}. The municipality of Campos dos Goytacazes, which ranks as one of the best for basic sanitation, ensures more than 90% of sewage collection and 100% treatment of it (GRUPO ÁGUAS DO BRASIL, 2019).

Another important issue to be highlighted is that although water quality monitoring stations receive the same quality rating according to INEA (2019) or ANA (2015), classification (Table 3), statistical differences have been observed. This identification of regions with critical water quality parameters assists the priority policies linked to water quality improvement without generalization.

Rainfall Analysis

When evaluating the rainfall station data, approximately 38% of the difference were observed in the rainfall totals between October and March (rainy period) and between April and September (dry period), especially at the stations upstream from PS044 (the difference between the rainy and dry period was 68%). Figure 5 shows the rainfall totals in the rain gauge stations in the rainy and dry seasons for the years of analysis (2014 to 2019). Annual variability in rainfall totals was perceived; the lowest values were observed in 2014, 2015, and 2017 for both the rainy and dry periods. The rainfall totals at stations 2141007, 2141100, and 2142007, located upstream from the other stations, at altitudes above 40 meters, showed higher rainfall totals, especially during the rainy season. In the dry period the rain gauges showed more similarity in rainfall totals when compared with the rainy period, but with higher totals at 2141007, 2141100 (located upstream from the others), 2141001, and 2141002 (located near the coast). Therefore, the assessment of rainfall in the analysis period confirms the orographic influence and the proximity to the ocean as influential factors on rainfall (BRITO *et al.*, 2017; BOHN *et al.*, 2020).

WQI_{NSF} was higher in the dry period at PS0434, PS036, and PS0441 water quality monitoring stations and the statistical difference followed the change in water quality classification according to INEA (2019) and ANA (2015), being PS0434 and PS441 classified as good quality in the dry period and medium in the rainy period. Differences between the rainy and dry periods were also observed from Turb, Col (except for PS0439), TDS (except for PS0434 and PS0436), T_{water} and T_{air} (except PS0434) parameters, with higher values in the rainy period (Table 5). Higher Turb, Col, and TDS values may be related to allochthonous materials transport into the body of water, caused by possible soil conservation issues. The rainfall increase favors surface runoff, which has an effective action in transporting pollutants to water bodies (ANDRIETTI *et al*., 2015; CHEN *et al*., 2016; MEDEIROS *et al*., 2018). T_{water} and T_{air} occur because of climate seasonality, as the rainy period coincides with seasons of higher incidence of solar radiation (BRITO *et al*., 2017; BOHN *et al*., 2020).

Table 4 shows differences in NO_3^- (except for PS0441) with higher values in the dry period. The highest concentrations of NO_3^- in the dry period indicate the influence of nitrogen pollution, as NO_3^- may derive from nitrogen compounds which reached the river during the rainy period, by surface runoff; and in the dry period, the highest concentration of polluting agents (nitrogen, phosphate, organic compounds, among others) because of the reduction of total precipitation (GROTT *et al*., 2018). Agricultural activities were identified as polluting agents having a more significant influence in the dry period (CHEN *et al*., 2016).

Box-plot Analysis

The notched box plot analysis (Figure 6) corroborates the Wilcoxon-Mann-Whitney test and shows minimal differences because of the notches overlapping between the stations of water quality in the same period (rainy or dry) as between the rainy and dry periods in the same water quality monitoring station. The exception was the T_{air} which showed a higher range in the rainy season

Figure 5. Seasonal rainfall totals in the annual analysis of the rain gauge stations located in the study area, in the Paraiba do Sul river

compared to the dry season, probably because of the transport of this nutrient from agricultural areas to the water body by surface runoff and domestic sewage, owing to superphosphate detergents in the fecal matter (BENVENUTI *et al.*, 2015). The data variability can be identified in the stations and during the rainy and dry periods. BOD, for example, varied only in the rainy season, and from some parameters (TP, Turb, and TDS), the number of outliers above the upper limit was higher in this period, demonstrating the transport effect of external agents from the surroundings into the water body. pH displayed slight spatial and seasonal variation, contradicting the hypothesis of the great variability of this parameter (RODRIGUES *et al.*, 2018; VAROL, 2020). Other minor differences between seasonal and spatial parameters were observed in comparison to similar studies (CHEN *et al.*, 2016; PIRATOBA *et al.*, 2017). The reason may be related to the great variability of water quality parameters in the rainy and dry periods, the rainfall behavior in the early years of analysis (2014 and 2015), and its consequences, contributing to a lesser seasonal difference. The 2014 drought, for instance, was considered one of the most severe droughts in the Southeast region

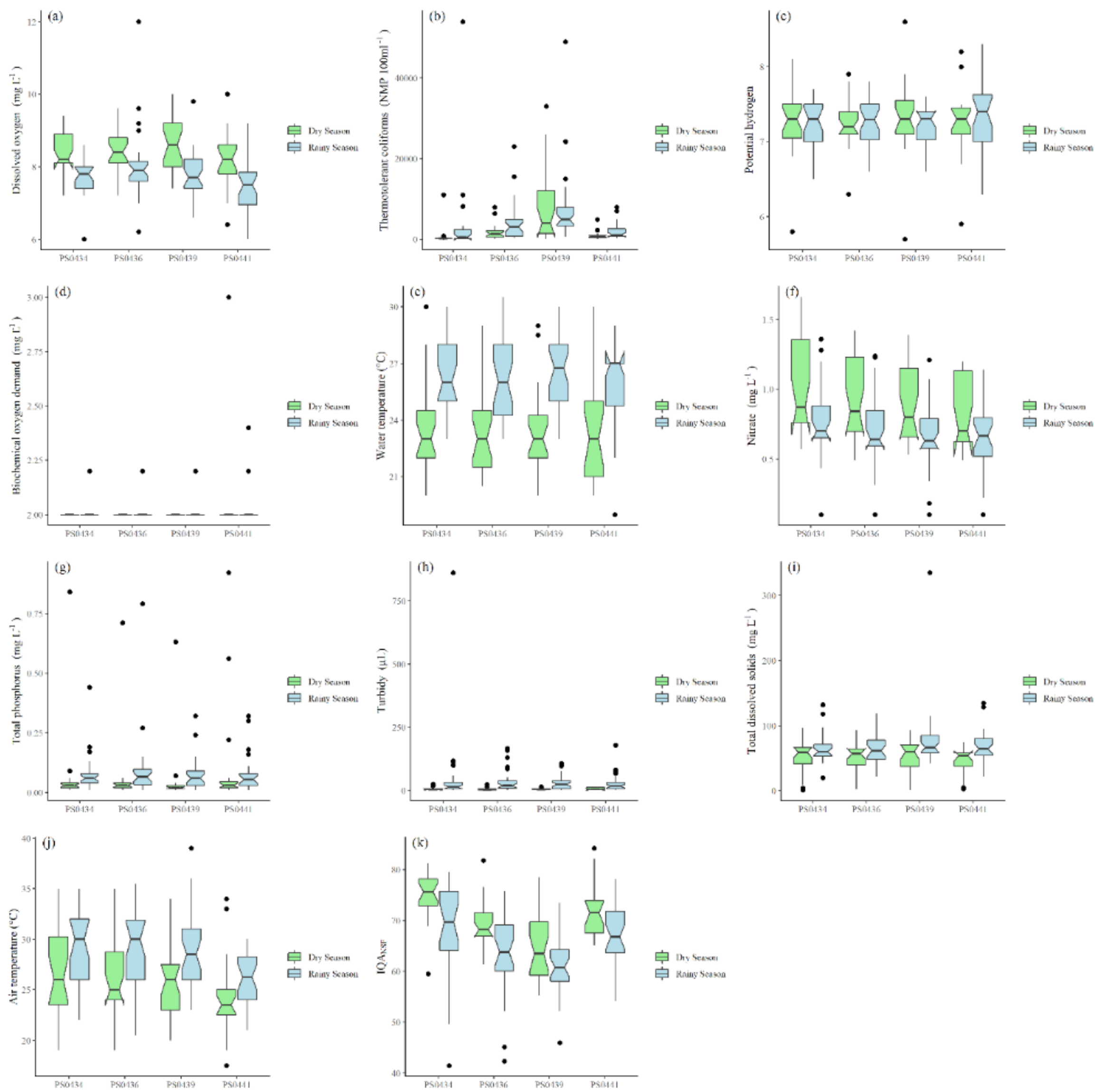

Figure 6. Notched box-plots of water quality parameters and water quality index (WQI) of the Paraíba do Sul river

of Brazil, in which several reservoirs reached dead volume, including the Cantareira water supplier system in the metropolitan region of São Paulo, compromising the water supply of approximately 9 million people (MELO *et al*., 2016; JESUS *et al*., 2020).

Spearman's correlation analysis

Spearman's correlation analysis (r) is showed in Figure 7 and some patterns on how water quality parameters related to different water quality monitoring stations in a generalized analysis (having data from both periods) and individually in the rainy and dry periods were perceived. In the analysis bringing all data together (dry and rainy periods and all water quality monitoring stations), the only correlation less than -0.7 ($r \leq -0,7$) was between Col and WQI_{NSF} in the dry period. The remaining correlations showed values between -0.69 and 0.69. The correlation analysis in each water quality monitoring station showed that the correlation pattern of all stations simultaneously analyzed has not been absolute in the analyzed area of the Paraíba do Sul river basin. Positive correlations greater than 0.7 ($r \geq 0.7$) were observed in the rainy season in stations PS0434 (between TP and BOD, Turb and BOD, Col and BOD, TP and Col, Turb and TP and T_{air} and T_{water}), PS0436 (between TP and BOD, Turb and TP and T_{air} and T_{water}), PS0439 (between Turb and TP and T_{air} and T_{water}) and PS0441 (between Turb and TP). The only correlation greater than 0,7 was between the T_{air} and T_{water} in The PS0441 water quality monitoring station in the dry season. Positive correlations between Turb and BOD have already been verified in other studies and justified because of increased nutrient concentrations causing growth in organic matter concentration, increasing respiration and organic matter degradation, boosting BOD (VAROL *et al*., 2020). On the one hand, Turb and Col are the main parameters that affect the water quality in the region. Because of the weight assigned to Col, its expressive negative correlation concerning the WQI_{NSF} is justified.

On the other hand, correlations less than -0.70 ($r \leq -0.70$) were observed in the rainy period at PS0434 (between Col and WQI_{NSF}, TP and WQI_{NSF}) and PS0436 (between Col and WQI_{NSF}, TP and WQI_{NSF}, Turb and WQI_{NSF}). In the dry period, correlations less than -0.70 were detected between Col and WQI_{NSF} in all the water quality monitoring stations, except in PS0441.

Correlation analysis allows identifying the water quality parameters that are most correlated with each other. For example, in the rainy season, the parameters most positively correlated were BOD and TP (except for PS0439) and Turb and TP, demonstrating that phosphorus is an important parameter in monitoring. This indicates the degree of the environmental degradation of the surrounding region of the Paraíba do Sul River and domestic sewages that may be discharged into water bodies. The highest negative correlations were between the parameters of TP, Turb, and Col, and the WQI_{NSF}. PS0434 and PS0436 are affected by the strongest influence of degraded pasture areas (Figure 3), having excessive nutrients in the water body, especially in the rainy season. As aforementioned, agriculture and urbanization aspects (domestic sewage) involve higher pollutant concentrations (BENVENUTI *et al*., 2015; PIRATOBA *et al*., 2017) and display erosive processes related to poor soil management by agricultural practice, allied to the absence of vegetation on the banks of watercourses (MEDEIROS *et al*., 2018). The study stretches of the Paraíba do Sul River has several disregarded riparian zone recommendations concerning environmental degradation and urbanization along the river.

In the dry period, the positive correlations were not expressive, although the correlations between T_{water} and Turb ($r = 0.6$) were observed at PS04441 and between T_{water} and Col ($r = 0.56$) at PS0434 water quality station drew attention. Higher temperatures may contribute to nutrient degradations (PIRATOBA *et al*., 2017) disposed into water bodies by increasing water turbidity. In contrast, the negative correlations between Col and WQI_{NSF}, between Turb and DO indicate expressive turbidity caused by a rapid transport route of suspended solids, surface runoff, and domestic sewage discharge into the river, for example. The number of deposited nutrients, especially organics, contributes to lower water oxidability (BARAKAT *et al*., 2018).

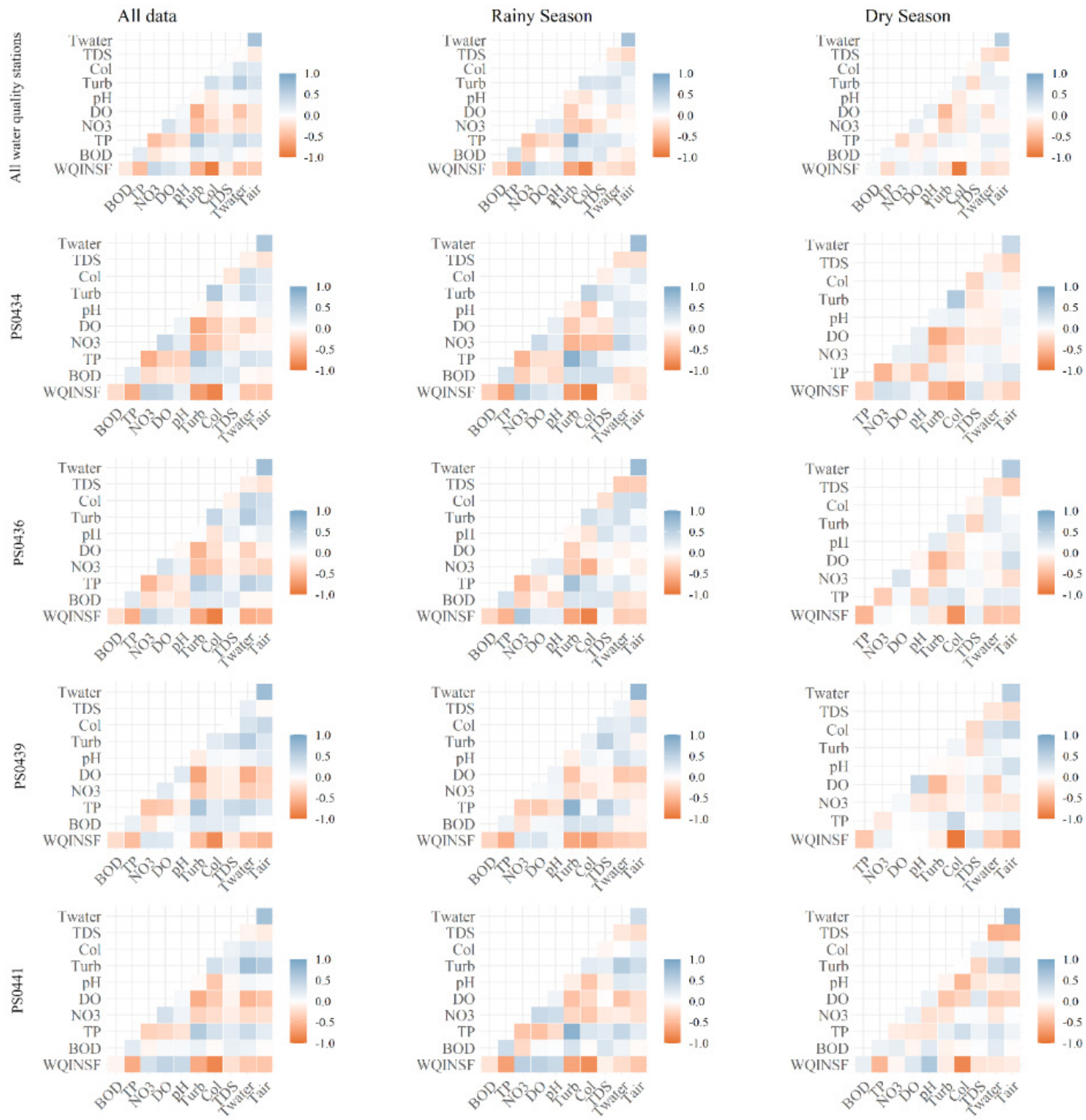

Figure 7. Spearman (r) rank correlation test relating to water quality parameter

Effect of rainfall seasonality and land use on the water quality of the paraíba do sul river

The water quality parameter and the WQI_{NSF} analysis allied to rainfall data establish an essential assessment tool, which offers conditions for the general diagnosis of the significant factors affecting the study area. However, limitations related to the relatively short analysis period and the number of observations make it difficult to show all the complexity in the aquatic ecosystem dynamics, which natural issues and anthropic actions may negatively or positively impact. This study has not conducted a spatial-temporal analysis of land use because of short data collection time interval. State environmental agencies responsible for collecting water quality parameters usually have financial and personnel limitations to conduct more comprehensive spatial and temporal collections. Thus, for more in-depth explanations and results about water quality parameters behavior (variation), a densification of the water quality monitoring network and a larger temporal scope would be necessary.

Disorderly growth of cities, overpopulation, and several deleterious unplanned anthropic activities have degraded Brazilian watersheds along the waterway (MANDARIC *et al.*, 2018). Among these activities, inadequate agriculture management and, mainly, degraded pastures are potential pollution sources of water resources. Hence, the study shows evidence that the anthropization and consequent degradation in the study watershed are closely intertwined with the water quality in the analyzed stretches of the Paraíba do Sul River. Therefore, restoration and mitigation measures are essential to increase the water quality, which will positively affect the ecosystem balance of this water body and the water quality for human consumption.

CONCLUSIONS

- There are no increases or decreases trends in water quality parameters and WQ_{INSF} in the studied stretches of the Paraíba do Sul River basin, except for pH, which an increasing trend by 0.1 $year^{-1}$ was detected, and Col at the PS0441 Station in Campos dos Goytacazes where there is a decreasing trend, probably because of the collection and treatment of domestic effluents.
- Land use, especially upstream of the PS0439 Station (municipality of São Fidelis), and the urban sites not connected to sewage treatment are the major modifiers of water quality in the stretch of the Paraíba do Sul River basin in the north and northwest regions of the state of Rio de Janeiro. As a result of several factors that affect, mainly, the concentrations of thermotolerant coliforms, phosphorus, turbidity, and nitrate, originated from the degradation of agricultural land, the lack of basic sanitation, and sewage discharged directly into rivers, without water pretreatment.
- The seasonal influence on water quality parameters and WQI_{NSF} shows thermotolerant coliforms, nitrate, turbidity, and air and water temperatures. The main polluting agents in each season were, in the rainy season, thermotolerant coliforms, phosphorus, and turbidity, and in the dry season, thermotolerant coliforms and nitrate.

AUTHORSHIP CONTRIBUTION STATEMENT

BOURGUIGNON, D.A.S.: Data curation, Formal Analysis, Investigation, Methodology, Writing – original draft; **FRAGA, M.S.**: Formal Analysis, Methodology, Supervision, Writing – original draft, Writing – review & editing; **LYRA, G.B.**: Supervision, Visualization, Writing – original draft, Writing – review & editing; **CECÍLIO, R.A.**: Supervision, Visualization, Writing – original draft, Writing – review & editing; **ABREU, M.C.**: Conceptualization, Formal Analysis, Methodology, Supervision, Writing – original draft.

DECLARATION OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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