caderno prudentino de geografia
Associação dos Geógrafos Brasileiros - Seção Local Presidente Prudente

SPACE-TEMPORAL ANALYSIS OF PHYSICO-CHEMICAL AND BIOLOGICAL VARIABLES OF WATER QUALITY IN THE ITAPECURU RIVER, NORTHEASTERN ATLANTIC HYDROGRAPHIC REGION, BRAZIL

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Abstract

The aim of the present study was to evaluate the surface water quality of the lower Itapecuru River in northeastern Brazil and investigate the spatiotemporal variations of physicochemical and biological variables. Twelve sampling campaigns at three-month intervals were conducted at five monitoring stations between 2012 and 2015. Significant changes were found from the upstream to downstream direction with regard to total suspended solids, transparency, turbidity and total iron, indicating that water quality was influenced by erosive processes in the sub-basins of the lower Itapecuru River. Iron (total and dissolved) and aluminum were frequently detected in the water, the concentrations of which were mainly related to the lithological characteristics of the region. No other metals or chemical pollutants, such as pesticides, hydrocarbons, phenols, free cyanide and artificial dyes, were detected in the section of the river investigated. The presence of thermotolerant coliforms and Escherichia coli indicate the direct discharge of sewage into the river. The principal component analysis demonstrated that 44.7% of the variability in the data was explained by the first three axes and the most representative variables were total suspended solids, iron (total and dissolved), transparency, total dissolved solids, temperature, true color and total phosphorus. The Itapecuru river is a strategic water resource for the development of the Northeast Atlantic Hydrographic Region of Brazil. The main pressure vectors identified in the research are associated with the discharge of sanitary sewage and the erosion processes of the sub-basins of the area of influence of the study, reducing the quality of the water in the stretch under investigation of the river. The information generated in the research is fundamental for the design of strategic actions for the planning and management of the Itapecuru river watershed.

Keywords: Water resource; Variability; Watershed.

ANÁLISE ESPAÇO-TEMPORAL DAS VARIÁVEIS FÍSICO-QUÍMICAS E BIOLÓGICAS DA QUALIDADE DA ÁGUA DO RIO ITAPECURU, REGIÃO HIDROGRÁFICA ATLÂNTICO NORDESTE, BRASIL

Resumo

A pesquisa foi desenvolvida para avaliar a qualidade da água superficial do Baixo Curso do Rio Itapecuru (BCRI), com o objetivo de compreender as variações espaço-temporal de variáveis físico-químicas e biológicas. Foram realizadas doze campanhas amostrais entre os anos de 2012 e 2015, em cinco estações de monitoramento, obedecendo periodicidade trimestral. Constatou-se que as variáveis: sólidos suspensos totais, transparência, turbidez e ferro total sofrem alteração de forma significativa no sentido montante/jusante, indicando que a qualidade da água foi influenciada por processos erosivos das sub-bacias hidrográficas do BCRI. Os constituintes ferro (total e dissolvido) e alumínio foram detectados frequentemente na água, cujas concentrações estão relacionadas, principalmente, com a litologia da região. Outros metais e poluentes químicos como os agrotóxicos, hidrocarbonetos, fenóis, cianeto livre e corantes artificiais não foram detectados no trecho investigado. As variáveis biológicas coliformes termotolerantes e presença da bactéria Escherichia Coli indicaram que existe lançamento de esgoto sanitário diretamente no rio. A análise de componente principal demonstrou que 44,7% da variabilidade dos dados são explicadas pelos três primeiros eixos, sendo as variáveis sólidos suspensos totais, ferro (total e dissolvido), transparência, sólidos dissolvidos totais, temperatura, cor verdadeira e fósforo total, mais representativas.

Palavras-chave: Recurso hídrico; Parâmetros; Variabilidade; Bacia hidrográfica.

ANÁLISIS ESPACIO-TEMPORAL DE VARIABLES FÍSICO-QUÍMICAS Y BIOLÓGICAS DE LA CALIDAD DEL AGUA EN EL RÍO ITAPECURU, REGIÓN HIDROGRAFICA DEL ATLÁNTICO NORDESTE, BRASIL

Resumen

La investigación fue desarrollada para evaluar la calidad de las aguas superficiales del Río Itapecuru Inferior (BCRI), con el objetivo de conocer los cambios espacio-temporal de las variables fisicoquímicas y biológicas. Se realizaron doce campañas de muestreo entre los años 2012 y 2015, en cinco estaciones de control, obedeciendo a una periodicidad trimestral. Se encontró que las variables: sólidos suspendidos totales, transparencia, turbidez y hierro total cambian significativamente aguas arriba/aguas abajo, lo que indica que la calidad del agua fue influenciada por los procesos erosivos en las subcuencas del BCRI. Los constituyentes hierro (total y disuelto) y aluminio se detectaron con frecuencia en el agua, cuyas concentraciones están relacionadas principalmente con la litología de la región. No se detectaron en el tramo investigado otros metales y contaminantes químicos como pesticidas, hidrocarburos, fenoles, cianuro libre y tintes artificiales. Las variables biológicas coliformes termotolerantes y la presencia de la bacteria Escherichia Coli indicaron que existe una descarga de aguas residuales sanitarias directamente en el río. El análisis de componentes principales mostró que el 44,7% de la variabilidad de los datos se explica por los tres primeros ejes, siendo las variables sólidos suspendidos totales, hierro (total y disuelto), transparencia, sólidos disueltos totales, temperatura, color verdadero y fósforo total las más representativas. El río Itapecuru es un recurso hídrico estratégico para el desarrollo de la Región Hidrográfica del Atlántico Nordeste de Brasil. Los principales vectores de presión identificados en la investigación están asociados a la descarga de aguas residuales sanitarias y a los procesos de erosión de las subcuencas del área de influencia del estudio, reduciendo la calidad del agua en el tramo investigado del río. La información generada en la investigación es fundamental para el diseño de acciones estratégicas para la planificación y gestión de la cuenca del río Itapecuru.

Palabras-clave: Recurso hídrico; Parámetros; Variabilidad; Cuenca hidrográfica.

Introduction

When occurring in an inadequate manner, human activities in the drainage regions of rivers have direct and indirect impacts on the physicochemical and biological properties of the water. Thus, understanding the variations of water quality in a river system is important to the evaluation of the ecological status of water resources as well as the establishment of management strategies for watersheds (SOARES et al., 2016; SOARES, et al., 2017; MACHADO et al., 2022).

According to Alatrista-Salas et al. (2015, p. 127), “the pollution of rivers is a phenomenon that can be observed by measuring physicochemical and biological indicators of water quality”. Fia (2015, p. 268) states that “the monitoring of surface waters constitutes an important management tool, independently of the size of the basin, enabling decision making on the part of environmental agencies”.

Marotta, Santos and Prats (2008, p.78) write that “monitoring plays a technical role in generating information and assisting in the improvement of methods; it is essential and irreplaceable for the effective execution of urban-environmental planning and management”.

However, the lack of continuous monitoring networks, difficulty in the access of data and the challenge of identifying interrelations between water quality and activities developed along a drainage basin make this an arduous task. Moreover, monitoring networks are costly and depend on an ample technological apparatus for the generation of reliable information that can assist in decision-making processes regarding the management of watersheds and water resources.

Despite these challenges, the evaluation of spatiotemporal patterns of the water quality of rivers and the understanding of these patterns in light of human activities conducted along watersheds constitute an essential tool for environmental management that can contribute to the maintenance of the integrity of aquatic ecosystems and guide the establishment of public policies directed at recovery and conservation, especially in freshwater environments (ANA, 2021).

In Brazil, which is a country with abundant water resources, there are gaps in scientific knowledge regarding the characterization of the water quality of major rivers. Few publications describe patterns of physiochemical and biological variables with a significant spatiotemporal design that seek to determine the correlation with human activities along drainage regions. Some recent examples involve rivers in the state of Goiás (BONNET; FERREIRA; LOBO, 2008), the Duas Mamas River in the state of Santa Catarina (PINHEIRO et al., 2014), the Cuiabá and São Lourenço Rivers in the state of Mato Grosso (LIMA et al., 2015), the Arari River in the state of Pará (ALVES et al., 2012) and Vermelho Creek in the state of Minas Gerais (FIA et al., 2015).

The lack of information is more evident in some hydrographic regions of Brazil, such as the northeast region on the western Atlantic Ocean. A report by the National Water Agency (ANA, 2013) summarized the water quality of the main rivers in Brazil in recent years through an evaluation of data from 2463 sampling sites in monitoring networks distributed among 17 states, but failed to present information on bodies of water in this region, such as the Itapecuru, Mearim and Grajau Rivers located in the state of Maranhão.

Among these rivers, the Itapecuru is a source of the public water supply in different cities, including the capital, São Luís. Activities of the primary sector linked to agriculture, livestock farming and fishing in the region are completely dependent on this water resource. The lower course of the river, in the stretch between the ITALUÍS water treatment facility and the municipality of Rosário, is subjected to a disorderly occupation process of the marginal sub-basins, with the expansion of urban and rural activities that have the potential to increase the organic load of nutrients and the discharge of untreated sewage, which can cause changes in the natural patterns of water quality.

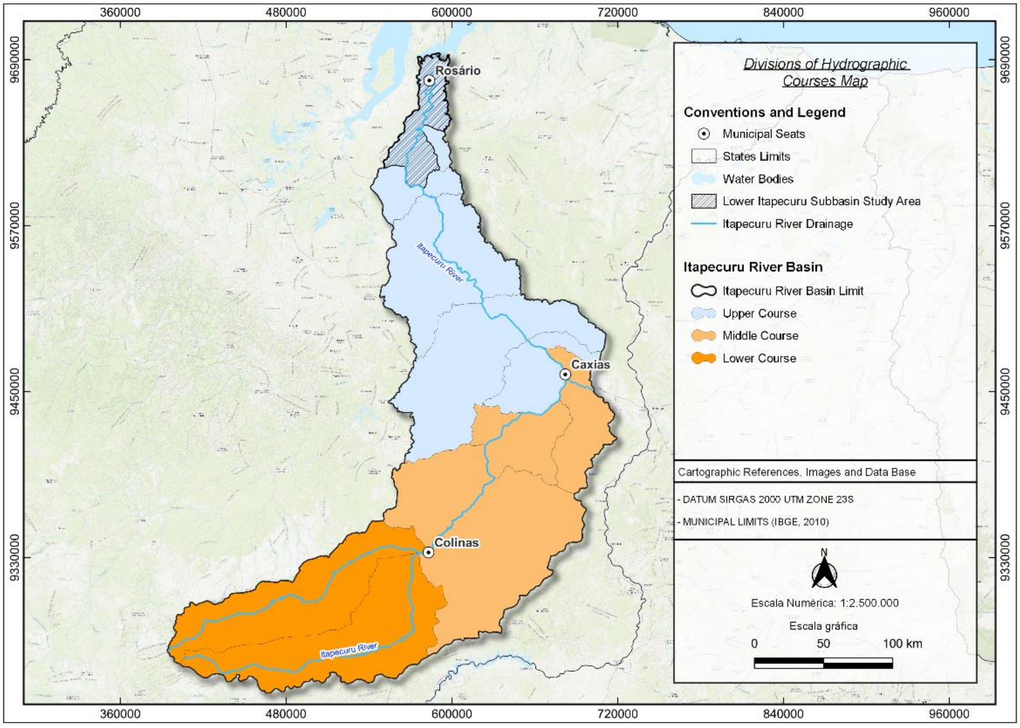
The aim of the present study was to analyze the spatiotemporal dynamics of the water quality of the Itapecuru River and investigate possible associations with human activities developed in the sub-basins situated along the lower course of this river.

Hydrographic Basin of Itapecuru River

The watershed of the Itapecuru River has an area of 53,216.84 km² and is the second largest drainage basin in the state of Maranhão (northeastern Brazil), passing through

57 municipalities with a total population of 1,019,398 inhabitants (NUGEO, 2011). According to Alcântara (2004), the river is divided into the upper, middle and lower courses based on differences in altitude (Figure 1). The lower Itapecuru River comprises the stretch between the municipality of Caxias and the mouth of the river in São José Bay, which is approximately 360 km in length (MEDEIROS, 2001). Due to the smaller slope of the lower Itapecuru River, the water flow is slower, characterizing it as a plain river (SILVA and CONCEIÇÃO, 2011).

Figure 01 - Location of watershed of Itapecuru River and division into upper, middle and lower courses. Source: Masullo and Soares (2019)



Source: The authors

The study area spans 35 km of the river, with the influence of ten sub-basins located in the lower course. These sub-basins total an area of 421.6 km^2 distributed within the municipalities of Rosário, Bacabeira and Santa Rita. Geographically, the sub-basins are situated in the microregion of Itapecuru Mirim in the northern portion of the state of Maranhão, approximately 50 km from the capital city (São Luís) and limited by UTM coordinates 598658/574822 E and 9678715/9653145 N (Figure 2). The main access roads are BR-135 and BR-402, which connect these municipalities to the capital city.

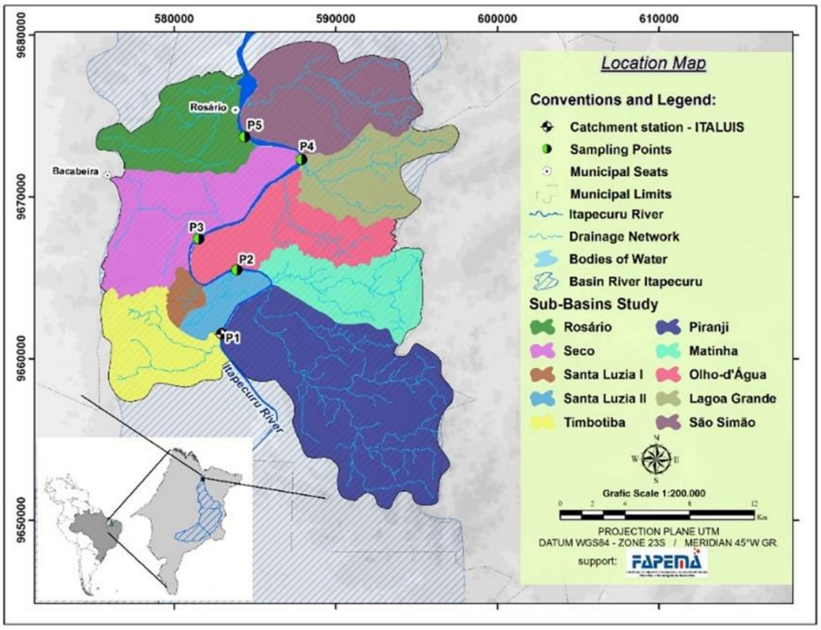
Based on the Thornthwaite climate index, the climatic pattern of the lower Itapecuru River is humid (LABGEO, 2002). Climate data from the region (1975 to 2015) register mean annual precipitation of 1998.8 mm/year, with two well-defined seasons: a rainy season that spans from January to July and a dry season that spans from August to December (INMET, 2015).

Methods

Sampling network

Twelve sampling campaigns were conducted between April 2012 and January 2015 at five monitoring stations (P1 to P5) distributed along 35 km of the lower Itapecuru River between the water treatment facility in the city of São Luís (ITALUIS) and the municipal center of Rosário (Figure 2). Sampling was performed at three-month intervals, with four samplings per each season: April (peak wet season); July (wet-dry transition); October (peak dry season); and January (dry-wet transition). The sampling stations were distributed to indicate possible changes in water quality from the upstream to downstream direction (P1 → P5) stemming from the variations of land use and occupation of the area of influence of the sub-basins.

Figure 02 - Location of sub-basins and sampling stations for monitoring of water quality of lower Itapecuru River.



Source: The authors.

Collection procedure

The sample collection and preservation procedures followed the guidelines of Brazilian Association of Technical Norms (ABNT NBR 9897 and ABNT NBR 9898), which determine the requirements for the sampling of domestic and industrial effluents, sediments and surface water from inland systems. All samples were collected from the surface of the water column in the morning period (8 am to 12 pm) with the aid of a watercraft.

Variables

The following variables were determined: water temperature, pH, alkalinity, hardness, conductivity, dissolved oxygen, transparency, turbidity, true color, chemical oxygen demand, total organic carbon, density of thermotolerant coliforms, presence of Escherichia coli, density of cyanobacteria, total suspended solids, total dissolved solids, chloride, fluoride, total nitrogen, nitrite, nitrate, total phosphorus, sulfate, sulfide, dissolved aluminum, antimony, arsenic, barium, boron, cadmium, lead, cobalt, iron (dissolved and total), lithium, mercury, vanadium, zinc, cyanide, hydrocarbons, phenols and pesticides. Water temperature (ºC), pH, dissolved oxygen (mg L^{-1}) and conductivity (mS cm^{-1}) were determined in situ using a multiparameter device (HANNA HI 9828). Turbidity (UNT) was determined using a turbidimeter (HANNA HI 93703) and water transparency (cm) was determined using a Secchi disk. The other water quality variables were determined in the laboratory following the recommendations of Standard Methods for the Examination of Water and Wastewater (APHA, 2012).

The assays for the physicochemical and biological variables were performed at the limnology and microbiology laboratories of the Federal University of Maranhão. Samples for the determination of metals, pesticides and hydrocarbons were duly fixed and sent to the Mérieux NutriSciences Laboratory in São Paulo for analysis following guidelines established by national and international environmental agencies.

Statistical analysis

The results were submitted to descriptive statistics for the determination of central and dispersion measures of the variables analyzed. After meeting the requirements of equal variance and normal distribution, analysis of variance with a 5% level of significance was used to determine temporal and spatial differences in the variables. When significant differences were encountered, a post hoc test was performed to demonstrate which groups exhibited these differences. When the presuppositions were not met for the use of ANOVA, the nonparametric Kruskal-Wallis test was used (CONOVER, 1990), which was followed by the nonparametric Mann-Whitney test when significant differences among groups were detected. Principal component analysis was performed to explain the structure and relationships among the variables. To determine the strength of correlations, a biplot was created among the principal components to explain the distribution of the points with response patterns and associations between the variables and sampling season. The cluster method was used to determine the spatiotemporal patterns of the water quality variables among the monitoring stations. This hierarchical analysis was established based on the Euclidian distance matrix, using the mean Euclidian distance as the cluster criterion (SIMEONOV et al., 2003). The basic units of analysis were rectangular matrices constituted by columns that represented the collection stations and lines the represented the duly standardized physicochemical and biological variables. The statistical analyses performed with the aid of the PAlaeontological STatistics (PAST), version 2.17 (HAMMER; HAPER; RYAN, 2001) and Statistica 10.0 (STATSOFT, 2010) statistical packages.

Results and discussion

Limnological studies that seek this understanding have been published in different countries, investigating the Loire River in France (MOATAR; MIQUEL; POIREL, 2001), rivers in northern Greece (SIMEONOV et al., 2003), the Gomti River in India (SINGH; MALIKA, SINHAB, 2005), Fuji River in Japan (SHRESTHA; KAZAMA, 2007), Han River in South Korea (CHANG, 2008), Bagmati River in Nepal (KANNEL et al., 2007), Ebro River in Spain (BOUZA-DEAÑO; TERNERO-RODRÍGUEZ; FERNANDEZ-ESPINOJA, 2008), St. Johns River in Florida (OUYANG et al., 2006) and Orinoco River in Venezuela (LARAQUE et al., 2013).

Tables 1 and 2 show the results of the descriptive statistics (annual mean and standard deviation [SD]) of the water quality variables in the lower Itapecuru River. Water temperature varied little throughout the sampling period (mean and SD: 30 ± 0.94 ºC; range: 27.4 to 31.3 ºC]. This pattern is characteristic of tropical rivers and indicates that the environment does not undergo fluctuations in water temperature as a result of human activities developed in the sub-basins of the lower Itapecuru River.

The pH ranged from 5.1 to 8.9. Alkaline tendencies occurred at P4 and P5 due to the closer proximity to the mouth of the river and the influence of salinity from São José Bay. In contrast, stations P1, P2 and P3 demonstrated a tendency toward slightly acid pH. The lowest values (6.74 ± 0.19) occurred in the wet period (April) (Tables 1 and 2). According to Maier (1987), the pH of the water of Brazilian rivers ranges from neutral to acid and can vary throughout the course of a river. For instance, the pH in the Amazon River increases gradually from 4.0 in the upper course to 7.8 at the mouth of the river.

Tabela 01 - Mean and standard deviation of variables monitored among sampling points in lower Itapecuru River, in the period between April 2012 and January 2015.

Variables	P1	P2	P3	P4	P5
Water temperature (ºC)	30.12±0.74	30.05±0.67	29.99±0.68	29.88±0.8	29.9±0.65
pH	6.97±0.15	6.74±0.37	6.91±0.21	7.24±0.53	7.4±0.51
Total alkalinity (mg L^{-1})	22.81±11.8	26.28±9.9	24.7±10.23	27.46±6.77	27.5±0.49
Hardness (mg L^{-1})	14.49±3.27	15.22±8.3	13.44±2.01	17.89±4.57	16.8±0.86
Conductivity (mS/cm)	0.0647±0.01	0.062±0.01	0.062±0.009	0.057±0.003	0.062±0.007
Dissolved oxygen (mg L^{-1})	6.0±0.13	6.11±0.27	6.17±0.58	6.49±0.55	6.29±0.82
Chemical oxygen demand (mg L^{-1})	10.43±6.47	14.59±6.47	13.5±4.84	17.15±2.41	16.39±6.75
Total nitrogen (mg L^{-1})	0.59±0.07	1.57±1.34	0.63±0.12	0.59±0.1	0.69±0.2
Total phosphorus (mg L^{-1})	0.09±0.03	0.1±0.05	0.094±0.009	0.14±0.075	0.14±0.0273
Total organic carbon (mg L^{-1})	2.47±1.58	3.14±0.96	2.78±1.05	3.65±0.79	3.17±1.59
Chloride (mg L^{-1})	8.1±1.93	7.97±1.94	7.97±2.9	9.12±3.74	11.08±3.03
Sulfate (mg L^{-1})	7.29±4.39	7.58±6.81	3.65±1.02	5.45±2.54	8.61±9.39
Dissolved aluminum (mg L^{-1})	0.088±0.05	0.20±0.14	0.145±0.112	0.22±0.13	0.23±0.077
Total iron (mg L^{-1})	0.89±0.46	1.1±0.4	1.33±0.57	1.66±0.48	2.46±0.63
Dissolved iron (mg L^{-1})	0.3±0.15	0.39±0.18	0.37±0.106	0.67±0.33	0.67±0.17
Barium (mg L^{-1})	0.0420±0.01	0.0468±0.01	0.046±0.009	0.051±0.009	0.0480±0.015
Total suspended solids (mg L^{-1})	20.58±9.95	29.75±15.8	51.08±17.19	81.91±79.46	71.83±19.54
Total dissolved solids (mg L^{-1})	63.33±10.05	59.3±7.84	70.33±19.61	84.6±26.45	168.33±143.6
Transparency (cm)	43.25±12.37	38.91±9.15	36.83±8.86	29.9±5.6	25.1±4.64
True color (Pt/Co)	30.12±18.21	29.69±19.4	32.81±21.08	32.2±18.95	35.69±17.93
Turbidity (NTU)	28.16±9.57	32.68±4.08	43.0±19.03	53.8±9.6	83.62±10.32
Cyanobacteria count (cells mL^{-1})	501±597.7	519.7±417.7	249.4±248	611.2±1039	142.1±113.7
Thermotolerant coliforms (NMP/100mL)	842.7±375.4	720.3±847.	943.4±722.8	1167.2±638	1538.25±395

Source: The authors.

The mean concentration of total alkalinity was 25.76 ± 15.6 mg.L^{-1}, with higher values in the wet months and at collection stations located downstream (P4 and P5). Although the river receives sewage discharge from the cities and communities along its banks, concentrations of total alkalinity were low, likely due to the high dilution capacity of the lower Itapecuru River. Siqueira, Aprile and Migués (2012) report a similar pattern in a monitoring study conducted in the Parauapebas River in the northern region of Brazil.

Water hardness concentrations ranged from 5 to 42 mg/L, with no spatiotemporal differentiation among the collection stations. Based on the classification proposed by Von Sperling (2005), the Itapecuru River has "soft water", since the concentration is lower than 50 mg.L^{-1}.

Electrical conductivity remained stable among the collection stations and throughout the sampling months, with values ranging from 0.015 to 0.129 mS cm^{-1} over the twelve campaigns (Tables 1 and 2). The highest values occurred at stations P4 and P5 in October 2012, October 2013 (dry season) and January 2014 (transition from dry to wet season), indicating that the reduction in water flow leads to a greater influence of tidal variations and salinity. For a better understanding of changes in conductivity in the environment, sampling should be performed in the deep part of the lower Itapecuru River during different phases of the lunar cycle to enable a detailed delineation of the influence of salinity and tidal variations.

Tabela 02 - Mean and standard deviation of variables monitored among sampling points in lower Itapecuru River, in the period between April 2012 and January 2015.

Variables	January	April	July	October
Water temperature (ºC)	30.37±0.32	28.96±0.61	30.15±0.2	30.3±0.5
pH	7.46±0.68	6.74±0.19	7.03±0.7	7.5±1.7
Total alkalinity (mg L^{-1})	23.18±12.82	36.73±19.09	23.09±5.3	27.7±8.8
Hardness (mg L^{-1})	13.09±4.01	20.73±5.06	14.5±6.3	17.6±3.5
Conductivity (mS/cm)	0.066±0.007	0.065±0.0011	0.071±0.029	0.057±0.04
Dissolved oxygen (mg L^{-1})	6.37±0.75	6.23±0.4	6.45±1.1	5.5±1.4
Chemical oxygen demand (mg L^{-1})	12.43±7.21	19.93±5.59	15.41±10.6	7.2±2
Total nitrogen (mg L^{-1})	1.179±2.158	0.716±0.227	0.794±1.174	0.677±0.225
Total phosphorus (mg L^{-1})	0.099±0.024	0.087±0.041	0.116±0.058	0.173±0.066
Total organic carbon (mg L^{-1})	2.49±1.23	4.56±0.98	3.13±1.6	1.3±0.3
Chloride (mg L^{-1})	8.33±0.85	8.68±0.93	11.95±4.2	11.9±7.3
Sulfate (mg L^{-1})	6.16±2.41	3.59±2.13	9.88±15.8	4.4±1.7
Dissolved aluminum (mg L^{-1})	0.199±0.205	0.232±0.216	0.092±0.048	0.185±0.027
Total iron (mg L^{-1})	1.361±0.471	1.911±0.307	1.293±0.933	3.167±1.439
Dissolved iron (mg L^{-1})	0.396±0.159	0.639±0.337	0.438±0.265	0.513±0.437
Barium (mg L^{-1})	0.045±0.07	0.061±0.005	0.046±0.008	0.031±0.007
Total suspended solids (mg L^{-1})	40.27±37.72	46.2±23.96	40.53±54.2	99.3±42.2
Total dissolved solids (mg L^{-1})	80.13±41	90.47±37.51	122±259.4	81.3±34.4
Transparency (cm)	28.93±6.6	27.6±4.37	43.2±10.2	39.53±12.35
True color (Pt/Co)	51.11±12.52	44.6±13.39	20.67±6.8	19.1±7.3
Turbidity (NTU)	54.94±22.33	57.32±21.15	41±23.2	83.3±41.7

Cyanobacteria count (cells mL^{-1})	653.7±781	351.4±232.4	584±552	3±0
Thermotolerant coliforms (NMP/100mL)	971±791	981±796	861.5±604.5	1753±1120

Source: The authors.

The mean concentration of dissolved oxygen (DO) was 6.2 ± 1.3 mg L^{-1}. DO remained at levels to allow the vital needs of the aquatic community, even in periods with an increase in suspended solids and turbidity. Monitoring the water quality of the Parauapebas River in the state of Pará, Siqueira, Aprile and Migués (2012) found that DO patterns remained lower than 5 mg L^{-1} and that low concentrations coincided with high turbidity (>24 NTU) and low transparency (< 0.50 m), stemming from the discharge of effluents containing large amounts of suspended material and organic matter.

The chemical oxygen demand (COD) ranged from 5 to 44 mg L^{-1}, with higher concentrations in the wet months (April 2013 and April 2014). COD concentrations were slightly higher at collection stations located downstream (P3, P4 and P5). This pattern suggests the existence of the discharge of organic matter in the municipality of Rosário as well as communities located along the banks of the Itapecuru River. Strohschoen et al. (2009) report a similar pattern for the Forqueta and Forquetinha Rivers in the state of Rio Grande do Sul (southern Brazil). According to the authors, the increase in COD from the upstream to downstream direction is due to the input of fecal matter from surface runoff in urban areas stemming from rainfall.

Low concentrations of nitrogen occurred among the collection stations and throughout the sampling months (Tables 1 and 2). Moreover, the nitrogen compounds nitrite and nitrate had levels below the analytical detection limit (0.02 and 0.1 mg L^{-1}, respectively) throughout the entire monitoring period.

Total phosphorus concentrations were low (0.01 to 0.41 mg L^{-1}), with a gradual increase from the upstream to downstream direction and higher concentrations in the dry period (Table 2). The concentrations at P4 and P5 are explained by the proximity of the collection stations to the municipal center of Rosário and more populated sub-basins, whereas the pattern for the dry period is related to the reduction in water flow.

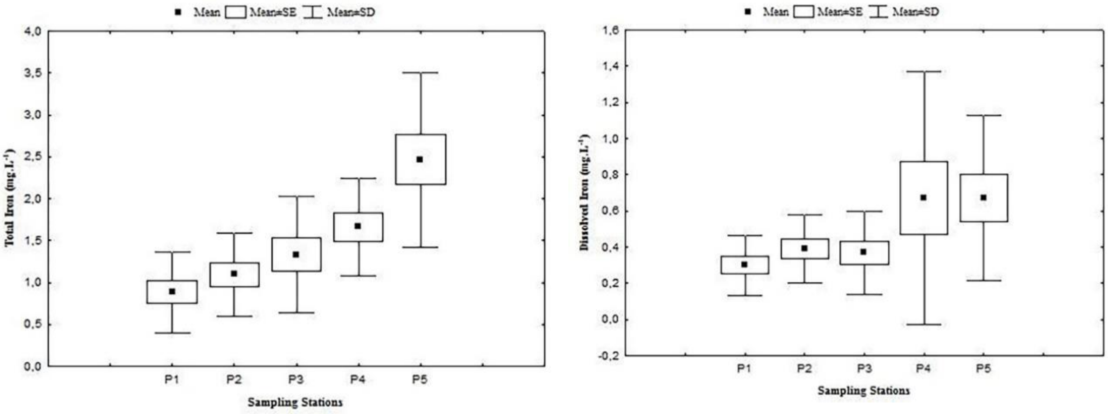
Concentrations of total organic carbon were low, with no spatiotemporal differences among sampling months or collection stations. The highest values occurred in April (4.56 ± 0.98) and at station P4 (3.65 ± 0.79) (Table 1).

Chloride concentrations were higher during the transition months (January and July) and dry period (October) at stations P4 and P5. This pattern is related to the influx of saline at the mouth of the Itapecuru River. No significant differences in mean sulfate (6.5 ± 9.8 mg L^{-1}) were found among sampling months or collection points and fluoride concentrations were lower than 1.4 mg L^{-1}.

The pattern for total dissolved solids demonstrated the influence of salinity at station P5, where higher concentrations and greater variation (mean: 168.3 ± 143.6 mg L^{-1}) occurred in comparison to the other monitoring stations. The means at the other stations ranged from 63.33 ± 10 mg L^{-1} at P1 to 84.6 ± 26.45 at P4. The concentration of total dissolved solids increased gradually from the upstream to downstream direction (Table 1). No significant differences were found between the wet and dry periods during the sampling months (Table 2).

Concentrations of dissolved aluminum ranged from 0.028 to 0.89 mg L^{-1} (mean: 0.16 ± 0.17 mg L^{-1}). No significant differences in this ion were found from the upstream to downstream direction. Regarding iron compounds (total and dissolved), higher concentrations were detected at stations P4 and P5 (Figure 3), but significant differences ($p < 0.05$) only occurred for total iron at P5 in comparison to P1, P2 and P3.

Figure 03 - Spatiotemporal variation in total and dissolved iron (mg L^{-1}) in water of lower Itapecuru River, in the period between April 2012 and January 2015.



Source: The authors.

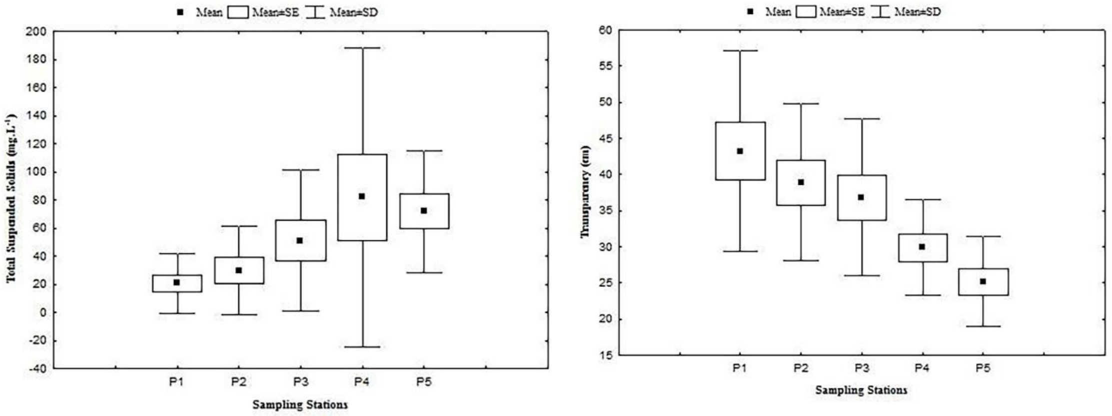
The variations for total aluminum and iron (total and dissolved) are associated with the lithology of the sub-basins of the lower Itapecuru River, since the main soil typologies are plinthosols, clay soils and latosols (IBGE, 2007). According to Lepsch (2010), plinthosols and latosols are rich in iron oxide, whereas clay soils are highly saturated with aluminum.

Barium concentrations were low (range: 0.022 to 0.086 mg.L^{-1}), with no spatiotemporal differences among the collection stations ($p < 0.05$). The other semimetals analyzed (antimony, arsenic, boron, lead, cadmium, cobalt, lithium, mercury and vanadium) were either at low levels or not detected during the monitoring, indicating that the quality of the water in the stretch of the Itapecuru River analyzed has not been altered due to the presence of these chemical constituents.

Regarding total suspended solids, lower concentrations were found at P1 and P2, with an increase from the upstream to downstream direction (Figure 4**Erro! Fonte de referência não encontrada.**). Significant differences ($p < 0.05$) were found between P5 and the other collection points. The highest values occurred in October (peak of the dry season) (Table 2). Evaluating the water quality of the Arari River in the state of Pará, Alves et al. (2012) report a similar relationship, with a higher amount of total suspended solids in the period with less rain.

Transparency ranged from 17 to 65 cm (mean: 34.8 ± 11.7 cm), with smaller Secchi disk visualization depths at collection stations closest to the mouth of the river (P4 and P5), indicating a reduction in transparency from the upstream to downstream direction and the possible influence of water runoff and human activities in the sub-basins on water quality in the Itapecuru River (Figure 4). Significant differences ($p < 0.05$) were found between P5 and all other sampling points as well as between P4 and P1. The lowest transparency occurred in the wet months (January and April) due to the presence of suspended and dissolved solids carried by the drainage basin.

Figure 04 - Spatiotemporal variation in total suspended solids (mg L^{-1}) and transparency (cm) in lower Itapecuru River, in the period between April 2012 and January 2015.

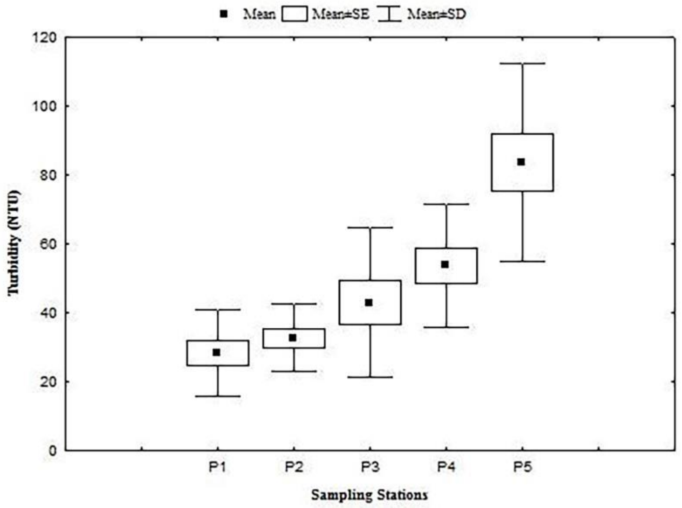


Source: The authors

The results for turbidity followed that same pattern as that found for total suspended solids and transparency, evidencing the influence of human activities in the sub-basins on water quality, with a gradual increase from the upstream to downstream direction (Table 1). Stations P4 and P5 differed significantly from stations P1 and P2 ($p < 0.05$) and higher readings (UNT) were found in the dry period (Figure 5).

The analysis of true color revealed a homogeneous pattern among the collection stations. Seasonally, higher readings were found in January and April, corresponding to the onset and peak of the wet period. Aguiar Netto et al. (2013) report the same pattern (increase in water color in the wet period) for the Proxim River in the state of Sergipe, Brazil, and the authors associated the hydrological behavior to the increase in dissolved organic matter and particulate matter from the drainage region of the river.

Figure 05 - Spatiotemporal variation in turbidity (NTU) of water in lower Itapecuru River, in the period between April 2012 and January 2015.



Source: The authors

The analysis of the density of cyanobacteria indicates the absence of blooms in the lower Itapecuru River. Thus, activities in the sub-basins are not leading to the development of populations of these organisms, which is further demonstrated by the low concentrations of nitrogen and phosphate compounds (Tables 1 and 2).

The analysis of thermotolerant coliforms (TCs) and the identification of *Escherichia coli* indicate the discharge of human fecal matter at specific points along the Itapecuru River as well as in a diffuse manner. Changes in the levels of TCs and the presence of *E. Coli* occurred constantly among the sampling stations and months throughout the entire study period. The highest densities of TCs were found in October at stations P4 and P5 (Tables 1 and 2). However, the identification of these organisms at P1 indicates that contamination begins upstream from the study area, probably due to precarious environmental sanitation services in the municipalities through which the Itapecuru River travels. A similar problem is reported for diverse water resources in Brazil, such as rivers in the state of Goiás (BONNET; FERREIRA; LOBO, 2008), the Arari River in the state of Pará (ALVES et al., 2012), Poti River in the state of Piauí (OLIVEIRA; SILVA, 2014) and Paraguaçu River in the state of Bahia (BARROS; CRUZ; SILVA, 2015). Water contamination renders a multiplicity of uses unviable and poses a risk to human health, especially among individuals who live in river communities and use the water without adequate treatment. In Brazil, this problem was confirmed by a study carried out by Ferreira et al. (2017), which proved inadequate conditions of access to water by quilombola communities in the state of Mato Grosso.

With regard to pesticides, only Acrylamide at P2 in January 2013 was detected at a concentration of 1.2 mg L^{-1}. The other groups analyzed, such as Aldrin, Alachlorine, Aldrin+Dieldrin, Carbaryl, Chlordane, Demeton, DDT (p,p'-DDT + p,p'-DDE + p,p'-DDD), Dodecachlorine pentacyclodecane, Endosulfan, Endrin, Glyphosate, Guthion, Heptachlor epoxide + Heptachloride, Hexachlorobenzene, Indene (1,2,3-cd)pyrene and PCBs, were not identified in the water of the lower Itapecuru River.

The analytical determinations performed for chlorinated hydrocarbons and chlorinated phenols (1,1,1-Trichloroethane, 1,1,2- Trichloroethane, Vinyl chloride, 1,2-Dichloroethane, 1,1-Dichloroethene, 2,4-Dichlorophenol, Dichloromethane, Tetrachloroethene, Pentachlorophenol, 2,4-Dimethylphenol, 2,6-Dichlorophenol, 4-Chloro-3-Methylphenol and 2,4,5 – Trichlorophenol), aromatic phenols (2-Methylphenol, 3+4 Methylphenol, 2-Nitrophenol and 4-Nitrophenol) and polycyclic aromatic hydrocarbons (Acenaphthylene, Fluorene, Anthracene, Phenanthrene, Benzo(g,h,i)perylene, Pyrene, Acenaphthene, Fluoranthene, Naphthalene, Benzene, Styrene, Ethylbenzene, Toluene, Xylene, Indene(1,2,3,cd)pyrene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, 2,4,6-Trichlorophenol, Hexachlorobenzene, Chrysene and Dibenzo(a,h)anthracene) indicated no changes in the environment, demonstrating the absence of an influence from human activities in the sub-basins on the water quality of the Itapecuru River in terms of these compounds.

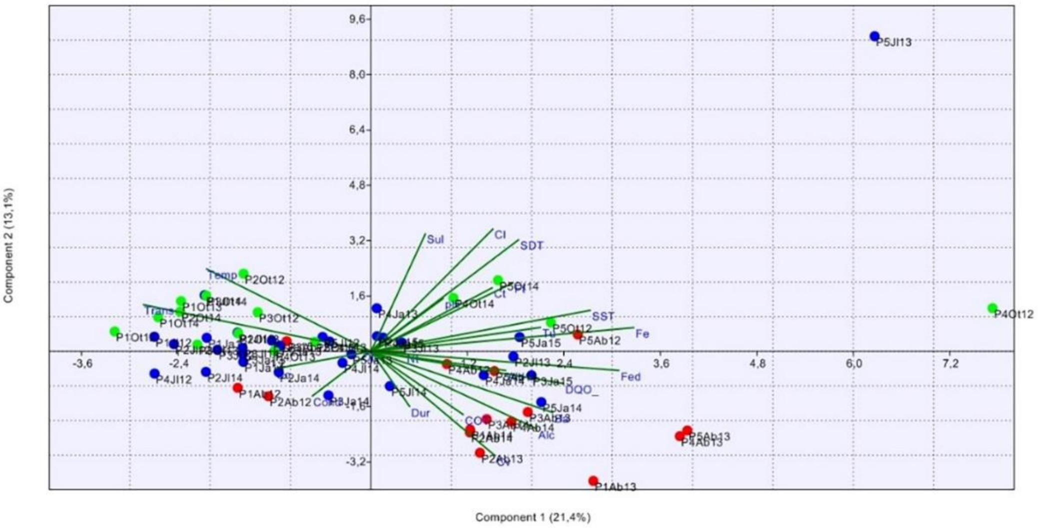
With regard to total petroleum hydrocarbons, no detection occurred in the gasoline (C8 to C11) or diesel (C14 to C20) ranges at any of the collection stations throughout the study. Motor oil (C20 to C40) was found at detection levels in July 2013 at P3 (0.07 mg L^{-1}), January 2014 at P5 (0.06 mg L^{-1}) and July 2014 at P4 (0.06 mg L^{-1}) and P5 (2.45 mg L^{-1}). The likely source was the boats that perform artisanal fishing in the region, motors very often have problems with leaking. Other toxic substances investigated, such as free cyanide, artificial dyes and phenols, were either absent or at concentrations below the limit determined by legal norms addressing water quality.

Exploratory analysis of data

Principal Component Analysis (PCA) are multivariate statistical procedures that perform significant statistical analysis, promoting the reduction of the number of variables with minimal loss of information (BHATTACHARYYA; KAPIL, 2012; SHEELA et al., 2016).

In the principal component analysis, the first three axes explained 44.7% of the variability in the data. Axis 1 accounted for 21.4%, Axis 2 accounted for 13.1% and Axis 3 accounted for 10.2% (Figures 6 and 7).

Figure 06 - Principal component analysis among water quality variables and sampling stations in lower Itapecuru River (Axes 1 and 2). Legend: Red dots (dry period: October); blue dots (wet period: April); green dots (transition periods: January and July). Sampling stations: P1, P2, P3, P4 and P5.

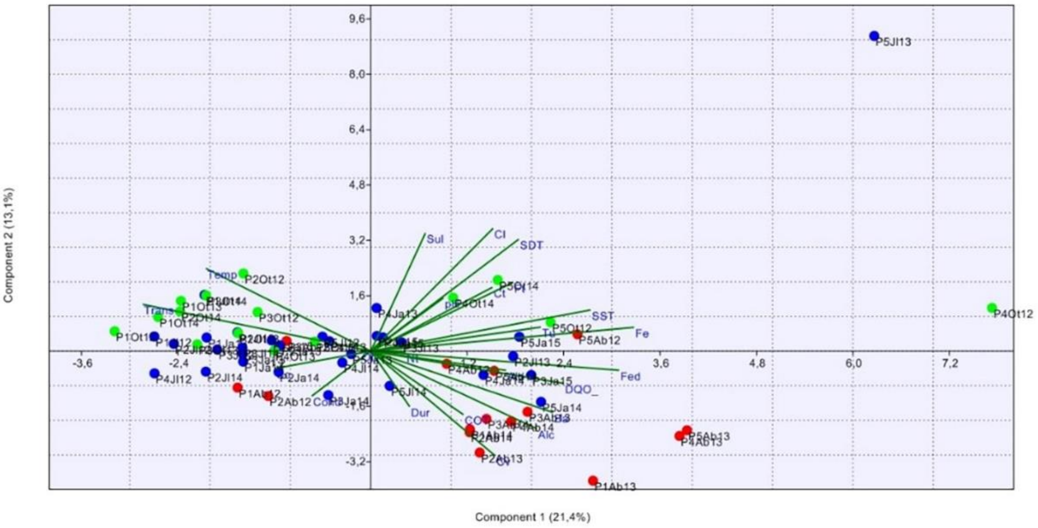


Source: The authors

The analysis of components 1 and 2 reveals a positive correlation on Axis 1 with total suspended solids, true color, total iron, total dissolved solids and total phosphorus. The main variables with a negative correlation were transparency and water temperature. With regard to Axis 2, the main variables with a positive correlation were total iron, chloride, total suspended solids, transparency, total dissolved solids and water temperature, whereas those with the strongest negative correlation were dissolved iron, alkalinity and barium (Figure 6).

The analysis of components 1 and 3 reveals the strongest positive correlations on Axis 1 with total iron, total suspended solids, total dissolved solids, chloride, dissolved iron, turbidity and alkalinity, whereas the strongest negative correlations were with water temperature and conductivity. On the third axis, total suspended solids, total iron, dissolved iron, total phosphorus and water temperature had positive correlations and total dissolved solids, chloride, total alkalinity and sulfate had negative correlations (Figure 7).

Figure 07 - Principal component analysis among water quality variables and sampling stations in lower Itapecuru River (Axes 1 and 3). Legend: Red dots (dry period: October); blue dots (wet period: April); green dots (transition periods: January and July). Sampling stations: P1, P2, P3, P4 and P5.



Source: The authors.

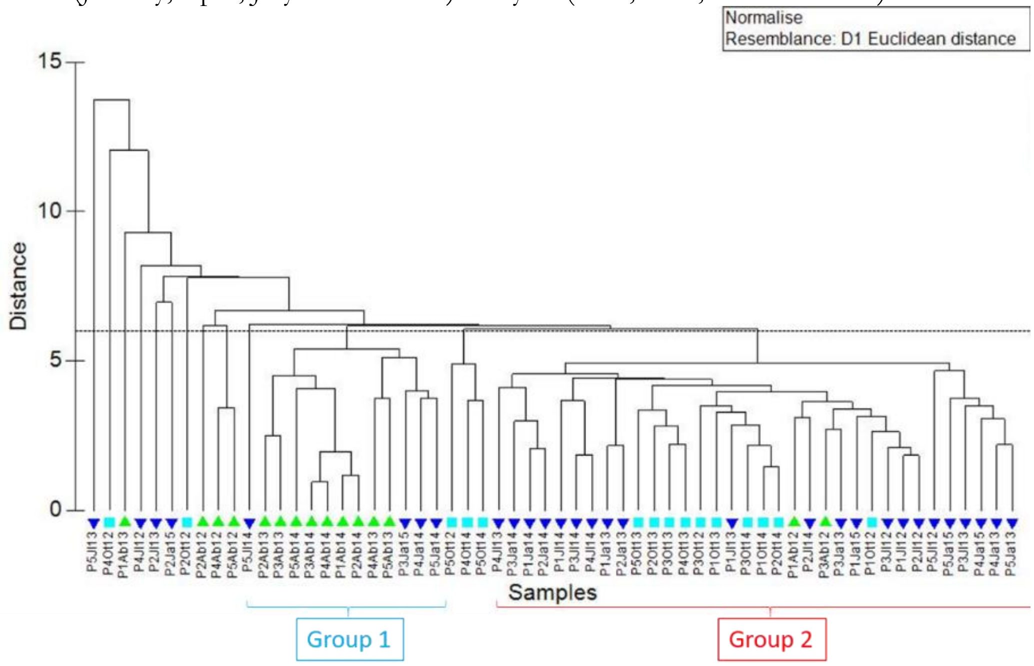
In the ACP analysis carried out by Rocha and Pereira (2015) in springs in the city of Juiz de Fora-MG, the results revealed that the limnological parameters that had the highest number of correlations had greater importance in the composition of the main components. When associated, the first three components explained about 73% of the total variance of the data, with 38.2% in Main Component 1 (PC 1) (the most expressive variable being color), 17.8% in PC2 (the most expressive were total phosphorus and chloride) and 17% in CP3, with greater representation of the variable Biochemical Oxygen Demand.

Medeiros et al. (2016) researching in the Inter-annual variability on the water quality in the Lower São Francisco River (NE-Brazil), identified the main component analysis revealed that the two first components at first axis explained 55.66% of the variance. The first factor grouped inorganic nutrients (except silicate), TSS, turbidity and conductivity. The high negative factors of turbidity and TSS are indicative of a dry period or precipitation reduction.

In the cluster analysis, the variables were distributed as a function of sampling station and seasonal period. P1 and P2 were grouped separately from the other sampling stations (P3, P4 and P5). The variables related to this spatiotemporal separation were water temperature, chloride, sulfate, total dissolved solids, total suspended solids, total iron, dissolved iron, COD, alkalinity, turbidity, pH and barium. Another trend regards the spatial distribution among the wet, dry and transition periods. The sampling stations clustered differently between the wet and dry periods and the transition periods exhibited intermediate characteristics between the two seasons (Figures 6 and 7). The main variables associated with the wet period were barium, alkalinity, total organic carbon and true color, whereas the main variables associated with the dry period were transparency, water temperature and, to a smaller degree, correlations were found with conductivity and pH.

The cluster analysis revealed the formation of two distinct groups in six distance units (Figure 8). The groups were formed as a function of season, with the first associated with samples from the wet period (April) and the second associated with samples from the dry period (October). These findings are in agreement with the results of the principal component analysis.

Figure 08 - Dendrogram for similarity analysis among sample units as function of water quality variables in lower Itapecuru River. Legend: Green Triangle: Rainy Period; Blue triangle: transition period; Blue square: dry season. Each object derived from location (P1, P2, P3, P4 and P5) in month (January, April, July and October) and year (2012, 2013, 2014 and 2015) of collection.



Source: The authors.

Conclusions

The majority of the physicochemical and biological variables in the water of the lower Itapecuru River had high dispersion measure values, indicating that these variables have ample seasonal variability. From the spatial standpoint, considerable differences were found between the upstream and downstream sites with regard to total suspended solids, transparency turbidity and total iron, indicating that the water quality at P4 and P5 was influenced by erosive processes. These variables are indicators of changes caused by human activities that potentiate erosive processes and the increase is directly related to the input of soil particles in bodies of water of the drainage basin.

Conductivity, pH, alkalinity, chloride and COD exhibited a gradual increase from the upstream to downstream sampling stations, but with no significant differences between P4 and P5 when compared to P1, P2 and P3. The results suggest that these variables may be related to the influence of salinity and tidal variations at stations P4 and P5 of the lower Itapecuru River.

The findings regarding total phosphorus and nitrogen compounds indicate that the river is not undergoing a process of eutrophication and has considerable dilution capacity in the stretch analyzed. This trend is strengthened by the absence of blooms and the low density of cyanobacteria.

The levels of thermotolerant coliforms and the presence of the bacterium *E. coli* indicate the discharge of sewage directly into the river. The results at P1 indicate that contamination begins upstream to the study area, but the high values detected at P4 and P5 suggest the occurrence of discharge from the municipality of Rosário and communities along the banks of the Itapecuru River. This underscores the need to prioritize a survey of users of the river, especially those that consume untreated water and make them aware of the care necessary prior to use due to the health risks.

The chemical elements antimony, arsenic, boron, lead, cadmium, cobalt, lithium, mercury and vanadium were either at low levels or were not detected during the monitoring. The results obtained for iron (total and dissolved) and dissolved aluminum are related to the lithology of the watershed of the Itapecuru River.

Pollution from pesticides, hydrocarbons, phenols, free cyanide and artificial dyes was not detected, demonstrating no influence from activities in the sub-basins on the quality of the water in the Itapecuru with regard to these substances.

The exploratory analysis of the 23 water quality variables demonstrated that the first three components explained 44.7% of the variability in the data. The results of the principal component analysis demonstrate that the variables selected have the same multidimensional trend on the first three axes, with the exception of conductivity, which had a negative correlation on Axis 2 and a positive correlation on Axis 3.

On the three axes analyzed, the variables tended toward the same multidimensional distribution, with the greatest contribution to the formation of these axes coming from total suspended solids, iron (total and dissolved), transparency, dissolved solids, water temperature, true color and total phosphorus. Thus, these variables should be considered important indicators for the monitoring of the water quality of the Itapecuru River.

The cluster analysis revealed the differentiation of the water quality of the river as a function of seasonality. The samples from the dry period clustered differently from those of the wet period.

The multivariate analyses revealed differences between the dry and wet periods as well as changes in the variables from upstream to downstream (P1→P5). Thus, as P1 is not influenced by the sub-basins determined in this study, the activities developed in its drainage region are probably causing changes in the water quality patterns in the stretch of the Itapecuru River investigated.

The Itapecuru River is a strategic water resource in the state of Maranhão. The maintenance of its ecological properties requires the continued monitoring of water quality. The information generated from this monitoring is fundamental to the identification of anthropogenic pressures on the system and the establishment of measures aimed at the recovery and/or maintenance of its natural properties, especially in the watersheds in its area of influence.

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Submetido em: janeiro de 2022
Aceito em: março de 2022