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Evolução da Qualidade das Águas da Bacia Hidrográfica do Rio Una-PE

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RESUMO

A qualidade dos ecossistemas aquáticos é uma preocupação da sociedade, uma vez que a deterioração dos corpos hídricos tem sido notória, principalmente daqueles que margeiam grandes centros urbanos. Por isso, vários parâmetros têm sido empregados no monitoramento da qualidade da água. Deste modo, objetivou-se avaliar a qualidade das águas da bacia do rio Una, Pernambuco, entre os anos de 2001 e 2019. Para tal, analisou-se os valores da temperatura da água (T), do potencial hidrogeniônico (pH), do oxigênio dissolvido (DO), da demanda bioquímica de oxigênio (BOD), da condutividade elétrica (EC), da quantidade total de fósforo, da turbidez e do volume das chuvas totais, disponíveis nos relatórios de monitoramento da qualidade da água de bacias hidrográficas do estado de Pernambuco. Pôde-se constatar que nenhuma das variáveis analisadas apresentaram um comportamento normal para o período estudado. Desta forma, utilizou-se os testes propostos por Kruskal-Wallis e por Nemenyi para se avaliar o comportamento de cada parâmetro. Os altos valores de T, EC, BOD, das concentrações de fósforo e da turbidez, junto aos baixos valores de DO encontrados durante vários momentos durante os anos analisados, indicam a intrusão de esgoto (doméstico e/ou industrial) no ecossistema aquático. Após uma análise estatística dos parâmetros indicadores concluiu-se que não foi possível identificar melhorias na qualidade das águas da bacia do rio Una-PE ao longo dos últimos 15 anos.

Palavras-chave: Rios, Esgoto, Temperatura, Ação Antrópica, Teste de Nemenyi.

Evolution of Water Quality in the Una-PE River Basin

ABSTRACT

The quality of aquatic ecosystems is a concern for society, since the interference of water bodies has been notorious, especially those that border large urban centers. Therefore, several parameters have been used to monitor water quality. In this way, the objective was to evaluate the quality of the waters of the Una River basin, Pernambuco, between the years 2001 and 2019. To this end, the values of water temperature (T), hydrogen potential (pH), dissolved oxygen (DO), biochemical oxygen demand (BOD), electrical conductivity (EC), total amount of phosphorus, turbidity and total rainfall volume, available in water quality monitoring reports from river basins from the state of Pernambuco. None of the verified variables showed normal behavior for the trained period. In this way, the tests proposed by Kruskal-Wallis and Nemenyi were used to evaluate the behavior of each parameter. The high values of T, EC, BOD, phosphorus concentrations and turbidity, together with the low DO values found at various times during the years analyzed, indicate an intrusion of sewage (domestic and/or industrial) into the aquatic ecosystem. After a statistical analysis of the indicators, it was concluded that it was not possible to identify improvements in the quality of water in the Una-PE River basin over the last 15 years.

Keywords: River, Sewage, Temperature, Anthropogenic Action, Nemenyi Test.

Introduction

It is not new that the quality of aquatic ecosystems is a concern for scientific society. More than twenty years ago, Tucci et al. (2001), already

highlighted that the main environmental problem to be faced by Brazil was the deterioration of the rivers that cross Brazilian cities.

Naturally, the water quality of a basin is influenced by the geological and pedological characteristics of the region in which it is located. The main anthropogenic impacts are water consumption, the discharge of domestic and industrial effluents and surface runoff from urban and rural areas. In other words, water quality reflects the different forms of land use and occupation (Liu et al., 2020; Shang et al., 2021; Ao et al., 2021).

Contamination by domestic sewage occurs, primarily, in cities where the collection and treatment system is insufficient, or non-existent, and it is then released into rivers. Oliveira et al. (2021), when analyzing the chemical parameters of the water at the entrance and exit of sewage treatment plants (ETE, in Portuguese) in the State of Pernambuco, found that even though there are no official connections between domestic sewage and water bodies, there are clandestine connections the rainwater collection network, which in turn is released into rivers.

There is also contamination of these water bodies due to the insertion of contaminants present in streets and avenues, resulting from the wear of tires, fuels and lubricants (Holanda & Soares, 2019).

Agricultural and farming activities also have a high potential to degrade the surface waters of a river basin. Many of the nutrients used to fertilize crops end up being carried by surface runoff to water bodies, increasing the concentration of nutrients, such as phosphorus and nitrogen (Menezes et al., 2016).

Furthermore, there is a high erosive impact of rainwater from the tops of hills and slopes without vegetation, with degraded pastures or those subjected to planting using conventional methods, which alters the water storage capacity in the basins, interfering with the regime river flow (Santos & Romano 2005).

The thermal behavior of a river's water is the sum of different environmental and anthropogenic factors to which this water body is subject. Surface waters naturally present seasonal variations in temperature, exerting a great influence on the growth, migration and reproduction of aquatic organisms that exist in them. The rise in temperature in a water body that is out of harmony with its natural behavior is generally caused by industrial dumping and thermoelectric plants (CPRH, 2020).

However, the characteristics of the rocky substrate may also be one of the factors responsible for the increase in the temperature of river surface waters, especially those that flow over mafic rocks

(Percebon, 2005). Furthermore, the removal of riparian vegetation has also been a major factor in increasing the temperature of water in water bodies (Cararo et al., 2022)

pH is a key physical and chemical characteristic for assessing the quality of water bodies. It governs the metabolism of aquatic organisms and species composition, affecting photosynthesis, enzyme activity in cells and nutrient absorption. Aquatic organisms can also suffer damage indirectly through changes in pH values, due to the possible increase in other toxic substances present in the water, such as heavy metals (Sorokin et al., 2014; Costa et al., 2016; Liang et al., 2023). According to CONAMA resolution 357, pH values must be between 6 and 9 to protect aquatic life (Brazil, 2005).

The DO level is essential for the existence of aquatic creatures and considerably reflects the health status of these ecosystems and is considered the most important parameter in the water quality of a river (Ho et al., 2019). Clean, flowing waters have high concentrations (above 5 mg.l⁻¹), varying throughout the course. Polluted waters exhibit low concentrations since DO is consumed during the decomposition of organic matter (Breitburg et al., 2018; Piatka et al., 2021; Xu et al., 2023).

There are some natural conditions in which there are changes in DO concentrations. In lakes where there is excessive growth of algae, oxygen concentrations exceed 10 mg.l⁻¹ during the day, due to photosynthesis. However, during the night, the breathing of organisms causes oxygen concentrations to decrease significantly, which can cause fish deaths.

Another parameter related to oxygen is BOD, which represents the amount of oxygen necessary to oxidize the organic matter present in the water through aerobic microbial decomposition, during five days at a temperature of 20 °C. The average value of BOD concentrations is 7 mg.l⁻¹. High BOD values in water bodies are most often caused by the release of organic loads, mainly domestic sewage. In this case, peak values above 50 mg.l⁻¹ can be observed (Ho et al., 2019). The occurrence of high BOD values causes a decrease in DO values, causing the mortality of fish and other aquatic organisms.

EC is another important parameter to control and determine the state and quality of water and can exhibit changes in the composition of water bodies (Piñeiro Di Blasi et al., 2013). In tropical regions it is related to the geochemical characteristics of the location and the periodicity of precipitation (Esteves, 2011). Natural waters have conductivity levels between 10 µS.cm⁻¹ and 100

$\mu\text{S}\cdot\text{cm}^{-1}$, and in environments polluted by effluents (domestic or industrial) values can reach up to 1000 $\mu\text{S}\cdot\text{cm}^{-1}$ (Von Sperling, 2007).

The EC presents different values with seasonality, with the lowest values being in the rainy season, due to the increase in ion dilution. Piratoba et al. (2017) observed in Barcarena-PA, that conductivity levels change from 45.08 to 68.08 $\mu\text{S}\cdot\text{cm}^{-1}$ in the less rainy season and from 35.77 to 43.22 $\mu\text{S}\cdot\text{cm}^{-1}$ in the rainy season. However, the release of industrial effluents can increase electrical conductivity values regardless of seasonality (Esteves, 2011).

In addition to being an important nutrient for biological processes, phosphorus is a chemical element used in industrial processes as a raw material, both in the composition and processing of products. In water bodies, its excess can cause water eutrophication. The largest sources are domestic effluents (orthophosphates), rainwater drainage from agricultural areas, and effluents from the fertilizer, food, dairy, and slaughterhouse industries. The concentration of phosphorus in domestic sewage is around 4 to 50 $\text{mg}\cdot\text{l}^{-1}$ (Glennie et al., 2002; Quevedo & Paganini, 2017). According to CONAMA resolution 357/2005, the recommended value is 0.05 $\text{mg}\cdot\text{l}^{-1}$.

The turbidity of water is defined as the measure of its ability to disperse solar radiation and indicates the degree of attenuation that a beam of light undergoes when crossing a column of water. It is a key parameter in monitoring the quality of surface waters, due to its relationship with the concentration of suspended material (silt, sand, clay, algae, debris, among others) and its influence on aquatic life, since turbidity can reduce water transparency, damaging the photosynthetic process of algae and submerged aquatic plants. Colloids, dissolved and particulate organic matter, microscopic organisms and algae are also factors that affect water turbidity (Wetzel, 2001; Göransson et al., 2013).

The main sources of turbidity in water are soil erosion, mining activities, and the release of domestic and industrial effluents. In an aquatic environment, turbidity varies spatially and temporally, mainly due to precipitation, flow, land use and vegetation cover (Silva et al., 2008; Hamilton & Luffman, 2009).

All these parameters are monitored, however, no comparisons are made to the data to determine whether there have been improvements in the quality of the water in this basin. Therefore,

the objective of this study was to evaluate the quality of water in the Una-PE River basin between 2001 and 2019. It is expected that the water quality of the basin has improved over the years. This hypothesis will be valid or not, based on a statistical analysis, which, if accepted, should present, in addition to different values between the beginning and end of the series, improvements in the values of the evaluated parameters.

Material and methods

Study area

The Una River basin is located between the states of Alagoas and Pernambuco, being of great importance for the south “Forest Zone” of Pernambuco, especially in terms of territorial reach (Figure 1). The basin covers an area of 6,740.31 km^2 , of which 6,262.78 km^2 are located in the State of Pernambuco, which corresponds to 6.37% of the State's total (EMBRAPA, 2021).

The source of the Una River is located in the municipality of Capoeiras, appearing intermittently until approximately the city of Altinho, when it becomes perennial. It has a length of around 290 km, with its main tributaries, on the right bank, being the Quatis stream and the Chata, Pirangi, Jacuípe and Caraçu rivers. The Jacuípe River serves as the boundary between the States of Pernambuco and Alagoas. On the left bank, the Riachão, Mentirosas and Sapo streams and the Camevô and Preto rivers stand out (EMBRAPA, 2021).

The basin has an intermediate climate characteristic between the “Forest Zone” and the semi-arid “Sertão”. The rainfall behavior of the basin is highly irregular, ranging from 800 mm in the west to 2200 mm in the east. The period between April and July has the highest rainfall, with a maximum monthly rainfall of 160 mm. The period of scarce rain runs from October to December, with a monthly average of just 25 mm (Melo et al., 2018). However, depending on the region, the rainy seasons have a time lag and in some years rain events may occur caused by atmospheric systems such as easterly waves, reaching the entire basin (Neto et al., 2015).

The relief of the Mata Sul region of Pernambuco, characterized by large slopes, drives surface runoff, causing extensive damage and flooding in riverside cities.

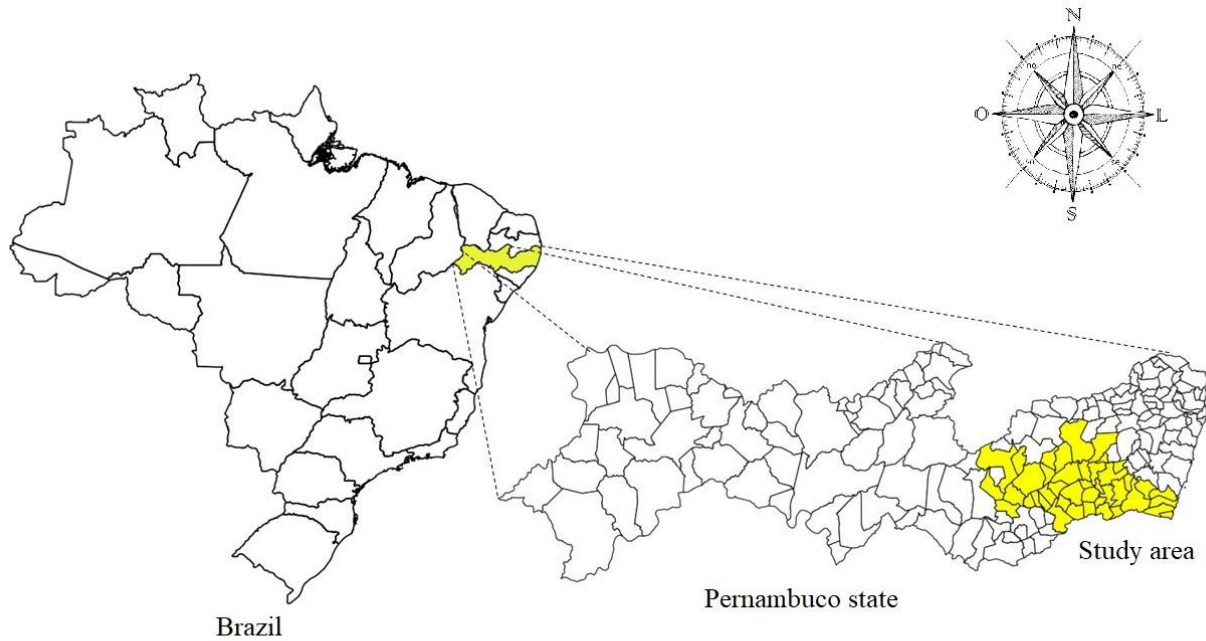


Figure 1. Map of the location of the municipalities in Pernambuco that make up the Una River basin.

Obtaining the data used

Data on the main environmental parameters, namely: water temperature (T), hydrogen potential (pH), dissolved oxygen (DO), biochemical oxygen demand (BOD), electrical conductivity (EC), quantity total phosphorus, turbidity and total rainfall were obtained from information available in water quality monitoring reports from river basins in the state of Pernambuco, between the years 2001 and 2019, available on the website of the state media agency environment (CPRH, 2020).

It is worth mentioning that although water quality reports have been available since 2001, it

was only in 2004 that rainfall data began to be made available, as well as turbidity data.

It is also important to note that data for the years 2011 and 2015 were not made available by the CPRH.

Data were obtained from six monitoring stations (Table 1), three of which were in their tributaries, on the Pirangí (UN-25) and Panelas (UN-27 and UN-30) rivers and three on the Una River (UN-04, UN -42 and UN-45). These stations were monitored with a bimonthly collection frequency, for the basic set (T, pH, DO, BOD, EC, Phosphorus and Salinity from September onwards.

Table 1 – Details of water body monitoring stations.

Station	Water body	Location
UN-18	Una River	In front of Sítio Barra de Timbó, downstream from the city of Batateira, in Belém de Maria.
UN-25	Pirangí River	On the PE-125 Bridge, downstream from the São Luiz Distillery, in Maraial.
UN-27	Panelas River	At the COMPESA catchment, on the road in the shadow of Barra, in the municipality of Belém de Maria.
UN-30	Panelas River	Downstream of the Catende Plant, in the City of Catende.
UN-42	Una River	On the PE-96 bridge, downstream of the city of Água Preta, in the municipality of Água Preta.
UN-45	Una River	On the bridge on PE-60, downstream of the city of Barreiros, in the municipality of Barreiros.

From 2004 onwards, monitoring of rainfall

in the Una River basin began to be carried out in

the municipalities of Água Preta, Belém de Maria, Barreiros, Catende and Jaqueira, all within the State of Pernambuco.

Data Analysis

Data normalities were tested using the Shapiro-Wilk test, with a significance level of 5%.

To analyze whether there were significant differences between each variable over the years, the ANOVA and Kruskal-Wallis tests (Kruskal and Wallis, 1952) were used for parametric and non-parametric data, respectively.

The hypotheses adopted for the Kruskal-Wallis's test were:

H_0 - There is no difference between the measured values of the variables over the years;

H_1 - There is a significant difference between the measured values of the variables in at least one of the years.

After applying one of these tests, the Nemenyi test (1963) was used in order to compare

pairs in order to verify which of the factors differ from each other.

The correlation between each parameter was calculated based on Equation 1:

$$r = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}} \quad (1)$$

Where r is the Pearson coefficient, x_i is the value x for each i , $\bar{x}$ is the mean of x , y_i is the value y for each i , $\bar{y}$ is the mean of y , and x, y are the analyses parameter, two at two.

Figure 2 shows a sequential scheme of the procedures followed in this research. All normality tests and statistical analyzes to determine whether there were statistically significant differences were performed with the R software (R Development Core Team, 2019).

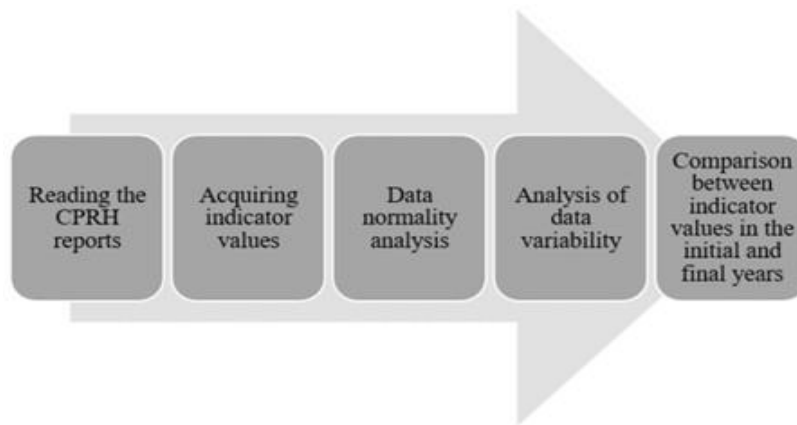


Figure 2. Schematic detail of data acquisition

Results and discussion

Table 2 shows the results of the Shapiro-Wilk and Kruskal-Wallis tests for the eight variables analyzed.

The results of the Shapiro-Wilk tests indicated that all variables present non-parametric

behavior, as they presented p-values lower than 0.05, that is, their data cannot be modeled by a Normal distribution. Therefore, the ANOVA test was not applied to any of the variables analyzed and the comparison between their behaviors each year was carried out using the Kruskal-Wallis test.

Table 2 – Result of the normality and variability test, year by year, for the eight parameters analyzed, at a level of 5%.

Variable	Shapiro-Wilk test		Kruskal-Wallis test	
	p-value	Normal Distribution	p-value	Hypothesis accepted
Temperature	5.5×10^{-7}	No	3.1×10^{-10}	H_1
Hydrogen Potential	6.5×10^{-7}	No	1.1×10^{-12}	H_1
Dissolved Oxygen	2.1×10^{-15}	No	1.5×10^{-11}	H_1
Biochemical Demand	2.2×10^{-16}	No	3.3×10^{-8}	H_1
Electric conductivity	2.2×10^{-16}	No	5.2×10^{-3}	H_1
Phosphorus	2.2×10^{-16}	No	8.7×10^{-14}	H_1
Turbidity	2.2×10^{-16}	No	5.0×10^{-10}	H_1
Rain	2.2×10^{-16}	No	2.2×10^{-16}	H_1

The p-values of the Kruskal-Wallis tests for the eight parameters presented values below the significance level ($\alpha = 0.05$), which leads us to reject the null hypothesis (H_0) that there is no difference between the values over the years.

Water Temperature

In Figure 3 we can observe the variations in water temperature over the years 2001 to 2019. Temperatures varied between 21 and 33 °C, with an average value of 27 °C, in accordance with the characteristic temperatures observed in the region, which are influenced by climatological conditions. These values are very close to those found by Melo et al. (2018) (minimum of 22.2 °C and maximum of 31.9 °C) when carrying out independent measurements of water temperature in the Pirangi and Una rivers, between 2006 and 2014 and 2015 (Gunkel et al., 2006; Melo et al., 2018).

However, from the year 2016 onwards, a tendency towards a decrease in the median values of water temperatures has been noticed, with greater emphasis on the year 2019. This was the year that presented the lowest temperatures in the analyzed period, with a minimum value of 21 °C, an amplitude of 7 °C and with 75% of the sampled values below 25 °C. 2013 was the hottest year, with values between 26 and 30 °C. According to Von Sperling (2014), the rise in temperature leads to an increase in the rates of chemical and biological reactions, thus reducing the solubility of gasses, causing an increase in the gas transfer rate.

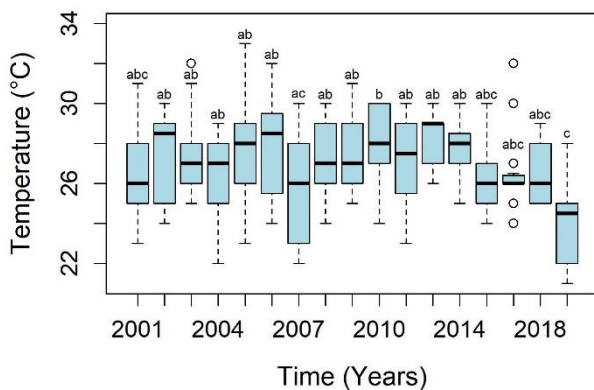


Figure 3. Boxplot of water temperature over the years 2001 to 2019. Groups that share the same letter are not significantly different from each other.

The Nemenyi test revealed that there were significant differences between the set of temperature values obtained year-by-year. The water temperature values were grouped into three categories, similar in variability (indicated by the letters “a”, “b” and “c”). Groups “a” and “c” are

made up of the years that presented the highest and lowest temperatures, respectively. This corroborates the downward trend in temperature values from 2016 onwards.

Still using the Nemenyi test, there were no significant differences in the measured values of water temperatures, when compared by collection points. It is worth noting that the unit in which the warmest values were obtained most frequently was in the Una River, in the municipality of Barreiros, close to the mouth of the waters of the Una basin into the Atlantic Ocean.

However, the highest temperature peak was found in the Panelas River (UN-30), located in the municipality of Catende, with a value of 33 °C, observed in February 2005. The second highest value found was 32 °C and was observed at various times in the Panelas River, and once in the Pirangi river (UN-25), located in the municipality of Maraial, in December 2017. These higher values are probably due to the industrial dumping of Usina Catende (sugarcane plant) in the river Panelas and the São Luiz distillery (ethanol production) on the Pirangi river.

Hydrogen potential

Under natural conditions, the water in a tropical river has a pH of approximately 6.5, enabling the survival of a wide variety of aquatic animals. If the pH of the water is reduced, the fish experience breathing difficulties and begin to capture air at the surface. Values below 5 would already result in mortality (CETESB, 2018).

In Figure 4, the hydrogen potential (pH) values can be seen, over the years 2001 to 2019. In this period, the pH values were between 5.6 and 9.1 with an average value of 7.04 and presented quite diverse variability. The values obtained are within the limits required by Brazilian legislation, which is between six and nine, according to CONAMA resolution 357/2005 (Brasil, 2005).

In general, there is a slight upward trend in median pH values over the years. This trend is confirmed by the Nemenyi test, which, when applied to analyze the variability of pH values each year, classifies them into five distinct groups (indicated by the letters “a”, “b”, “c”, “d” and “e”).

Group “a” represents the years where the water in the basin presented a large number of values below neutrality. Years such as 2003 presented pH values below seven in more than 75% of measurements, with a minimum of 5.7. In general, this condition is closer to the natural conditions of a river.

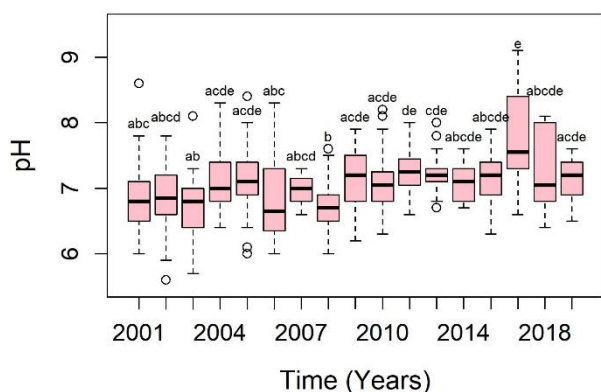


Figure 4. Boxplot of hydrogen potential (pH) over the years 2001 to 2019. Groups that share the same letter are not significantly different from each other.

In group “e” the highest pH values are found. However, it is worth highlighting that only one element of this group, in 2017, presented a single value of 9.1, which is higher than the upper limit.

By analyzing the variability of pH values per collection point, it was possible to classify the data into three distinct groups (“a”, “b” and “c”). Group “a”, formed by the pH values collected in the waters of the Una River collected in the city of Belém de Maria (UN-18), which presented the most alkaline values, with more than 75% of them above seven. Group “b”, with three collection stations (UN25, UN42 and UN45), with intermediate values between those presented by the other two groups, which presented median values equal to or greater than seven. And finally, group “c”, where the stations showed the opposite behavior to that shown by group “a”. A representative of this group is presented by the data obtained at the collection point of the Panelas River (UN-27), which had more than 75% of its values between six and seven.

Among the possible causes that may be influencing the increase in pH are the presence of organic matter, the type of soil on which the water flows, the life cycle and decomposition of aquatic plants, in addition to the dumping of domestic effluents into water courses. (Meybeck et al., 1996; Borges et al., 2003; Bueno et al., 2005; Souza, 2006; Américo-Pinheiro et al., 2021; Storto et al., 2021; Ribeiro et al., 2022, Isaac et al., 2023).

Dissolved oxygen

In Figure 5 we can observe the Boxplot of the concentration of oxygen dissolved in water (DO), over the years 2001 to 2019. The values obtained presented a minimum value of 0.5 mg.l⁻¹ and a maximum value of 10,4 mg.l⁻¹. Even though

there was a slight downward trend in median values until 2016, all were above the minimum required (5 mg.l⁻¹). Large fluctuations in DO values were observed, mainly in the years 2006, 2010 and 2016. If outliers are considered, in all years the DO presented values lower than the minimum required. If they are disregarded, only the years 2001, 2007, 2012 and 2018 would meet the minimum values required.

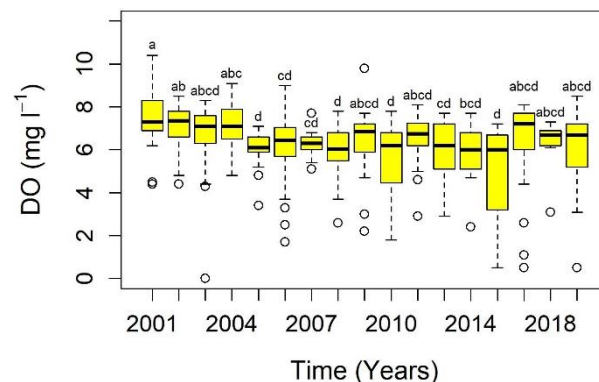


Figure 5. Boxplot of dissolved oxygen (DO) concentration, over the years 2001 to 2019. Groups that share the same letter are not significantly different from each other.

It is noteworthy that in practically all years (with the exception of 2001, 2007 and 2012) values lower than 4 mg.l⁻¹ were found, a value at which most fish species cannot resist (Kato and Piveli, 2006)

The values measured year-by-year were grouped into four distinct categories, indicated by letters from “a” to “d”, corresponding to the group with the highest and lowest concentration, respectively. Conversely to what was found in the analyzes of pH values, the median values of DO concentration showed a slight decrease over the years. DO is a parameter strongly related to the presence of organic matter in water ecosystems. Low concentrations of DO are associated with high microbial activity, which use oxygen to decompose organic matter (Santos et al., 2020; Valentini et al., 2020). The depletion of oxygen in water can be the result of an excessive discharge of organic material (Thomaz et al., 2023).

When analyzing the data on a spatial scale, it is clear that values lower than the minimum required were observed at all collection points. However, the values obtained at the collection points on the Una River (UN-18, UN-42 and UN-45) and on the Pigangi River (UN-25) presented more than 75% of the values above the minimum. The waters of the Panelas River (UN-27 and UN-30) showed different behavior from the others,

presenting the lowest values. In the case of the UN-27 collection point, half of the values were less than 5 mg.l⁻¹.

Biochemical oxygen demand

In Figure 6, you can see the Boxplot of biochemical oxygen demand, over the years 2001 to 2019. The presence of outliers is notable, both in terms of the quantity and values found. In the first five years, BOD showed a different behavior, with no values lower than 2 mg.l⁻¹ being observed. From 2017 onwards, lower values were found every year.

Disregarding the outliers, in all years the BOD values were below the limit established by CONAMA resolution 357/2005 (5 mg.l⁻¹), with the exception of 2017. Considering all measures, the maximum limit was exceeded in every year, except for 2013 and 2014. It is worth noting that in 2006, 25% of the values observed were less than 2 mg.l⁻¹. And in 2007, 2008 and 2018, practically 100% of the data obtained were less than 2 mg.l⁻¹, a value well below the maximum allowed. Only the outliers presented values above the maximum limit allowed in these years.

The possible causes that contributed to this scenario were the human influence of riverside cities and the presence of organic matter, as, generally, high levels of BOD are found when organic materials are released into the water (Ferreira et al., 2015). Also, according to Cunha and Ferreira (2019), the increase in organic matter may be related to nutrients present in effluents, animal feces, leftover leaves and branches and other organic nutrients present in the soil.

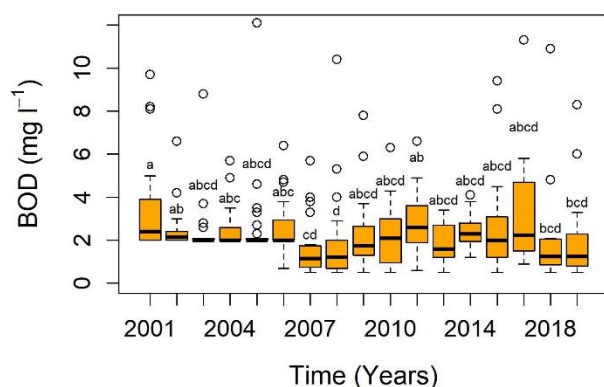


Figure 6. Boxplot of biochemical oxygen demand over the years 2001 to 2019. Groups that share the same letter are not significantly different from each other.

The BOD data did not show similar behavior over the time studied and were statistically classified into four different groups. A slight downward trend in median values can be

seen from 2007 onwards.

Group “a” is made up of the years where median BOD values concentrated around 2 mg.l⁻¹ were observed. A good representative of this group is the year 2001, where 50% of the values are between 2 and 4 mg.l⁻¹. The year 2008, representative of group “d”, has more than 75% of BOD values below 2 mg.l⁻¹.

When comparing the BOD values per collection point, it was possible to notice different behaviors, classified into three groups. The collection station located on the Panelas River (UN-30) was the one with the largest amplitude and the highest value in the analyzed period (106 mg.l⁻¹), in 2010.

Electric conductivity

Electrical conductivity (EC) is determined by the amount of salts present in the water, indirectly indicating the concentration of pollutants. In Figure 7 we can see the EC Boxplot, over the years 2001 to 2019.

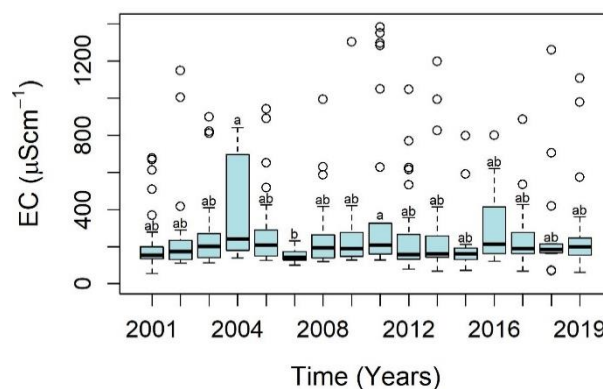


Figure 7. Boxplot of electrical conductivity over the years 2001 to 2019. Groups that share the same letter are not significantly different from each other.

The years that presented the most atypical EC values were 2004 and 2006. Except for these two years and 2010, all others presented statistically equivalent behavior. Group “a”, formed by the years with the highest EC values, is represented by the year 2004, which in addition to presenting the highest value for the median also presented 50% of the values above 200 µS.cm⁻¹.

Group “b” corresponds to the years in which the lowest EC values were observed. The year 2007 satisfactorily represents this group. In it, the lowest value for the median was measured (142 µS.cm⁻¹), in addition, more than 80% of this year's EC values were lower than 200 µS.cm⁻¹.

Spatially the differences are even greater. For the six collection points, it was possible to

classify the values into four groups. Group “a”, whose only member was UN-18, had the greatest amplitude. Values between 264 and 3786 $\mu\text{S.cm}^{-1}$ were observed. Group “b” was composed of units UN-25, UN-27 and UN-42. UN-27 presented the lowest amplitude, with values between 77 and 423 $\mu\text{S.cm}^{-1}$. Groups “c” and “d”, composed of just one unit each, UN-30 (121 – 622 $\mu\text{S.cm}^{-1}$) and UN-45 (91 and 627 $\mu\text{S.cm}^{-1}$), respectively.

According to Medeiros et al. (2018), high values for electrical conductivity, in urban areas, probably come from the discharge of untreated domestic effluents, and in rural areas, from the transport of ionic compounds used in agriculture, such as potassium, phosphorus and nitrogen.

CONAMA resolutions 357/05 and 430/11 do not establish values for electrical conductivity. According to Von Sperling (2007), natural waters have conductivity levels between 10 and 100 $\mu\text{S.cm}^{-1}$, and in environments polluted by domestic or industrial sewage values can reach up to 1000 $\mu\text{S.cm}^{-1}$.

In practically all EC measurements, the values found were greater than 100 $\mu\text{S.cm}^{-1}$, which highlights the unnaturalness of the water. And at several times, the values were higher than 1000 $\mu\text{S.cm}^{-1}$, indicating water contamination by sewage.

Phosphorus

In Figure 8 we can see the phosphorus Boxplot over the years 2001 to 2019. Concentrations ranged from 0.01 to 1.48 mg.l^{-1} , with values well above 0.03 mg.l^{-1} , the limit established by CONAMA Resolution 357/2005 (Brazil, 2005).

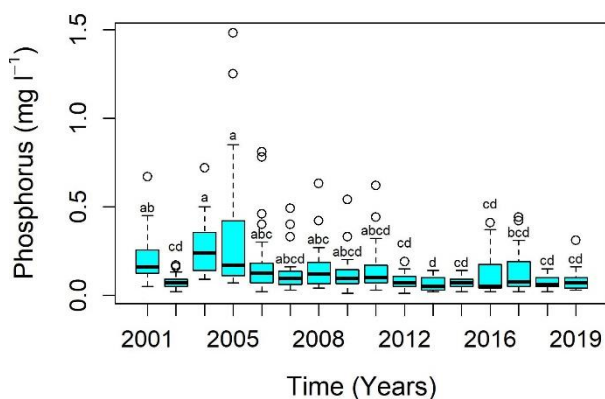


Figure 8. Boxplot of phosphorus over the years 2001 to 2019. Groups that share the same letter are not significantly different from each other.

Temporally, there were significant differences between the values of phosphorus concentrations, using the Nemenyi test. Thus, four

categories were created, where groups “a” and “d” represent the years in which the highest and lowest values were observed, respectively.

The median values were greater than 0.03 mg.l^{-1} in all years. However, the median values show a slight downward trend, especially from 2012 onwards.

Spatially, great differences were observed between the phosphorus concentration values at the collection sites. Four groups were categorized. The collection station located on the Una River (UN-18), the only member of group “a”, was the one with the greatest amplitude, with a range of values from 0.02 to 1.48 mg.l^{-1} and a median value of 0.17 mg.l^{-1} . These values are quite contrasting with the values observed for the collection station located on the Panelas River (UN-27), which was the one with the lowest amplitude, varying between 0.01 and 0.37 mg.l^{-1} . The median value in this collection unit was 0.06 mg.l^{-1} .

The increase in phosphorus concentration levels may come from the weathering of phosphate rocks, domestic waste, industrial effluents and even fertilizers (Alves et al., 2017; Santos et al., 2021; Zhang et al., 2023). All four of these possibilities are found throughout the Una basin. However, Thomaz et al. (2023) emphasize that anthropogenic factors are the main reasons for the increase in phosphorus concentrations in waters close to urban centers.

This thought is corroborated by Fia et al. (2015), when they state that the causes of the increase in the concentration of total phosphorus in water ecosystems are due to i) anthropogenic agricultural activities and ii) the release of domestic effluents.

Phosphorus enrichment in aquatic ecosystems accelerates the phytoplankton found in more superficial waters, which leads to an increase in turbidity. As a result, algae that are at a greater depth receive less light, reducing photosynthesis and causing the death of algae that enter a state of decomposition, which reduces water quality (Von Sperling, 2014; ANA, 2021).

Turbidity

In Figure 9 we can observe the Boxplot of water turbidity, over the years 2004 to 2019. Apart from the discrepant data, in all years the values observed were below the limit allowed by Brazilian legislation (100 UNT), CONAMA Resolution 357/2005 (Brazil, 2005), except for the year 2005. It is observed that the presence of discrepant values above the maximum limit allowed in the years 2005, 2007, 2010 and 2017.

The turbidity values were grouped into three categories, with group “a” being those with the highest values. The year 2007 stands out for presenting a median of 35 UNT, the highest of all years, and a range in the range of 3 UNT to 150 UNT. The values established this year are in complete contrast to the values observed in 2013, which had a median of 4.5 UNT and a range of 1.5 UNT to 30 UNT.

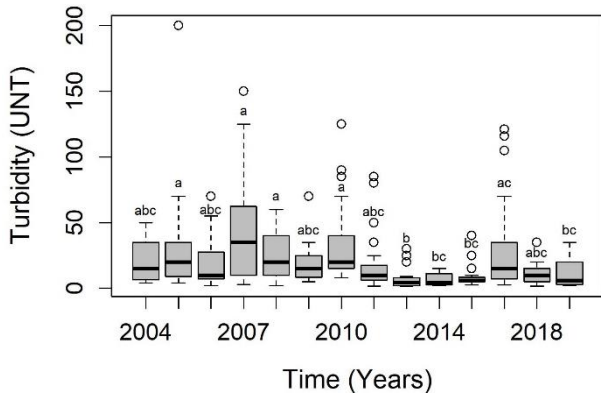


Figure 9. Boxplot of turbidity over the years 2001 to 2019. Groups that share the same letter are not significantly different from each other.

Discrepant high turbidity values may be due to the improper discharge of domestic and industrial sewage (Santos et al., 2023). Increases in turbidity contribute to the reduction of photosynthesis and plant development in the aquatic environment, thus harming existing species. (Von Sperling, 2014; CETESB, 2018).

When analyzing the data on a spatial scale, it can be seen that in UN-18, UN-25 and UN-27 the measured values were lower than or equal to the maximum allowed. In the other three, the maximum values were always higher. Thus, it was possible to statistically group the collection units into two categories.

In UN-18, the lowest median was observed (6.4 UNT), a maximum value of 90 UNT and with 75% of values below 15 UNT. This collection unit is a member of group “a”. These numbers are quite different from those presented for UN-30, which obtained a median value of 20 UNT, a range in the range of 4.0 UNT to 200 UNT.

Rains

When observing the Boxplot of rainfall over the years 2004 to 2019 (Figure 10), the year 2008 was the year with the highest median value, with 178 mm. In 2005, it was the year with the lowest rainfall compared to the median, with around 54 mm.

The month with the highest rainfall

recorded in the period analyzed was May 2017, with a total rainfall of 725 mm, in the city of Barreiros. On this occasion, there was a series of floods and floods, causing rainwater to mix with black and gray water from domestic and industrial effluents (Figure 11). Thus, favoring the increase of other indicators, such as turbidity, phosphorus and BOD levels, while EC values decreased.

As expected, the annual rainfall values throughout the period present statistically significant differences and can be grouped into three categories, according to the Nemenyi test.

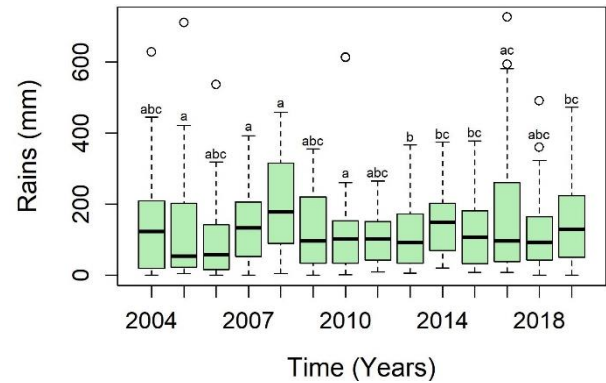


Figure 10. Boxplot of rainfall over the years 2004 to 2019. Groups that share the same letter are not significantly different from each other.



Figure 11. Floods in the municipality of Barreiros in May 2017. Source: Deyvson França-Diário de Pernambuco.

The water quality of aquatic ecosystems is influenced by river runoff and has a short response time, due to a rain event, mainly by leaching existing attributes in the soil on the banks of the river basin (Girardi et al., 2016).

With increasing rainfall, the pH tends to rise and approach neutrality, due to greater dilution of dissolved compounds and faster runoff (Carvalho et al., 2000). EC also depends on rainfall volume, as it depends on the ionic composition of water bodies (Esteves, 2011). There is also an influence on concentration values (DO, BOD,

phosphorus), since the number of diluents present increases. In this case, the entry of rainwater into aquatic ecosystems generates a reduction in BOD, pH and total suspended solids (TSS) values (Oliveira et al., 2021). With the increase in rainfall, the transport of organic and inorganic material drained from the banks of the rivers increases, which provides an intensification of the color, changing its turbidity (Piratoba et al., 2017).

In Figure 12, you can see the draftsman's plot of temperature, pH, DO, BOD, EC, phosphorus and turbidity. It is showing the histogram and the value of the correlation coefficient (r) between each parameter. The p-value indicates whether the correlation is statistically significant ($p\text{-value} \leq 0.05$) or not ($p\text{-value} > 0.05$).

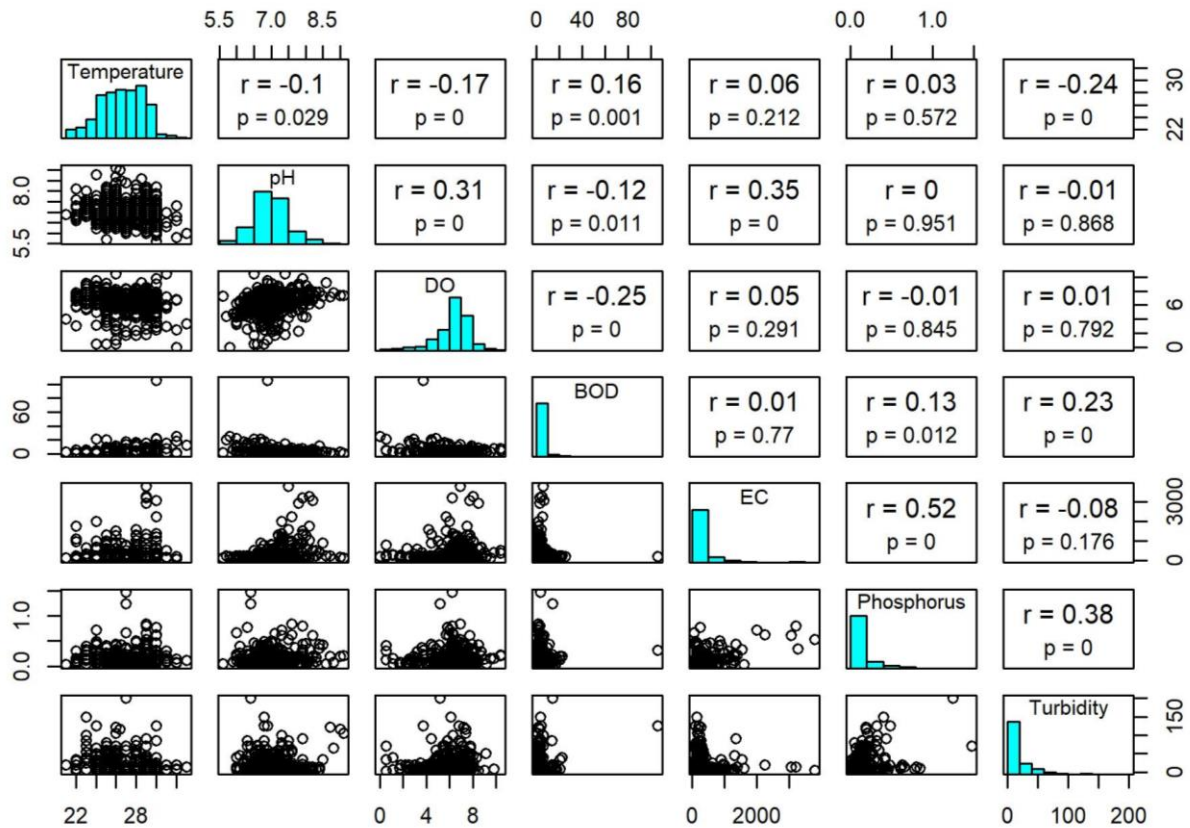


Figure 12. Draftsman's plot of evaluated water quality indicators.

The correlation coefficient always measures the relationship between the dependent and independent variables. If the correlation coefficient is +1 or -1, it shows the perfect linear relationship between the variables.

There was a moderate positive correlation between the phosphorus and EC ($r = 0.52$), weak positive correlation between phosphorus and turbidity, BOD and turbidity, EC and pH, DO and pH parameters ($r = 0.38$, 0.23 , 0.35 and 0.31 , respectively). Weak negative correlation between temperature and turbidity and DO and BOD ($r = -0.24$ and -0.25 , respectively) and very weak positive and negative correlations were observed between all other parameters analyzed. This lack of correlation between variables indicates that all parameters are important in determining water quality, and that none of them can be suppressed (Ramos-Pacheco et al., 2023).

Conclusion

No parameter analyzed showed normal behavior for the period studied. In this way, the tests proposed by Kruskal and Wallis and by Nemenyi were used to evaluate the behavior of each parameter.

As the data does not present a normal distribution, it is not possible to express the parameters in terms of others.

Over time, significant differences were found in the values measured in all variables analyzed. Spatially, only water temperature did not show statistically significant differences.

However, a slight tendency towards a decrease in temperatures, dissolved oxygen, biochemical oxygen demand, electrical conductivity and phosphorus in the waters of the

basin can be seen, as well as a slight tendency towards an increase in hydrogen potential.

The waters of the Una River basin were severely damaged by human actions, both due to the activity of the sugar-energy sector (sugar and ethanol production) and the inadequate disposal of domestic effluents.

The high values of temperature, electrical conductivity, biochemical oxygen demand, phosphorus concentrations and turbidity, together with the low values of dissolved oxygen found at various times during the years analyzed, indicate that there is continued dumping of effluents (domestic and/or industrial) in the aquatic ecosystem.

In general, it was not possible to identify improvements in water quality in the Una-PE River basin over the last 15 years.

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