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USE OF MULTIPARAMETRIC PROBE TO DIAGNOSE WATER QUALITY IN THE HYDROGRAPHIC REGION OF MIDDLE PARAÍBA DO SUL

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Abstract: Located in one of the most developed industrial areas in the country, the Paraíba do Sul hydrographic region plays a prominent role in the implementation of the National Water Resources Policy. The Paraíba do Sul River serves several conflicting uses, including collecting water from public supplies, receiving domestic and industrial effluents, in addition to being essential for the maintenance of several ecosystems. Therefore, monitoring water quality in the region is a public and environmental health issue. Despite this, the number of systematic monitoring points existing in this region is insufficient to meet management demands. This work presents the results of the partnership between the Middle Paraíba do Sul Hydrographic Basin Committee (CBH-MPS) and ``*Universidade do Estado do Rio de Janeiro*``(UERJ) to carry out water quality diagnosis in this hydrographic region using a Multiparametric Probe. Analytical results were obtained indicating the seasonality of the most critical issues in the basin in terms of water quality and photographic records of sampling points in the four seasons of the year. The interaction between the basin's actors brought a new perspective to the management of water resources.
Keywords: Water quality, Water resources management, Environmental analysis, Environmental Chemistry.

INTRODUCTION

Water is a finite and essential natural resource for maintaining life on Earth, being fundamental for the survival of all species. However, water availability is compromised due to human actions that have caused severe impacts on the environment, whether due to disorderly urban and population growth or an unsustainable lifestyle. [1]

According to Telles and Costa, [2] in the last 500 million years it is believed that there have been no significant changes in the volume of water on the planet, so that drought and flood scenarios are closely related to volume variations in reservoirs and geographic distribution of climate events. Despite the large volume of water on the globe, around 1.4 billion km^3, only 2.5% of this is fresh, with only 0.3% of the total volume available for human activities. [3] It is estimated that Brazil holds between 12% and 16% of the planet's fresh water, however the country presents large biogeophysical, economic and social differences within its territory, thus varying the volumes of water per capita by region. [1]

The Paraíba do Sul river basin, located in the Southeast region, extends across the territories of three states, occupying an area of 57,000 km^2, between São Paulo (13,605 km^2), Rio de Janeiro (22,600 km^2) and Minas Gerais (20,500 km^2). [4] In the state of Rio de Janeiro, for the purposes of water resources management, nine hydrographic regions were defined, through Resolution number: 107/2013 of the Rio de Janeiro State Water Resources Council (CERHI-RJ), [5] of which are the Middle Paraíba do Sul Hydrographic Region (RH-III). RH-III is still located in a heavily industrial area, in the Paraíba Valley, covering 19 municipalities and presenting a high potential for pollution and environmental degradation. [6]

During its course, the Paraíba do Sul River passes through cities with progressive urbanization, where in many of them sewage treatment is inadequate or non-existent, releasing its effluents directly into the water source. Furthermore, the intense use of water resources in this region contributed to the increase in water demand, which, together with other factors, indicates a serious compromise in the quantity and quality of the basin's waters. [4] According to the 2022 Environmental Scenario Report of RH-III, [6] the water quality balance presented sections of the basin with high values of the analyzed parameters, indicating that the basin needs better monitoring and monitoring water quality, in compliance with CONAMA resolution 357/2005 [7] which provides for the classification of water bodies and water quality standards for each class.

For an environmental diagnosis of the basin, one of the main aspects to be considered is monitoring water quality. [8] In relation to RH-III, this monitoring represents a public and environmental health issue due to the relevance of the Paraíba do Sul River in the region, serving both domestic and industrial purposes, directly and indirectly impacting the lives of millions of people. Even so, there is no real-time monitoring system for water quality in the basin nor any type of alert for chemical pollution that could affect the capture of water for public supply and the number of existing monitoring points is insufficient for the implementation of effective water resources management measures.

Statistical analysis was used to process the data and obtain the best results with data optimization [12 13 14]

In this work, the results of water quality monitoring carried out through a partnership between the Middle Paraíba do Sul Hydrographic Basin Committee (CBH-MPS) and ``*Universidade do Estado do Rio de Janeiro*``(UERJ) with a Multiparametric Probe at 34 will be presented. points of RH-III during the year 2023. The results obtained in four collection campaigns for the parameters pH, turbidity, dissolved oxygen and conductivity, may assist management in implementing effective environmental protection measures, pollution remediation and waste treatment. contaminated areas, in order to guarantee the safety of the community that consumes the water and the survival of fauna and flora.

EXPERIMENTAL PART

MATERIALS

- YSI PRO DSS Multiparameter Probe
  - pH meter
  - Conductivity meter
  - Turbidity sensor
  - Optical DO Meter
  - Thermometer
  - Barometer
  - GPS
- Bucket

METHODOLOGY

To diagnose water quality in different tributaries and in the Paraíba do Sul River itself, 40 collection points were initially defined by the Middle Paraíba do Sul Hydrographic Basin Committee (CBH-MPS), using location criteria, restriction of use and alignment with what is foreseen in the Basin Plan. [9]

The points were divided into reference points, impact points and strategic points. Collections were carried out in four campaigns during 2023, in different seasons, the first between February and March, the second in May, the third between August and September and the fourth in December. Each campaign was carried out over four days, two days in the cities of Resende, Itatiaia, Quatis, Barra Mansa and Volta Redonda and two days in the cities of Vassouras, Rio das Flores, Três Rios, Paraíba do Sul, Barra do Piraí and Pinheiral.

Due to problems not foreseen in the initial mapping, but found in the field work, such as difficult access, security, restricted access on private property and lack of water, some points were eliminated and others replaced after the first two campaigns, reaching a total of 34 points that were maintained in

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subsequent campaigns. Thus, six points were defined in Volta Redonda, four in Resende, four in Itatiaia, three in Barra Mansa, two in Pinheiral, three in Barra do Piraí, five in Paraíba do Sul, two in Rio das Flores and one in Três Rios. Figure 1 shows the distribution of points on the map and table 1 shows the 34 collection points, their location, reference point and the water body analyzed.

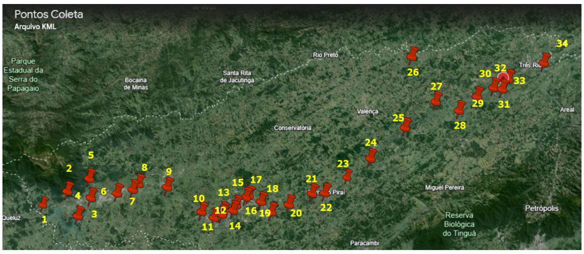

Figure: Distribution of the 34 Water Quality Monitoring points with the Multiparametric Probe in the Médio Paraíba do Sul Hydrographic Region. [10]

The analyzes were carried out in the field with a YSI ProDSS multiparametric probe, acquired by CBH-MPS, coupled with Turbidity, pH, Dissolved Oxygen, Conductivity sensors, as well as GPS and a temperature and barometric pressure meter. Calibration of the equipment was carried out before each sampling campaign in the Environmental Analysis laboratory of the Resende Regional Campus of UERJ.

Water samples were collected through a bucket thrown by ropes into water bodies. The probe was then introduced into the samples and after waiting for the sensors to stabilize, readings began. To perform each reading, the probe takes 30 s, so, to obtain at least 10 readings from the same point, it was left in contact with the sample for a minimum period of 5 min. At each point and during each collection campaign, photographic records and notes were made about the conditions found.

RESULTS AND DISCUSSIONS

Due to the collections being carried out in different seasons of the year, it was possible to observe the variation in parameters due to periods of flood and drought and to carry out a statistical study to evaluate the trends in the basin. The results of each campaign were presented at the CBH-MPS Plenary meetings, with photographic records of the most critical issues observed, such as the drastic change in the flow of the Paraíba do Sul River between March and May at the point of Três Rios, as shown in the figures 2 and 3.

Figures 2 and 3: Paraíba do Sul River Point in Três Rios in the months of March and May, respectively.

Seasonality influenced the analysis of each parameter studied differently. For turbidity, the flood times caused an increase in its values, with the high rainfall the sediments at the bottom of the bed move and the high flow causes sliding of slopes which increased the number of particles suspended in the water and consequently light scattering and turbidity. Furthermore, during this period the

Point	Place	Reference	Water Body	Coordinates
1	Resende	Engenheiro Passos	Ribeirão da Água Branca	- 22°29’55”; -44°40’31”
2	Itatiaia	Hotel de Trânsito	Rio Campo Belo	- 22°27’39”; -44°35’58”
3	Itatiaia	Funil	Rio Paraíba do Sul	- 22°31’42”; -44°34’7”
4	Itatiaia	Hyundai	Rio Belo	- 22°28’44”; -44°31’50”
5	Itatiaia	Penedo	Ribeirão das Pedras	- 22.42558; -44.53413
6	Resende	Sesmarias	Rio Sesmarias	-22°28’ 1 “; -44°27’6”
7	Resende	Pirapetinga	Rio Pirapetinga	- 22°27’23”; -44°24’13”
8	Resende	Lagoa da Turfeira	Lagoa da Turfeira	- 22°26’26”; -44°23’12”
9	Barra Mansa	Quatis X Floriano	Rio Paraíba do Sul	-22°27’ 1 “; -44°18’0”
10	Barra Mansa	Rio Bananal	Rio Bananal	-22°31’7 “; -44°11’48”
11	Barra Mansa	Rio Barra Mansa	Rio Barra Mansa	- 22°32’50”; -44°9’35”
12	Volta Redonda	Ponte alta	Rio Paraíba do Sul	- 22°31’35”; -44°8’8”
13	Volta Redonda	Córrego Bugio	Córrego Bugio	-22°31’7 “; -44°7’58”
14	Volta Redonda	Laranjal	Ribeirão Brandão	- 22°30’53”; -44°6’7”
15	Volta Redonda	Aterrado	Rio Paraíba do Sul	-22°30’ 1 “; -44°5’35”
16	Volta Redonda	Escória CSN	Rio Paraíba do Sul	- 22°28’43”; -44°3’48”
17	Volta Redonda	Dom Bosco - Ribeirão	Ribeirão do Inferno	- 22°28’26”;-44°3’18”
18	Pinheiral	Parque Fluvial	Rio Paraíba do Sul	- 22°29’23.7”; -44°01’03.8”
19	Pinheiral	Pinheiral – Rio Cachimbal	Rio Cachimbal	- 22°31’12.5”; -43°59’14.9”
20	Barra do Piraí	Estrada Vargem Alegre	Rio Paraíba do Sul	- 22°29’56”; -43°56’4”
21	Barra do Piraí	Ponte preta	Rio Ipiabas	-22°28’6 “; -43°51’53”
22	Barra do Piraí	Barra Do Pirái Centro	Rio Piraí	-22°28’ 1 “; -43°49’36”
23	Vassouras	Vassouras - Lucio Meira	Rio Paraíba do Sul	- 22°25’26”; -43°45’39”
24	Vassouras	Barão de Juparanã	Córrego das mortes	- 22°22’16”;-43°41’23”
25	Vassouras	Sebastião Lacerda	Rio Paraíba do Sul	- 22°17’08.9”;-43°35’09.1”
26	Rio das Flores	Rio das Flores	Rio das Flores	- 22°5’22”;-43°33’59”
27	Rio das Flores	Abarracamento	Rio da Divisa	- 22°12’48”;-43°27’42”
28	Vassouras	Andrade Pinto - Ponte	Rio Ubá	- 22°14’17”;-43°25’25”
29	Paraíba do Sul	Posto imperador	Ribeirão da Boa Vista	- 22°11’56”;-43°22’11”
30	Paraíba do Sul	Rio Chacarinha	Rio Chacarinha	- 22°10’29; -43°19’12”
31	Paraíba do Sul	Paraíba do Sul - Bridge	Córrego do Covanca	- 22°10’29”;-43°19’12”
32	Paraíba do Sul	Paraíba do Sul - Pedestrians	Córrego do Inema	- 22°10’42”;-43°17’38”
33	Paraíba do Sul	Cerâmica	Rio da Barra do Rio Novo	-22°9’ 1 “; -43°16’32”
34	Três Rios	Três Rios - Piracanjuba	Rio Paraíba do Sul	- 22°6’17”;-43°10’7”

Table: Location, reference and water body of the 34 Water Quality Monitoring points with the Multiparametric Probe in the Médio Paraíba do Sul Hydrographic Region contribution of diffuse sources of pollution also increases. In times of drought, turbidity presented lower values with less variation, and can be used as an indicator for human interference, with low values in points with little interference and high values in points with a lot of interference.

On the Piraí River, in the center of Barra do Piraí, there was a significant variation in turbidity in December after the implementation of the ``*Limpa Rio*`` Program of the State Institute of the Environment of Rio de Janeiro (INEA), as shown in figures 4 and 5, where at the beginning In September there was growth of various aquatic macrophytes and the water was clearer, even during the dry season, and in December the entire bed was turned over after the cleaning machines passed through.

Figures 4 and 5: Piraí River Point in Barra do Piraí in the months of September and December, respectively

Dissolved oxygen (DO) was affected, especially by the lack of rain, presenting its lowest values during periods of drought, since it is an indicator of pollution due to organic load, mainly coming from sewage, and varies depending on the flow of the water body and its capacity for self-purification. In Três Rios, a point on the Paraíba do Sul River after transposition to the Guandu Basin, dissolved oxygen varied so much depending on the flow that it could be classified, according to CONAMA Resolution 357/200 5 [7], as Class 1 (above 6 $mg.L^{-1}$) in March and December, as Class 3 (between 4 and 5 $mg.L^{-1}$) in August and as Class 4 (above 2 $mg.L^{-1}$) in May. Due to the drought, the flow in May at this point was so low that it was not enough to dilute the sewage released into the region, so the bacteria consumed the available oxygen, leaving a low level for the maintenance of aquatic life.

In the boxplot in figure 6 it can be seen that, as happened in Três Rios, other points also varied the DO content depending on the flow of the water body between campaigns, so that they could be classified in different classes throughout the year, such as in Barra do Piraí on the Piraí River, on the Córrego Bugio in Volta Redonda, on the Funil dam in Itatiaia and on the Barra Mansa River in Barra Mansa. In the field, fish were observed in some of these points going to the water surface to breathe due to the level of dissolved oxygen being very low, forming circles of water due to this movement. The diagram in figure 6 also points to another situation that serves as a warning, which is the case of Lagoa da Turfeira in Resende, where the DO content was below 2.5 $mg.\ L^{-1}$ in the four campaigns, being outside the class range of CONAMA resolution 357/2005. [7]

The pH was the only parameter that did not suffer significant variation between the rainy and dry periods, showing only a small variation between points and seasons due to changes in temperature and pollution, but without leaving the range between 6 and 9. stipulated by CONAMA 357/2005. [7]

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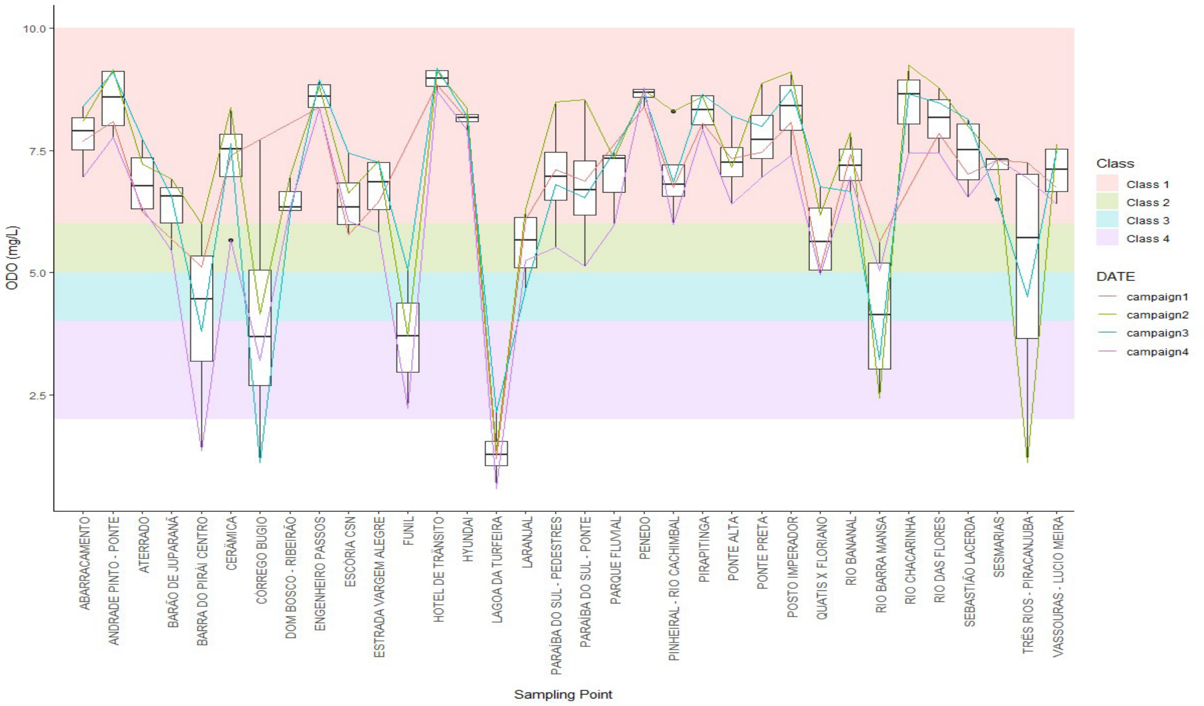

Figure 6: Boxplot of Dissolved Oxygen of the 34 points in the 4 collection campaigns of 2023 according to CONAMA 357/2005.[7]

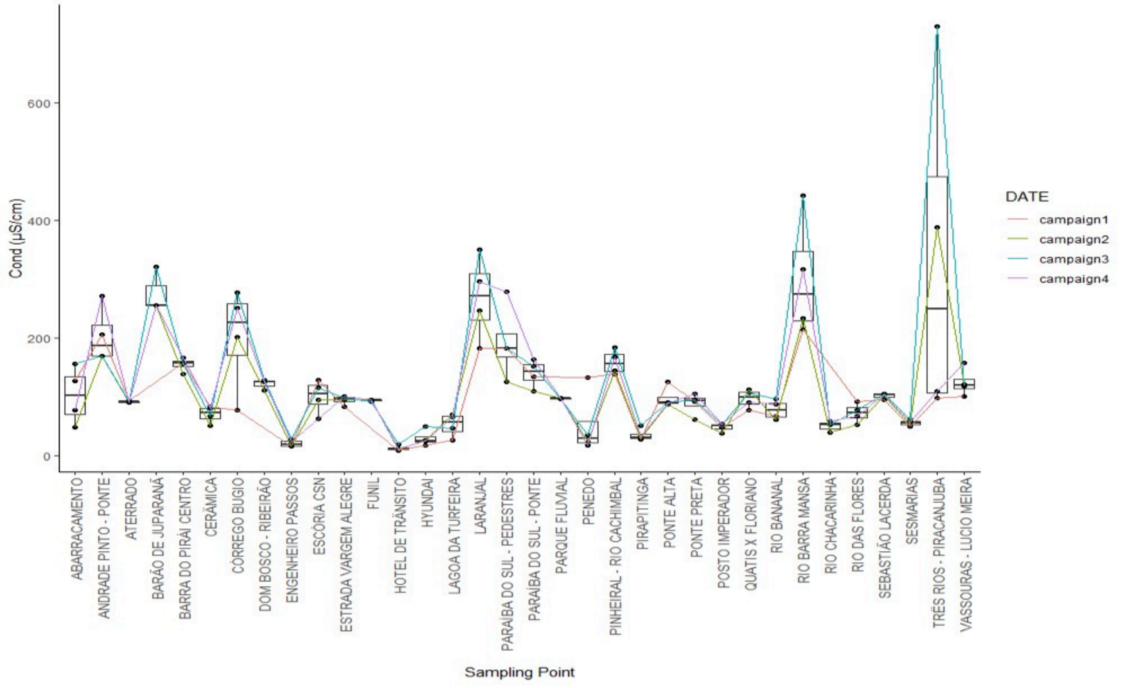

Figure 7: Boxplot of the Conductivity of the 34 points in the 4 collection campaigns of 2023 according to CONAMA 357/2005.7

Conductivity is an extremely important parameter as an indicator of both the presence of sewage and metals, serving as a basis for defining the points that require deeper investigation as it is a region with a strong presence of steelmaking. Although there is no standard in legislation, Von Sperling [11] indicates values between 10 and 100 $\mu S.cm^{-1}$ for natural waters and values above 100 $\mu S.cm^{-1}$ indicate contamination.

The boxplot in figure 7 shows that several points presented values greater than the Von Sperling range, [11] mainly in tributaries that pass through urbanized regions such as Ribeirão Brandão in Laranjal in Volta Redonda, the Rio Barra Mansa in Barra Mansa and the Córrego Bugio in Round Round. In Três Rios, the variation in conductivity is related to the change in flow, but in an inversely proportional way, in which the higher the conductivity, the lower the flow found.

CONCLUSIONS

The evaluation of the analyzed parameters showed how much the change in the flow of water bodies and urban and industrial pollution affect the basin, potentially interfering with the ecosystem and harming use by the population. The results obtained served as a basis for defining the points that require more detailed monitoring with sample collection for laboratory analysis and also for defining the real-time monitoring points, which are the next stages of the research.

Monitoring also contributed to warning about the effects of the transposition of the Paraíba do Sul River in the basin, serving as an important instrument for water resources management. Furthermore, monitoring brought a new perspective as a water resources management tool, integrating the various actors in the basin such as CBH-MPS, ``*Associação Pró-Gestão das Águas da Bacia Hidrográfico do Rio Paraíba do Sul*`` (AGEVAP), UERJ and the riverside community.

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