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Evaluation of physical and chemical parameters of two rivers crossed by PR 508 highway in Paranaguá/Brazil

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Abstract

Rivers are widely used by societies and have been degraded due to environmental impacts caused by human action over the years. This factor influences the extinction or decrease of the biological diversity of rivers and nearby regions. The anthropization on the rivers in the coastal region of Paraná causes impacts that can be evaluated through physical-chemical parameters of the local water resources. The objective of this work was to quantify the concentration of phosphate, ammonia and nitrate ions present in water samples from the Santa Cruz River and the Ribeirão River (Paranaguá - PR), which are crossed by PR 508 - Alexandra - Matinhos. The space-time sample collection took place in March and September of the year 2020. The values of turbidity, air and water temperature, concentration of phosphate, ammonia and nitrate ions were evaluated, in addition to the measurement of pH values, dissolved oxygen, electrical conductivity, total dissolved solids, in the four sampling points, being two points in each one of the evaluated water resources. The analytical investigation was carried out at the Laboratory of Environmental Impact Assessment of the Paranaguá Region (LAVIMA) using potentiometric, turbidimetric, conductometric and spectrophotometric methods. The results obtained in each of the parameters evaluated were compared to those established by National Council for the Environment (Conama) Resolution No. 357/2005. It was observed that the phosphate values obtained in the tests were higher than the maximum value recommended by the aforementioned normative resolution, and the other results presented results considered normal.

Keywords: Anthropization; Physical-chemical parameters; Spectrophotometric Method; Nitrogen Compounds; Phosphate Compounds.

1. Introduction

The occupation and use of the soil stand out as the main anthropic interferences that alter the quality of the soil and water resources. Rivers are essential for regional economic development, and range from leisure tourist activities to agro-industrial activities, this can be seen throughout the history of human beings on planet Earth. Always the development of a society emerged close to some water resource [1].

The anthropization process on aquatic ecosystems promotes the incorporation of substances that can cause its eutrophication, as well as other forms of pollution. In the specific case, the nutrients in low concentrations gradually affect the biological diversity and in higher concentrations, they can cause the decrease or extinction of the ecosystems of the water body due to the proliferation of algae or micro-algae on the surface of this resource.

The high introduction of macro-nutrients in rivers can generate problems in water quality. In this way, the systematic and continuous evaluation of these water resources is of fundamental importance for the control and possible investments in the recovery of degraded areas [2].

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The quantification of physical-chemical parameters of river water is important to prevent the eutrophication process, evidenced by silting up and excess flowering in the superficial region of the water resource. Thus, this anthropic process promotes a decrease in the penetration of sunlight into the deepest parts of the water, causing a decrease in dissolved oxygen and, as a consequence, also a decrease in aquatic species. From the negative impacts comes the degradation of aquatic ecosystems, affecting the environment and consequently human life [3]. In surface waters, eutrophication is triggered mainly due to high rates of nutrients that have in their composition the chemical elements nitrogen and phosphorus, in their soluble ionic forms.

Nitrogen reaches water bodies through the solubilization of gaseous species in rainwater; as well as the biological fixation, and also, by the allochthonous origin. The levels of concentration of this element are observed by anthropic activities and by the type of vegetation.

Reis et al [4] points out that nitrogen is fundamental for the development of plants, and in the aquatic system the most oxidized species of nitrogen prevails, that is, in the form of the nitrate ion [5]. For this to occur, organic matter is oxidized to the ammonium ion and its weak base ammonium. Subsequently these chemical species are oxidized by nitrosomonas bacteria forming the nitrite ion, which in turn are oxidized by nitrobacter bacteria forming the nitrate. Thus, favouring the presence of oxidized chemical species. In these cases, the ionization of weak acids or weak bases, combined with the Châtelier Principle, promotes the oxidation process [6].

The main substance of the atmosphere is nitrogen in its gaseous form (N_2) comprising 78% of atmospheric gases. Ammonification or mineralization, nitrification, de-nitrification, fixation, reduction and synthesis of organic forms are phases of the biogeochemical cycle of the element nitrogen, and all these processes occur for the formation of nitrate, that is, for the formation of element nitrogen in its most oxidized form [7]. Not forgetting that the element nitrogen is a basic component in the composition of proteins, nucleic acids and different biochemical species that are very important for the development and conservation of biological activities [8]. This element is also used in the production and use of commercial fertilizers and when they are used in excess, they cause impacts of their concentration in water bodies [9]. Although eutrophication is a natural process of increasing algal populations [10], when the concentration of the element nitrogen found in the form of ammonia (NH_3), nitrate (NO_3^-) and nitrite (NO_2^-) is exacerbated [11] and, together with excess phosphorus, causes artificial eutrophication [12].

Another important element is phosphorus, which has a limited soluble, available and particulate presence in the atmosphere and soil. Since erosion and leaching of rocks and soil remove the little soluble phosphorus, in the form of phosphate ion, and take it to water bodies [13]. Due to this limited availability and its need for plant development, phosphorus is also recurrently used as a fertilizer, and it is estimated that between 75% and 90% of the product used ends up in water resources [14] . The disposal of untreated domestic and industrial sewage, combined with the excess of fertilizer deposited in agricultural regions, aggravates the concentration of this element in water resources.

The National Council for the Environment (Conama) through Resolution No. 357/2005 deals with the classification of bodies of water and establishes standards for releasing effluents into them. Through the parameters established for the elements phosphorus and nitrogen, where it is possible to show whether anthropization is promoting negative impacts on the limnic environment [15].

Carpenter et al [16] comments that these ions in excess and in combination with climatic, physical, biological and chemical factors alter the river's metabolism causing an increase in phytoplankton biomass and toxic species. As well as the proliferation of gelatinous zoo-plankton, benthic algae and epiphytes, the alteration of the macrophyte population. As well as the death of coral reefs, the decrease in water transparency, the depletion of oxygen levels and the death of fish species [10].

The quantification of the mentioned elements in their ionic forms is carried out through diversified analytical techniques. However, in this work spectrophotometric determinations were carried out, and the methodologies used are considered official for the quantification of these nitrogen compounds and this existing phosphate compound.

The samples come from two sampling points for the waters of the Santa Cruz River, as shown in Figure 1:

Figure 1 Santa Cruz River sampling points. Source: Adapted from Google Maps

And two sampling points for water from the Ribeirão River (Paranaguá - PR), as shown in Figure 2:

Figure 2 Ribeirão River sampling points. Source: Source: Adapted from Google Maps

The geographic projections were carried out based on the spatial data available on the website of the Institute of Lands and Cartography (ITCG) and on the Geomorphological Chart - Curitiba's Leaf, which makes up the Geomorphological Atlas of the coastal Hydrographic Basin, thus outlining the sample points located in the Paranaguá city, which were produced by the Water and Land Institute (IAT) [17], as shown in Figure 3:

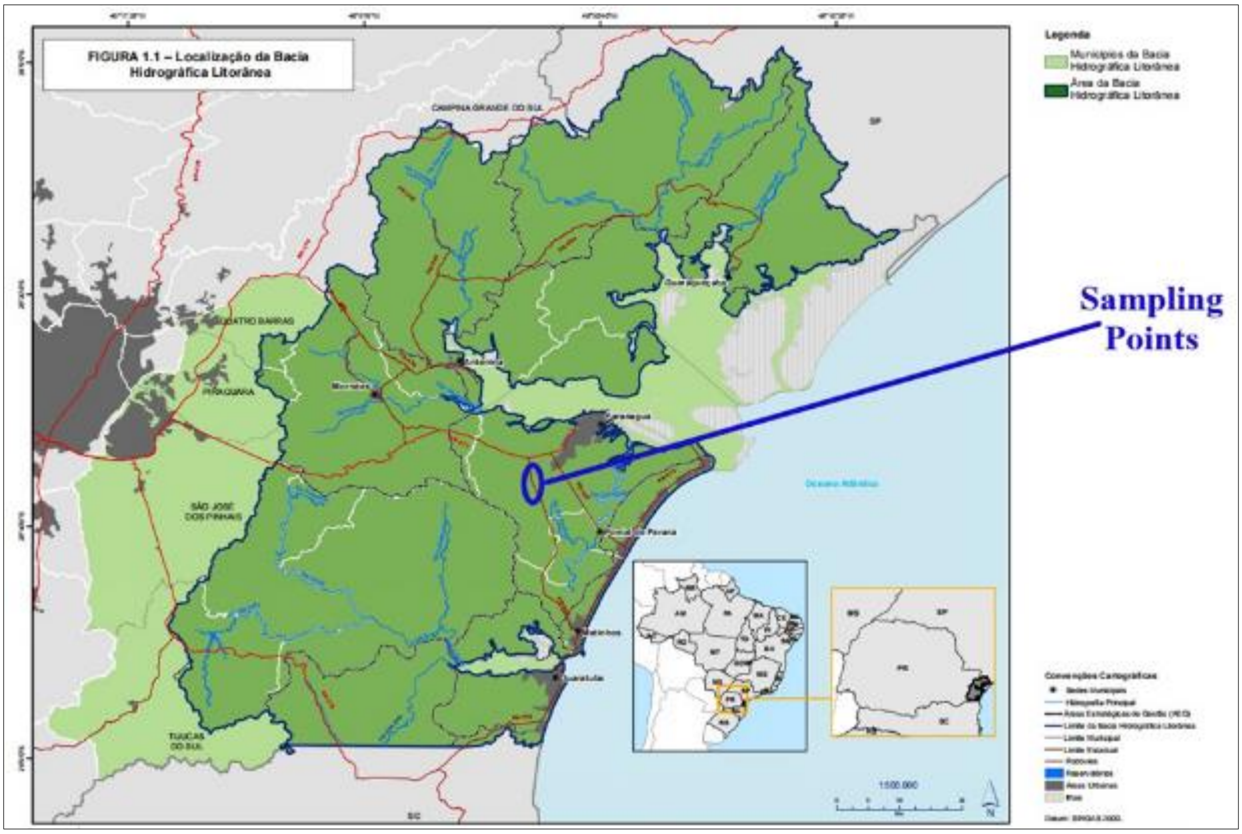

Figure 3 Sampling points in Paranaguá-PR. Source: Adapted from IAT [17]

Both rivers are close and crossed by the PR 508 Highway, an important highway with constant access to the beaches of the State of Paraná and the State of Santa Catarina. The sampling process, and analytical procedure, took place in the space-time cut in the year 2020.

2. Material and methods

This research was carried out on the Santa Cruz and Ribeirão rivers cut by PR 508, located in Paranaguá - PR. The highway that crosses these rivers is an important access from the coast of Paraná to the metropolitan region of the state capital (Curitiba). The riverside population uses the soil for plantations and the rivers for water uses and echo-tourism

The time frame of this study is from the year 2020 and the collections took place in March and October.

The water samples were collected in plastic containers and the temperature was measured using a glass thermometer in the locations shown in Table 1:

Table 1 Location referring to the four sampling points on the Santa Cruz and Ribeirão rivers

	Sampling Point	Coordinate
Santa Cruz River	P1	25°58’11’’ 48°61’81’’
Santa Cruz River	P2	25°58’03’’ 48°61’34’’
Ribeirão River	P3	25°59’48’’ 48°61’67’’
Ribeirão River	P4	25°59’49’’ 48°61’94’’

The river water samples were transported in 1.5L plastic bottles to the Environmental Impact Assessment Laboratory (Lavima) at the State University of Paraná – Paranaguá Campus for analysis.

The determination of dissolved oxygen concentration (DO) in mg L^{-1} was performed using a Lutron DO5519 oximeter. Electrical conductivity and total dissolved solids (TDS) were determined using the mCA150 MS TECNOPON conductivity meter, with the results expressed in µS cm^{-1} and mg L^{-1}, respectively. The turbidity parameters were performed using a Lutron TU430 portable digital turbidimeter. The equipment calibration was previously performed with solutions ranging from 0 NTU to 800 NTU.

After calibrating the bench-top pH meter (model PHS-3E PHTEK) with a pH 7.0 buffer solution and a pH 4.0 buffer solution, potentiometric tests were performed. Determinations were performed with five replicates in order to minimize analysis errors.

Using the Griess method, the concentration of the nitrite ion is determined, adding a solution of sulfanilamide and naphthyl-1-ethylenediamine dihydrochloride (NED) in an acid medium. This fact allows the reaction of the nitrite and a pink solution is obtained, where the intensity is greater at the wavelength of 540 nm in relation to the monochromatic light incident on the initial sample [18, 19, 20].

To quantify the nitrate ion, the nitrite ion method was used, preceded by prior reduction of nitrate to nitrite [21]. The reduction process was carried out using the reducing agent zinc metal [4]. The method adopted for the NH_4^+ ion was the indophenol one (Berthelot reaction) which consists of the reaction of the ion in the presence of fenic acid, sodium nitroprusside, sodium dichloroisocyanurate dihydrate and sodium hydroxide [22], using the wavelength equal to 630 nm [23].

For phosphorus quantification, the molybdenum blue spectrophotometric method was used in the visible region at 660 nm. In this way, orthophosphate ions combine with solutions of ascorbic acid, glycerin, ammonium molybdate and nitric acid, forming the blue molybdenum complex, quantified when producing an analytical curve of phosphorus in the form of phosphate. Therefore, monochromatic light is focused on each of the standard solutions produced, the absorption process obeys the Law of Lambert-Beer [24].

3. Results and discussion

Table 2 presents the representation of the water and air temperature values on the days of sample collection. This measurement is important, as it is an indication of the anthropic process. If there is a significant difference in the equilibrium temperature, values greater than four between the temperature of the air and the temperature of the water resource, it is an indication that substances have been added, and thus some chemical process is taking place in the waters of the rivers.

Table 2 Air and water temperature values, in ºC, obtained during the four samplings

Temperature values / ºC					
Sampling points		**T. Air / March**	**T. Water / March**	**T. Air / October**	**T. Water / October**
P1	Santa Cruz-going	25.0	25.0	25.0	25.0
P2	Santa Cruz-return	25.0	24.0	26.0	26.0
P1	Ribeirão-going	23.0	23.0	25.0	25.0
P2	Ribeirão-return	23.0	23.0	25.0	25.0

Taking into account Conama Resolution No. 357/2005 [15] for the pH which is from 6.00 to 9.00, part of the values obtained oscillate below the minimum value indicated in the indicated norm (Table 3). The incident acidity may come from the leaching of acidic substances into the soil, the use of products added to the crop or other chemical processes that influence the change in the pH of the water, since the collections were carried out at points close to the bridges of Highway PR 508 strategically before and after the passage of water along the highway, but still close to the Highway.

Table 3 Space-time distribution of pH values (PHS-3E PHTEK). Data represented as mean ± standard deviation

pH							
P1-March	**P1-October**	**P2-March**	**P2-October**	**P3-March**	**P3-October**	**P4-March**	**P4-October**
5.64	6.02	5.47	6.15	5.49	6.38	5.45	6.16
5.49	6.45	5.41	6.25	5.43	6.27	5.48	6.17
5.52	6.25	5.50	6.33	5.46	6.24	5.41	6.22
5.60	6.12	5.48	6.28	5.48	6.09	5.43	6.28
5.55	6.24	5.43	6.26	5.47	6.28	5.41	6.28
5.56 ± 0.06	6.22 ± 0.16	5.46 ± 0.04	6.25 ± 0.07	5.47 ± 0.02	6.25 ± 0.10	5.44 ± 0.03	6.22 ± 0.06

As for total dissolved solids (TDS), the values found are in line with the values stipulated by Conama Resolution No. 357/2005 [15], which indicates that, for inland waters, the values obtained should not exceed 500 mg L^{-1}, as shown in Table 4.

Table 4 Space-time distribution of total dissolved solids (TDS) values in mg L^{-1} (MS TECNOPON mCA150). Data represented as mean ± standard deviation

Total dissolved solids (TDS) / mg L^{-1}							
P1-March	**P1-October**	**P2-March**	**P2-October**	**P3-March**	**P3-October**	**P4-March**	**P4-October**
17.34	31.21	17.43	23.61	17.81	25.01	17.36	24.73
17.33	31.45	17.39	23.45	17.80	24.91	17.54	24.73
17.35	31.42	17.39	23.39	17.81	24.90	17.53	24.67
17.33	31.40	17.45	23.41	17.85	24.87	17.45	24.68
17.34	31.38	17.40	23.35	17.80	24.90	17.48	24.68
17.34 ± 0.01	31.37 ± 0.09	17.41 ± 0.03	23.44 ± 0.10	17.81 ± 0.02	24.92 ± 0.05	17.47 ± 0.07	24.70 ± 0.03

Electrical conductivity (Table 5) is linked to ionic species dissolved and solvated in water and closely linked to the concentration of total dissolved solids. The legislation does not establish values for this parameter specifically, however, in agreement with the other variable that this parameter is related to, TDS, it can be understood that the values obtained from the samples represent values considered normal.

Table 5 Space-time distribution of electrical conductivity values in μS cm^{-1} (MS TECNOPON mCA150). Data represented as mean ± standard deviation

Electrical conductivity values / μS cm^{-1}							
P1-March	**P1-October**	**P2-March**	**P2-October**	**P3-March**	**P3-October**	**P4-March**	**P4-October**
34.34	63.00	34.58	48.50	35.29	49.88	34.71	49.84
34.44	62.79	34.50	46.75	35.21	49.50	34.74	48.95
34.41	62.78	34.47	46.64	35.42	49.49	34.69	48.99
34.40	62.61	34.57	46.71	35.33	49.43	34.77	48.99
34.35	62.51	34.48	46.74	35.30	49.37	34.72	49.10
34.39 ± 0.04	62.74 ± 0.19	34.52 ± 0.05	47.03 ± 0.83	35.31 ± 0.08	49.53 ± 0.20	34.73 ± 0.03	49.17 ± 0.38

The next parameter evaluated was turbidity. When this process intensifies, it can harm the photosynthesis process and, in turn, the oxygenation of the water. The results obtained are represented in Table 6, where it is observed that the values obtained are below the maximum limit recommended by the Conama Resolution [15], which is 50 NTU. It is also observed that the results obtained do not change significantly between the samples from the collection points.

Table 6 Space-time distribution of turbidity values in NTU (TU430 Lutron). Data represented as mean ± standard deviation

Turbidity / NTU							
P1-March	**P1-October**	**P2-March**	**P2-October**	**P3-March**	**P3-October**	**P4-March**	**P4-October**
23.5	24.2	23.7	26.7	25.5	27.7	26.0	27.5
23.4	25.3	24.1	26.2	25.7	27.5	26.3	26.4
23.6	26.0	23.8	24.7	25.2	28.7	26.3	25.2
23.5	26.0	23.6	24.5	25.4	28.2	26.3	26.9
23.5	26.0	23.9	26.0	25.3	28.2	26.2	25.3
23.5 ± 0.1	25.5 ± 0.8	23.8 ± 0.2	25.6 ± 1.0	25.4 ± 0.2	28.1 ± 0.5	26.2 ± 0.1	26.3 ± 0.1

The dissolved oxygen concentration (Table 7) showed significant variation between the sample periods. The values observed in March showed higher values than in October. The Conama Resolution [15] considers that they are adequate when they are not less than 6 mg L^{-1}.

Table 7 Space-time distribution of dissolved oxygen (DO) values in mg L^{-1} (DO5519 Lutron). Data represented as mean ± standard deviation

Dissolved oxigen (DO) / mg L^{-1}							
P1-March	**P1-October**	**P2-March**	**P2-October**	**P3-March**	**P3-October**	**P4-March**	**P4-October**
7.9	6.6	7.6	7.2	6.6	7.5	8.2	7.0
7.4	6.8	7.5	7.5	7.0	8.0	7.6	6.9
7.7	7.5	7.5	7.0	7.4	7.6	7.4	7.4
7.5	6.9	7.5	7.1	7.5	7.7	7.5	7.7
7.5	7.0	7.6	7.3	7.5	7.5	7.7	6.9
7.6 ± 0.2	7.0 ± 0.3	7.5 ± 0.1	7.2 ± 0.2	7.2 ± 0.4	7.7 ± 0.2	7.7 ± 0.3	7.2 ± 0.4

Table 8 Space-time distribution of HI727 PCU True Color values. Data represented as mean ± standard deviation

True colour values (PCU or mgPt L^{-1})							
P1-March	**P1-October**	**P2-March**	**P2-October**	**P3-March**	**P3-October**	**P4-March**	**P4-October**
35	15	30	10	95	85	95	90
25	10	25	10	90	80	95	80
25	10	35	10	85	80	90	85
30	15	30	10	90	85	90	85
25	10	35	15	90	85	85	80
28 ± 5	12 ± 3	31 ± 4	11 ± 2	90 ± 4	83 ± 3	91 ± 4	84 ± 4

The results obtained in the True Color parameter (Table 8) of the Santa Cruz River showed values below those recommended by the Conama Resolution [15], which are values lower than 75 PCU. The results obtained in the Ribeirão River samples were superior, probably because there is a higher concentration of dissolved organic matter in this water resource.

The results obtained from the spectrophotometric parameters were performed using solutions with known concentrations. For the element phosphorus in the form of phosphate, the concentrations of standard solutions were 0.15; 0.30; 0.60; 0.90; 1.20 and 1.50 mg L^{-1} and thus the standard curve was traced (Figure 4) where data referring to phosphate Abs = 0.07855 + 0.1997 [P], with linear correlation coefficient R^2 = 0.99889. A similar procedure was performed to quantify ammonium and nitrate ions in different samples. So for the ammonium ion prepared standard solutions of ammonium chloride in the following concentrations: 0.01; 0.05; 0.10; 0.20 and 0.40 mg L^{-1}. As for the nitrate ion, standard solutions were prepared with a concentration equal to 0.1; 0.5; 1.0; 3.0 and 5.0 mg L^{-1}.

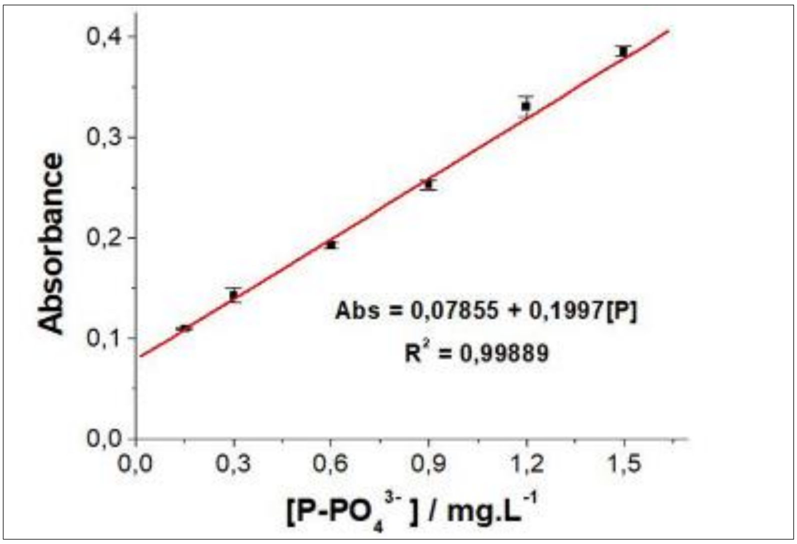

Figure 4 Graphic representation of the standard curve of the element phosphorus, in the form of phosphate, obtained by the molybdenum blue method at 660nm

For the ammonium ion (Figure 5), which is the parameter whose maximum concentration is 3.7 mg L^{-1}, according to Conama Resolution No. 357/2005 [15], it was verified that it presented values below the maximum allowed concentration.

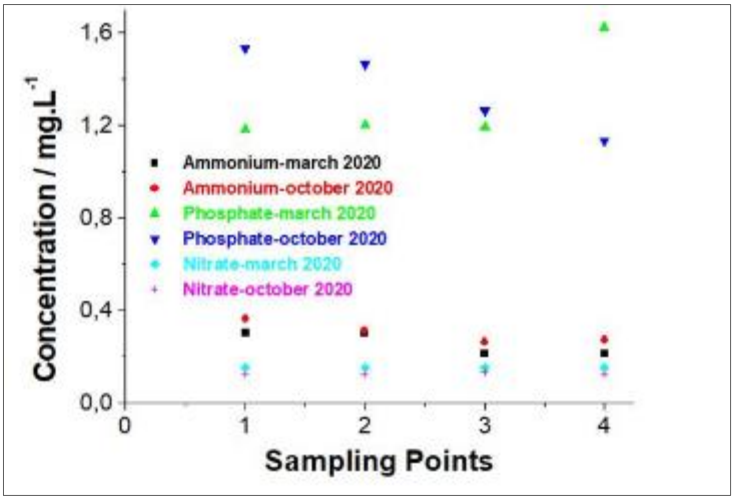

Figure 5 Graphical representation of the concentration values of Ammonium, Phosphate and Nitrate (mg L^{-1}) in samples taken from the Santa Cruz River (1 and 2) and the Ribeirão River (3 and 4)

The nitrate ion (Figure 5) detectable in environments with an anthropization process, as it is consumed by the flora for its development, showed values below those stipulated by Conama Resolution No. 357/2005 [15], which is 10 mg L^{-1} of NO_3^-.

In Figure 5, it is observed that phosphate has a concentration well above the maximum parameter of the legislation of Resolution No. 357/2005 of Conama [15]. The increase in phosphorus concentration is one of the consequences of anthropization linked to the demographic expansion along the rivers and the use of fertilizers in the surrounding crops.

4. Conclusion

It is concluded that the water bodies of the Santa Cruz River and the Ribeirão River in the municipality of Paranaguá - PR, crossed by the PR 508, have been suffering a gradual impact caused by the flow of transport and human actions, which occurred around the PR 508 Highway, because, Phosphorus in the collected samples presents relatively high values.

The increase in phosphorus concentration is not only due to the intense flow of vehicles on Highway PR 508, but also to the use of fertilizers used in plantations on the banks of the referred rivers.

Ammonium did not present values above that established by the Conama Resolution No. 357/2005, however, the samples from the last collection point to an increase in concentration, perhaps due to the presence of the few head of cattle existing on the properties around the sampling points.

This research is important, in order to promote the evaluation of temporal changes suffered by water bodies, by human action verified on a spatial scale, as well as assisting in the anthropic information of the coastal region.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare no conflicts of interest regarding the publication of this paper.

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