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Physical-Chemical Characterization of Peri River, Pontal do Paraná, PR, Brazil

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***Abstract*— *Rivers always went too utilized for the population's benefits, however, environmental impacts caused by humans have resulted in aquatic ecosystems degradation. This fact decreases biological diversity and impairs water availability. Amongst elements which could be quantified to evaluate the impact caused anthropically are phosphorus and nitrogen since the increase of their levels in rivers could result in artificial eutrophication. Thus, the aim of this work was to evaluate the Peri River (Pontal do Paraná – PR) in a spacetime perspective, between 2018 and 2019. It was measured the pH, dissolved oxygen, electric conductivity, total dissolved solids, turbidity, air and water temperature, phosphorus, nitrate, and ammonium in 8 samples points. The majority of the parameters got compatible values with the established with 357/2005 CONAMA's resolution, even the results of the ammonia ion in May 2019 in the points 1, 2, 3, and 4 have shown high values, likely as consequence as leachate from the dump. The parameter pH in point 8, localized in the river source has shown acid values due to soil leaching or the introduction of chemical substances adjacent to this place. As well as past studies, phosphorus has been showing elevated values, which in this set sample collections, data are 50 folds higher than to the established by the CONAMA's resolution, making the Peri River susceptible to eutrophication and environmental deterioration. We concluded that Peri River has been suffering gradually with anthropic impacts, thus, preventive and palliative actions must be taken immediately against the anthropic actions.*

***Keywords*— analytical chemistry, Parana's coast, pollution, water quality.**

I. INTRODUCTION

Rivers always went too used to the population's benefits, allowing the development of several sectors, from recreation activities to industrial purposes, being essential for both local community and tourists (Carvalho, Balduino & Figueiredo, 2016). This importance raises a big dependence upon the rivers, resulting in several impacts in it, changing their physical-chemical and biological features (Kramer, Pereira Filho & Faccin, 2018).

Many of these impacts are caused by human activities, which they were intensified since the industrial revolution, promoting the accelerated development of cities and industries, besides the exponential population's growth (Cunha, Lucena & Sousa, 2017). These impacts have been resulting in aquatic ecosystems degradation, which in turn impair the water availability, affecting not only the environment but also the human quality of life (Filho & Nunes, 2017).

The Resolution nº357 of the Brazilian National Environmental Council (CONAMA, 2005) dispose of the hydric body classification and the environmental guidelines for their categorization, besides establishing the conditions and patterns of waste release. It is possible through this resolution to verify how much a river has been affected by anthropic activities. In the case of parameter's values be in discordance to established values and substance concentrations, the river could be considered impacted. Amongst the elements that could be quantified are phosphorus and nitrogen.

Phosphorus is a limited element in the atmosphere and part of its soluble available form is removed from the soil to the oceans and rivers by erosion and rock lixiviation (Mekonnen, Mesfin M. & Hoekstra, 2017). Furthermore, this element is a key component of the nucleic acids and it is responsible for energy transport through ATP, being for this reason, much used as a fertilizer in crops (Conley et al., 2009). Besides, it is estimated that about 75 to 90% of the phosphorus utilized

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as a fertilizer é carried to the rivers (Sharpley et al., 2003). Together with excessive fertilizer usage, sewage discharge in rivers is another factor that contributes to the increase of phosphorus concentration in aquatic environments (Conley et al., 2009).

Nitrogen in its most steady gaseous form (N_2) is the main substance in the atmosphere, comprehending about 78% of present gases. Its biogeochemical cycle involves the ammonification or mineralization, nitrification, denitrification, fixation, reduction, and synthesis of organic forms steps (Stein & Klotz, 2016). This element has very important functions to living beings because it is an essential component of the nucleic acids and proteins (Conley et al., 2009). Due to its importance to the biota, processes such as production and usage of commercial fertilizes, and energy production, increasing the nitrogen levels in aquatic environments (Vitousek et al., 1997). Nitrogen could be found in rivers as ammonia (NH_3), nitrate (NO_3^-) and nitrite (NO_2^-) (Spiro & Stigliani, 2009). The increase of these substances levels with phosphorus concentration could promote the exacerbated populations' growth of plants and algae, culminating in artificial eutrophication, since these substances are limiting factors in rivers (Anderson, Glibert & Burkholder, 2002).

Although eutrophication is a natural process, which occurs the increasing of the algae populations, artificial eutrophication is a process that occurs when there is an increase of the nutrient's concentration due to human activities (Ghaly & Ramakrishnan, 2017). According to Carpenter et al. (1998), the adverse effects of the artificial eutrophication are (1) increasing of the phytoplankton biomass, (2) switch of phytoplankton population to other toxic species, (3) proliferation of the gelatinous zooplankton, (4) increasing of benthonic and epiphytic algae biomass, (5) changes of macrophyte population, (6) death of the coral reefs, (7) diminished water transparency, (8) depletion of oxygen levels and (9) fish species death. Although the artificial eutrophication occurs as a result of a combination among climate, physical-chemical, and biological factors, the availability of nutrients seems to play a key role in this process (Ghaly & Ramakrishnan, 2017).

Thus, the aim of this study was to evaluate the nitrogen and phosphorus species concentrations, besides other physical-chemical parameters of water quality, along the Peri River (Pontal do Paraná-Brazil).

II. MATERIAL AND METHODS

2.1. Area and sample collection

The study was conducted in Peri River, which is localized near to a dumping ground of Pontal do Paraná city. This river is the only affluent placed at the left of the Guaraguaçu River Margin. Guaraguaçu River has extreme importance locally due to fishing activities and its big water supply. Sample collection was done during August and November 2018 and February and May 2019, in 8 different sampling points representing in Figure 1.

Fig 1 – Aerial image of Peri River (Pontal do Paraná – PR/Brazil) and the eight sampling points.

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The sampling points 1, 2, 3, and 4 are near to houses and the dumping ground. On the other hand, the 5, 6, and 7 sampling points are near to a road. About the 8 sampling point, it is adjacent to the river's source. During the sampling, the air and water temperature were taken by a digital thermometer and the water samples were conditioned in plastic recipients. The river samples were transferred to plastic bottles of 1,5 litters and, posteriorly, carried to the Laboratory for the Evaluation of Environmental Impacts (LAVIMA) at the State University of Parana.

2.2 Potentiometric and turbidimetric analyses

The potentiometric and turbidimetric assays were performed in 5 replicates in the following equipment: pH determination in a bench pHmeter (PHS-3E PHTEK), water turbidity in a mobile digital turbidimeter (TU430 Lutron), dissolved oxygen in the oximeter (DO5519 Lutron), electrical conductivity and total dissolved solids (TDS) in a conductivity meter (mCA150 MS TECNOPON).

2.3 Spectrophotometric analyses

The official method for the nitrite quantification is the Griess' reaction. In this process, the acid medium allows the reaction between nitrite with sulfanilamide solution's and the naphthyl-1-ethylenediamine dihydrochloride, obtaining a pinky-colored solution. The nitrite concentration was quantified in a spectrophotometer at 540 nm (Green et al., 1982; Moorcroft, Davis, & Compton, 2001; Ramos et al., 2006). We used the same methodology to quantify the nitrate ion, however, initially, nitrate was reduced to nitrite using metallic zinc, because of this ion does not react with these substances described above (Reis et al. 2015).

Ammonia quantification was done by the indophenol method (Berthelot's reaction), which consists of the reaction of ammonia with phenolic acid, sodium nitroprusside, sodium dichloroisocyanide dehydrate and sodium hydroxide (Staden & Taljaard, 1997). The solution was read at 630 nm (Rice, Baird, Eaton & Clesceri, 2012).

About phosphorus method, orthophosphate ions combine with ascorbic acid, glycerine, ammonium molybdate, and nitric acid solutions, generating the molybdenum blue complex, which is read at 660 nm (Masini, 2008).

III. RESULTS AND DISCUSSION

The water and air temperature measurements are shown in Table 1. Besides the temperature can influence the metabolism of some organisms, it also could be used as an indicator of pollution. When in situ measurements display a big difference between them, it may indicate the occurrence of thermal pollution in the river, which could be a result of the discharge of heated effluents or removing of riparian vegetation (Dallas & Day, 2004). It seems that is not the case, because we cannot see any big difference between them. The higher temperature measurement was seen at P1 (32ºC) in February 2019, whereas the minimum value was observed at P5, P6, and P7 in August 2018.

Table 1 – Air and water temperature measurements obtained during the four samplings in Peri River, Pontal do Paraná - PR.

	TEMPERATURE							
Sampling Points	Aug/air	Aug/water	Nov/air	Nov/water	Feb/air	Feb/water	May/air	May/water
P1	20	20	26	26	32	32	21	22
P2	19	20	24	24	30	31	21	21
P3	20	20	26	27	31	31	22	22
P4	20	20	27	28	31	31	22	21
P5	19	19	24	23	26	26	20	19
P6	19	19	24	23	26	26	20	19
P7	19	19	24	23	26	26	20	19
P8	19	20	24	24	26	27	20	19

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The pH values are shown in Figure 2. A part of the data oscillated within the recommended by CONAMA's nº357 resolution for continental waters (6.0 to 9.0). The samples obtained values lower than 6.0 could be explained by the influence of some chemical substance or the lixiviation of acid substances in the soil, which is intensified due to the region's pluviometric intensity in some months of the year. According to the Brazilian National Institute of Meteorology (INMET), the months of August and November 2018 were less rainy when compared to February and May 2019, being August 2019 the less rainy period and February 2019 the rainiest month amongst the four samplings taken. We observed at point 8 the most constant values during the year. Although this point is one of the sources of the Peri River, it is localized near to roads, becoming it susceptible to anthropic impacts, once the point 8 has a considerable vehicle flow, including trucks carrying loads of fertilizers and several other chemical substances.

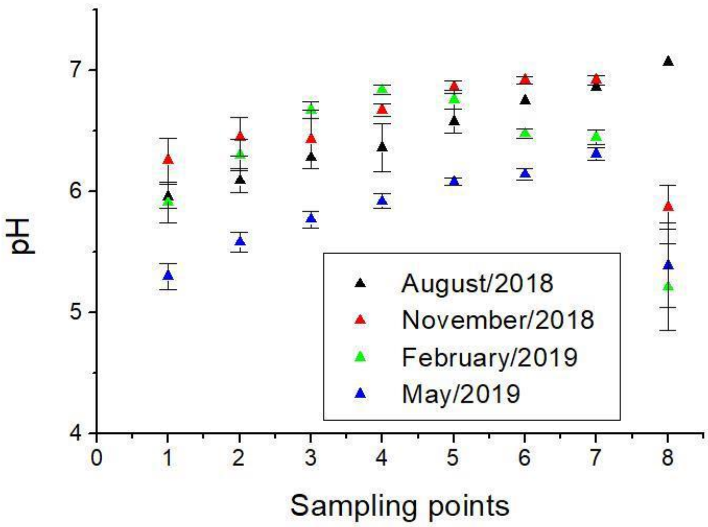

Fig 2 – Space-time distribution of the pH values obtained along Peri River, Pontal do Paraná – PR. Data expressed as mean ± standard deviation

About TDS, we reported that all values are lower than the maximum value recommended by the CONAMA's resolution (500 mg.L^{-1}). The highest measurements were seen during the windy period, making part of the solid substances were carried to the Peri River. TDS values are represented in Table 2.

Table 2 - Space-time distribution of the total dissolved solids values obtained along the Peri River, Pontal do Paraná – PR. Data expressed as mean ± standard deviation.

TOTAL DISSOLVED SOLIDS (mg.L^{-1})				
Sampling Points	August	November	February	May
P1	80.77 ± 1.2	65.5 ± 1.0	115.8 ± 1.5	107.2 ± 1.0
P2	81.01 ± 0.4	78.0 ± 0.8	119.6 ± 2.6	66.3 ± 0.9
P3	82.33 ± 0.7	67.5 ± 0.5	74.4 ± 1.6	66.5 ± 0.6
P4	83.30 ± 0.5	69.1 ± 0.7	74.8 ± 0.6	67.3 ± 1.0
P5	91.80 ± 1.2	74.8 ± 0.3	57.1 ± 0.3	49.7 ± 0.5
P6	97.87 ± 1.1	81.4 ± 1.0	109.5 ± 1.3	52.4 ± 0.5

P7	102.47 ± 1.3	82.3 ± 0.6	56.7 ± 0.8	88.2 ± 0.5
P8	97.17 ± 0.4	31.1 ± 0.2	93.0 ± 1.9	94.1 ± 1.7

Electrical conductivity (Table 3) is directly related to the presence of ionic species in the water. These data trend to represent a part of the values linked to the pH and another part linked to TDS. High values of this parameter in summer could be related to domestic and industrial sewage discharge, agricultural run-off, and organic matter, which in turn, increase the ionic concentration of Ca^{2+}, Mg^{2+}. and Cl- (Hassan, Parveen, Bhat, & Ahmad, 2017). Even though there is no maximum or minimum recommended value for this parameter, we observed that, as most of the pH data showed normal results according to the current Brazilian legislation, so, the electrical conductivity also exhibited values considered normal.

Table 3 – Space-time distribution of the electrical conductivity values obtained along the Peri River, Pontal do Paraná – PR. Data expressed as mean ± standard deviation.

ELECTRICAL CONDUCTIVITY (µS.cm^{-1})				
Sampling Points	August	November	February	May
P1	184.0 ± 1.2	151.4 ± 0.6	227.2 ± 5.7	206.7 ± 1.9
P2	184.3 ± 1.1	172.8 ± 1.9	227.4 ± 2.2	126.8 ± 0.9
P3	190.2 ± 2.4	151.6 ± 0.6	144.1 ± 0.7	127.1 ± 2.3
P4	189.9 ± 1.4	153.6 ± 0.6	143.6 ± 0.6	129.1 ± 1.5
P5	276.5 ± 2.7	160.9 ± 1.1	109.2 ± 0.3	95.1 ± 0.7
P6	277.8 ± 0.9	171.4 ± 1.1	210.6 ± 1.8	102.2 ± 1.0
P7	279.0 ± 2.5	173.1 ± 1.3	110.8 ± 0.7	170.0 ± 2.3
P8	127.7 ± 0.3	65.8 ± 0.3	181.2 ± 4.6	185.1 ± 2.7

The turbidity could be understood as a resistance of light passage through a solution, so, if a river was too cloudy, it can inhibit that sun rays pass through the river surface, impairing the photosynthesis (Dallas & Day, 2004). Thus, we observed that all values (Table 4) are below the maximum threshold, which is 50 NTU. The data during the year does not show much seasonal variation, however, at points 5, 6, and 7, which are near to Engenheiro Argus Thá Heyn Road (PR-407), displayed higher values to the other points, by the higher flow of vehicles, dust, and solid residues of the road.

The concentration of dissolved oxygen, as well as other parameters, showed some variations in its values due to seasonal regimen, receiving the direct influence of the amount of rain in certain periods of the year, temperature, and other factors. We reported the most values are above of minimum threshold (6 mg.L^{-1}). When the dissolved oxygen concentration is lower than recommended by CONAMA's resolution, the biota can die by hypoxia (i.e. depletion of oxygen). The data of dissolved oxygen are shown in Table 5.

Table 4 – Space-time distribution of the turbidity values obtained along the Peri River, Pontal do Paraná – PR. Data expressed as mean ± standard deviation.

TURBIDITY				
Sampling Points	August	November	February	May
P1	21.0 ± 0.55	21.0 ± 1.06	22.2 ± 1.7	20.52 ± 0.2
P2	21.5 ± 0.81	27.5 ± 1.10	23.1 ± 2.4	21.56 ± 0.1
P3	21.6 ± 0.64	20.5 ± 0.26	23.2 ± 1.6	22.7 ± 1.0
P4	21.8 ± 1.06	21.0 ± 0.79	21.6 ± 1.0	21.8 ± 0.2

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P5	27.6 ± 0.59	27.1 ± 1.60	27.5 ± 1.6	22.88 ± 0.2
P6	27.8 ± 0.39	28.0 ± 1.30	26.9 ± 1.7	22.7 ± 0.4
P7	26.7 ± 0.48	28.2 ± 0.37	26.1 ± 1.6	24.32 ± 0.6
P8	26.5 ± 0.41	23.1 ± 0.88	20.6 ± 1.1	0.0 ± 0.0

Regarding the spectrophotometric parameters, assays with standardized solutions were first performed. For phosphate, concentrations of 0.15 were used; 0.30; 0.60; 0.90; 1.20 and 1.50 mg.L-1. Together with the average absorbance values that were quantified in each of these standard solutions, a standard curve was plotted. Figure 3 shows the data referring to phosphate, in the period of May 2019, where the equation of the straight line obtained was represented by Abs = 0.05309 + 0.1841. [P], with linear correlation coefficient R^2 = 0 , 99945. By obtaining the absorbance values of the eight sample points, it was possible to determine the phosphate concentrations in the Peri river. The same procedure was used to quantify ammonium and nitrate, however, with different concentrations of the standard solutions and the reagents used. Subsequently, the mean values of the samples were also determined.

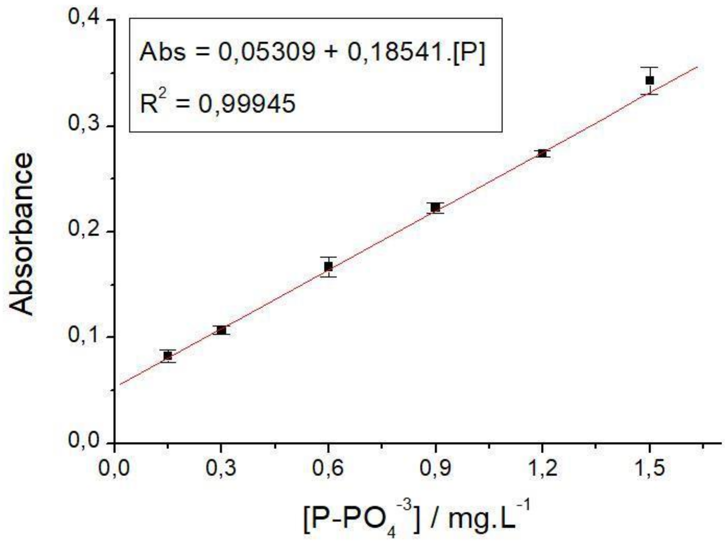

Fig 3 - Representation of the deviation curve of the phosphate, obtained by the molybdenum blue method at 660 nm, in the sampling performed in May 2019.

The ammonia concentration is represented in Figure 4. This ion showed values below to the maximum threshold allowed (3.7 $mg.L^{-1}$, when pH is lower than 7.5). However, in May 2019 we observed a considerable increase in points 1, 2, 3, and 4, likely by the presence of the apparent leachate in the surface of the river since these points are near to the dumping ground. Besides, it is worthy to mention that the February 2019 sampling, the river displayed exacerbated smell and foam. Moreover, (Souza, Gonçalves, Carvalho & Rocha, 2019) indicated that Peri River showed a considerable increase of ammonia concentration from one year to the next, corroborating that Peri River has been suffering even more with pollution.

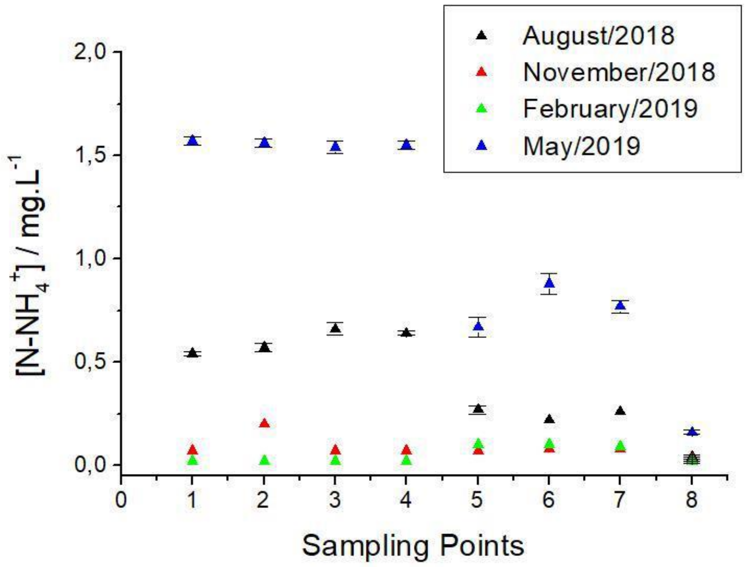

Fig 3 - Space-time distribution of the ammonia concentrations along the Peri River. Data expressed as mean ± standard deviation

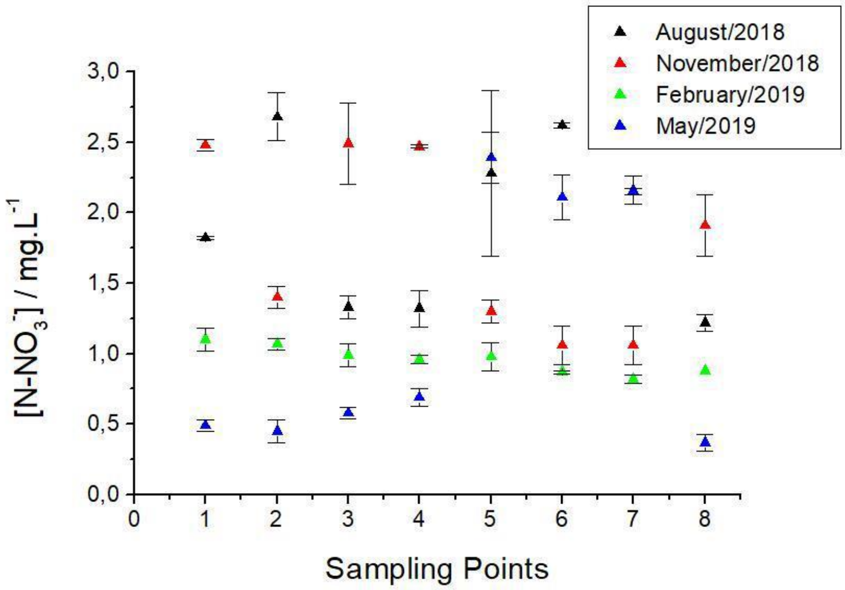

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Fig 5 - Space-time distribution of the nitrate concentrations along the Peri River Data expressed as mean ± standard deviation

Nitrate data are shown in Figure 5. It is only detectable in anthropogenic-impacted rivers, once it is easily incorporated by the plants. Thus, its presence might be considered as a marker of pollution (Hassan et al., 2017). CONAMA's resolution established that the maximum threshold as 10 mg.L^{-1} for nitrate.

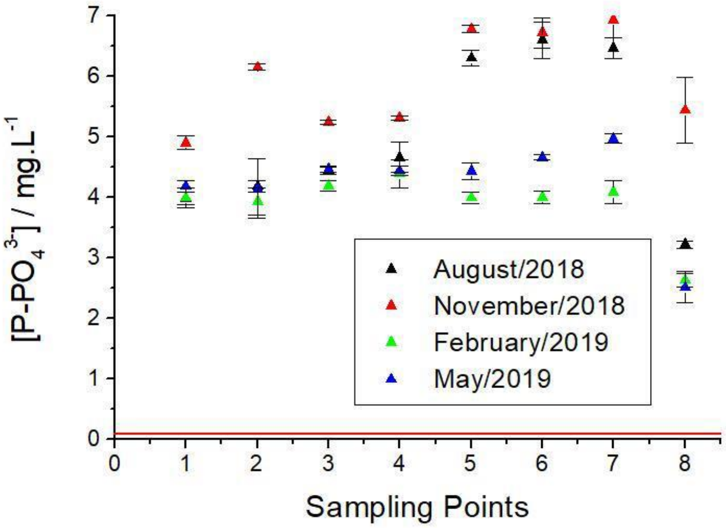

Fig 6 - Space-time distribution of the phosphorus concentrations along the Peri River, Pontal do Paraná - PR. Data expressed as mean ± standard deviation.

Table 5 – Space-time distribution of the dissolved oxygen values obtained along the Peri River, Pontal do Paraná – PR. Data expressed as mean ± standard deviation.

DISSOLVED OXYGEN (mg.L^{-1})				
Sampling Points	August	November	February	May
P1	6.4 ± 0.3	9.5 ± 0.3	9.8 ± 0.1	6.3 ± 0.3
P2	6.5 ± 0.3	8.9 ± 0.7	9.5 ± 0.1	6.3 ± 0.2
P3	6.8 ± 0.6	9.8 ± 0.4	9.7 ± 0.2	6.3 ± 0.2
P4	6.6 ± 0.6	11.1 ± 0.4	9.6 ± 0.2	6.8 ± 0.3
P5	6.8 ± 0.7	8.3 ± 0.3	9.9 ± 0.3	6.5 ± 0.2
P6	6.4 ± 0.8	7.5 ± 0.6	9.7 ± 0.2	6.2 ± 0.2
P7	6.2 ± 0.4	10.7 ± 0.4	9.4 ± 0.3	6.0 ± 0.5
P8	6.5 ± 0.6	9.9 ± 0.5	9.1 ± 0.2	5.9 ± 0.2

In Figure 6, we reported the most phosphorus measurements are about 60 times higher than the maximum threshold recommends by CONAMA's resolution (0.150 mg.L^{-1}). These data are similar to reported by Reis, Cavallet & Rocha, (2011), and Lopes, Carvalho, Gomes & Rocha, (2019), which researches were done in the same coast region of our study. Thus, this high phosphorus concentration can be a consequence not only by the flow of tourists or demographic expansion near to the river but mainly by the mismanagement of transport and storage of fertilizers in the Port of Paranguá, the second biggest in Brazil. Besides of that, previous results of our research group (Souza et al., 2019) reinforce the hypothesis that these high phosphorus levels are related to the tidal cycle and strong influence of the Paranagua's Port. Finally, Souza, Gonçalves, Carvalho & Rocha (2019) also indicated an additional factor of contamination in Peri River is the presence of the dumping ground, localized adjacent to this river.

IV. CONCLUSION

We concluded that Peri River has been suffering gradually with impacts caused by humans, once phosphorus has shown extremely high values. Previous studies reported are a result not only by the flow of tourists in summer and domestic waste but also by the tidal action, carrying the fertilizers from the Paranaguá's Port. Although ammonia does not exhibit values higher than the maximum threshold by the local legislation, in the last sampling it was observed a considerable increase in its levels. Researches as ours are important to evaluate the temporal changes in rivers caused by human impacts, and also examine such effects in a spatially-scale.

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