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Evaluation of Physical-Chemical Parameters of Water Resources Quality from Paranaguá City, PR

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Abstract: *In this work the analytical results of water samples taken from Itiberê River and its affluent Village River are presented. The settlement of Paranaguá occurred, among other places, along these two rivers, which caused deforestation of Atlantic Forest areas for residential construction and commerce in general. To evaluate this environmental impact, analytical tests were carried out in which the nitrogen and phosphorus macronutrients, considered the eutrophic agents, were quantified as well as other physical and chemical parameters such as pH, turbidity and the total residue. For that, we used the potentiometric, turbidimetric, gravimetric and spectrophotometric analytical techniques. These analytical results showed that in some sample points the degradation process is relatively high due to the alteration of pH values and ammonium ion. The excessive presence of the phosphate ion in some sample points, that is, values close to 40 times higher than the values recommended in CONAMA Resolution 357/2005 [1], may be due to uncontrolled demographic expansion, where sewage is directly dispensed into the riverbed.*

Keywords: *anthropogenic activity, nitrogenous compounds, phosphate compounds.*

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I. Introduction

The analytic unit of this study is the water quality in some water resources of Paranaguá city. Localized in the coast of Paraná state, where the municipal head office is between the following geographic coordinates 25°31'12" south latitude and 48° 30'32" west longitude of Greenwich Meridian. The same is limited to the north with Antonina and Guaraqueçaba through Paranaguá Bay, to the south with Guaratuba and Matinhos, to the east with Pontal do Paraná and to the west with Morretes. The county occupies an area of 826 652 square kilometers and is 91 Km from the main city (Curitiba).

As to Paranaguá Seaport, it has 52,9% of Paraná coast population, in a total of 140.469 inhabitants. Paranaguá Seaport is considered the biggest bulk carrier port of Latin America, where there are considerable ship flows [2, 3].

Paranaguá city started with a little population near of Cotinga Island (1550). Afterwards, the same was transferred (1575-1580) to the left bank of Itiberê River. The main reason to occupy this territory was the gold exploration in Paranaguá Bay. The population of the region was formed by a mix of Europeans, mainly Portuguese, Indigenous and Blacks, being the two last in slave conditions. In 1648, it was installed as an administrative unit. In 1841, this administrative unit was rised to the Village category and then, in 1842, to the town category [4].

The urban and economic development of Paranaguá has always been associated to the region rivers throughout the history (Paranaguá Bay and the Seaport). So, since the second half of the century XIX, the port activity has become the focus in economy and definition of urban space organization of Paranaguá. This process rose the city urbanism, without planning and separating physically the town from Seaport. The Seaport operated originally on the Itiberê sides, where it was later settled. The transference of Seaport to Paranaguá Bay started in the final of the century XIX. At last it was inaugurated in 1935 as Dom Pedro II Port. The spatial and environmental changings resulting from the Port function followed the new location of the Port, which resulted in urban expansion to the north. Paranaguá has become responsible for hosting one of the most important Seaports for the movement of foreign Brazilian trade flows. This characteristic affects the structure and the local environment a lot, but economic alternatives aim at the social and ecologically balanced development. By contrast, we have a sad scenery showing that while the port is moving an increasing volume of wealth, it is observed the city's capacity reduction to withhold and transform it significantly for the development, with increasing social returns to the local population. It is observed the necessity to reduce the county dependence from an activity that has high environmental impacts and decreasing social results over the time. In this way, the city will be open to new ideas for sustainable development that will improve regional living conditions [4].

It stands out for some time that the modern ideology was connected to Curitiba because of an archaic and unhealthy image that began to characterize Paranaguá. According to Scheiffer [5], under the hygiene influence that marked the end of the XIX century and the beginning of XX, the image of the Port city generated constraints, associated to dirt and disease.

Guided by the beauty ideology from the beginning of the century, the city center was the main target of the public policies actions under sanitation perspective [5]. The peripheral position of the new Port structure, however, made it possible for migrant workers to occupy less valued areas, being more distant from the central urban and distributed irregularly through the city, without urban planning. These precarious occupation areas were effectively excluded from the urban reforms and in some cases represented by the fragile ecosystem of mangroves already anthropized [6]. Their expansion has also been colliding with the Port area over the years and becoming a problem. Today is even more relevant from the point of view of territorial management due to the lack of planning in the use and occupation process of the soil. Thus, we can consider the need to rethink the planning of the city, since the territorial weight of the port over the city has been superior to the benefits that brings to it.

With the use and illegal occupation of the soil, brings other problems such as environmental degradation and destruction, contamination of water resources and even the emergence of diseases and epidemics. It´s evident that need becomes considering that within the context of the use of water is for drinking, recreation or fishing in it is included the daily lives of individuals who occupy these areas in Paranaguá. With this is in mind we need to see that the areas of the city are not homogeneous, because within them coexist different social categories that even standing in the same spatial context, have different means to find answers to the problems that arise. The health of individuals for example, expressing the impact of material problems on the body, and allows, in a way, a reading of these relations of conflict between the individual and their physical environment. The behavior of man depends largely on the structures in which they are inserted and the system of values and norms conveyed by the social environment to which they refer, and which govern the relations between environment and health and society. Thus the health status of a population is a reflection of "passive" of their living conditions, and where they reside and attend. It is essential to take into account the social responses that are given to problems that arise in the form of social management, not only of health and disease, but also the daily life as a whole [7].

Today, of course, we understand the importance of water for living beings, specially on issues related to their quality of life. It is apparent that the first living organisms appeared on earth surface born in an aquatic environment. By observing the course of life evolution, it is realized that it was shaped by the properties of the aqueous medium in which life began. Thus, to realize the importance of studying and understanding the physical and chemical parameters which shape those concepts are crucial to water quality in both amenable aspects to life, such as their use by humans [8].

Even if you understand the importance of water for the life of living beings, unfortunately the human activity degrades the man, destroys and causes even the scarcity of this resource so essential to life, mainly because these days have increased pollutant emissions significantly in different environmental compartments, i.e. atmosphere, lithosphere and hydrosphere. Despite of the significant efforts to reduce contamination of water resources, to observe the end of this contamination by pollutants is virtually impossible. Most of the time, the water-related problems are related to human impacts caused by human activities, but sometimes these changes are caused by natural activities [9].

So, according to a human perspective, until a few decades ago, it was believed that water was an infinite good and that its self-purification capacity also was. But in the past decades, the fast industrial development, the significant increase in the world population and agricultural productivity brought, as a result, awareness about the quality and availability of water for human consumption. These facts provoke a fast degradation of water bodies. Thus, it was possible to verify the fragility of such auto depurative capacity of the water cycle by the great demand required by the socio-economic systems of contemporary society. It was realized that water is a finite good and therefore, it requires special attention in the management of its use. In addition, the feeling of need to promote the rehabilitation of urban sewage and strict control in industrial waste disposed in water bodies.

Thereby, to evaluate the water qualitative and quantitative manner through different physical, chemical and even microbiological ways, establishes results which are compared with quality standards set by supervisory bodies as in the CONAMA. We can get subsidies to determine the possible activity causing the pollution from the moment we know the quality of the water. And, in more complex cases, even to plan mitigating actions to repair the damage, which can cause changes in the quality of water resources. Specially when we talk about the water quality which can always be related to the natural conditions, therefore the quality refers to a pattern close to the natural before human contact these resources [10].

According to Marques *et al* [11], the constant use of water resources and the introduction of toxins in aquatic ecosystems have required greater number of studies to assess and maintain their quality. So, it is justified the importance of research related to the study of water resources, stressing that water quality can be defined as the set of physical, chemical and biological properties of certain body of water, which quality evaluation criteria depends heavily on purpose of its use.

It is necessary to monitor all these factors and then find these water resources that are constantly damaged by human activities.

II. Materials And Methods

All the samples were collected on the surface of the water resource, in other words, the depth was not more than 30cm. The ten selected geographical points were in the city of Paranaguá coastal region in Paraná State using accessibility criterion, as well as the connection between the sample points. It was also selected a collection point that was located in conservation and protected area, since this region has no significant human activities. This site was identified as a point 10 where the pier is sometimes the palm heart forest park. All nine collection points go around the city with strong human activity, such as the presence of waste from household, including sewage; use of these areas for fishing and housing construction; other forms of contamination, drastically changing the landscape in these regions. Among the nine sample points, three are located in the Rio da Vila and five samples beyond the point 10 are located in Rio Itiberê. The first sampling point is located in the Bay of Paranaguá, specifically in the neighborhood of Rocio, near Paranaguá Port Dom Pedro II. The ten sampling points are better observed through the map shown in the Figure 1.

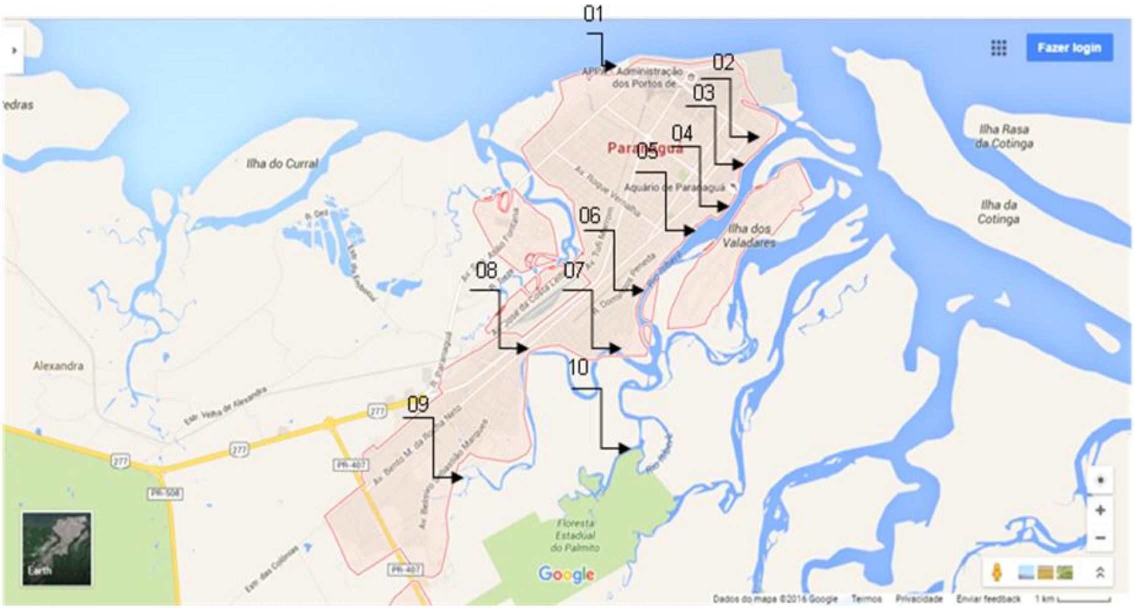

Figure 1. Map of Paranaguá City where the arrows represent the ten sampling points (Source: adapted from Google Maps).

The analytical tests were performed in samples taken at two collection periods with methodologies considered official [12]. The first colleting sampling occurred on 04.19.2016, in a period of high tide. The second gathering took place on 07.02.2016, in a very low tide period. After the collection, the samples were transported to the Environmental Impact Assessment Laboratory (LAVIMA) of the State University of Paraná, *Campus* of Paranaguá, and stored in the refrigerator. During the sampling process, the geographic location of the sampling points was determined (Table 1), and also, each one was determined by its temperature and air in relation to the sample. Analytical tests performed in the laboratory were determined with five replicates, to increase the confidence of the results obtained due to statistical analysis, and minimize the possible errors that are usually verified in all analytical process.

Table 1. Geographic coordinates of the ten sample points verified by GPS During the collection of water samples in Paranagua.

Sample Points	Geographic Coordinates
01	- 25,503508 – 48,531517
02	- 25,515965 – 48,300259
03	- 25,519173 – 48,503567
04	- 25,524216 – 48,505627
05	- 25,527567 – 48,509228
06	- 25,534174 – 48,520622

07	- 25,541641 – 48,524563
08	- 25,551502 – 48,546818
09	- 25,581999 – 48,564016
10	- 25,569498 – 48,529549

A spectrophotometer U2M Quimis was used for the spectrophotometric determinations of this study making it possible to determine the concentrations of ammonium and phosphate ions by the indophenol blue method [13, 14] and molybdenum blue [15, 16], respectively. In both methods absorbance values in the visible region were determined and from these values were determined the concentrations of the studied ions. Recalling that these methodologies relate to Lambert-Beer's Law, that is, the higher the concentration of the species in solution the greater the amount of light absorbed will be [17].

For gravimetric tests were used: a heater plate (DB model), the Biomixer (IVAC model greenhouse and DeLeo A1SH) and a bio-accurate analytical balance of the FA2101 model. In the potentiometric assays was used the benchtop pH meter (PHS-3E model PHTEK), calibrated with solutions of pH 4.01 and 7.00. Conductivity Measurements were realized with the Bench Conductivity Meter (ITMCA-150). The salinity determinations were performed using the optical refractometer (CHR 200ATC). The turbidity determinations of the samples were realized in the digital portable turbidity meter (TU2106 AKSO), after the calibration of the equipment with 0 NTU solution and then with solution 100 NTU.

III. Results and Discussion

The first tests showed measurements of the air temperature values and the water sample in situ. While many parts of Vila River and Itiberê River banks were busy due to the real estate expansion in the results obtained (Table 2) it is clear that large or reducing concentrations of oxidizing agents were not made because of the temperature balance between the two environmental compartments in the sampling points, during the two sampling periods, which did not exceed 2°C.

Table 2. Obtained results in the measurement of water and air temperature, in situ, samples collected in April and July of 2016, respectively.

Collecting points	*First Sampling*		*Second Sampling*	
	Water Temperature / °C	*Air temperature / °C*	*Water Temperature / °C*	*Air temperature / °C*
1	28,0	28,0	19,0	18,5
2	30,0	30,0	19,0	18,0
3	29,0	29,5	18,5	18,0
4	29,0	30,0	18,5	18,0
5	31,0	29,0	19,0	18,0
6	30,0	31,0	21,0	20,0
7	31,0	30,0	19,5	19,0
8	30,0	30,0	20,0	18,5
9	27,0	27,0	18,0	16,0
10	28,0	28,5	18,0	17,5

When we look to the Table 3 it is clear that the values of pH are directly related to the values of the concentration of ammonium ion, since the tendency is the higher the concentration of ammonium ion in aqueous medium, the lower the water pH [16] will be. This is associated with ammonium ion hydrolysis process in an aqueous average (1), which occurs due to release of protons in the water resources, changing the pH of the medium [18].

$$NH^{+}_{4(aq)} + 2H_2O_{(\ell)} \rightleftarrows NH_4OH_{(aq)} + H_3O^{+}_{(aq)} \qquad (1)$$

The few values that come in clash with this premise may be related to other substances that were launched in the water resources due to illegal sewage networks as well as in the official sewerage system.

Table 3. Results obtained in pH values and nitrogen element concentration, in the form of the ammonium ion in the samples collected in April and July of 2016, respectively.

Collecting points	*First Sampling*		*Second Sampling*	
	pH	*Ammonium / mg L^{-1}*	*pH*	*Ammonium / m L^{-1}*
1	7,45±0,45	0,27 ± 0.00	6,98±0,09	0,30±0,01
2	7,08±0,19	0,24 ± 0.02	6,84±0,05	0,25±0,02
3	7,40±0,28	0,22 ± 0.00	6,79±0,05	0,23±0,00
4	7,35±0,15	0,21 ± 0.01	6,86±0,02	0,22±0,02
5	7,29±0,06	0,25 ± 0.01	6,67±0,25	0,26±0,01
6	7,05±0,08	9,28 ± 0.24	7,08±0,09	9,52±0,03
7	7,28±0,08	0,56 ± 0.01	7,02±0,13	0,63±0,01
8	7,08±0,14	0,51 ± 0.00	7,24±0,06	0,57±0,00
9	6,77±0,09	11,86 ± 2.60	7,41±0,05	12,24±0,30
10	6,76±0,11	0,15 ± 0.01	6,79±0,14	0,15±0,01

The two sample points (6 and 9) with higher values in ammonium concentrations are those where the population of the city makes illegal connections to the sewer system. Next to the sample point 6 there is a single sewer system, and periodically the sludge of this system is removed by trucks, but the liquid portion, when in excess, overflows and reaches the Itiberê River depositing a considerable concentration of urea and ammonium. The tests results evaluating the turbidity in the samples are shown on Table 4. These results make clear that higher values are obtained on the sample points 6 and 9, although these are still proposed according to the CONAMA and its resolution 357/2005 [1].

Table 4. Results obtained from the turbidity values of the samples collected in April and July of 2016, respectively.

Sample Point	*First Sampling / NTU*	*Second Sampling / NTU*
1	7,18±0,50	2,10±0,05
2	3,91±0,08	3,69±0,76
3	4,79±0,44	3,38±0,04
4	9,62±0,43	4,69±0,67
5	7,24±0,40	8,32±0,24
6	34,62±0,09	30,65±0,13
7	4,69±0,75	2,49±0,10
8	7,24±0,35	1,56±0,18
9	10,00±0,64	5,63±0,37
10	14,91±0,17	3,02±0,58

The Table 5 shows the results of three linked physical and chemical parameters: conductivity, salinity and total dissolved solids.

These results clearly show that all sampling points suffer influence of the tide, with the exception of point 9. This sample point is located on the village river bed region that is not influenced by the tide. But the sampling point 6 is positioned in a small part of Itiberê River, so the influence of the tide occurs on a smaller scale.

Table 5. Results obtained in the electrical conductivity, salinity and the total dissolved solids values, in the samples collected in April and July of 2016, respectively.

Sample Point	*First Sampling*			*Second Sampling*		
	Conductivity / μS cm^{-1}	*Salinity /%*	*STD / mg.L^{-1}*	*Conductivity / μS cm^{-1}*	*Salinity /%*	*STD / mg.L^{-1}*
1	38 120±286	31,6± 0,9	28,9±2,2	43 892±773	27,5±1,2	25,0±0,4
2	38 025±685	29,6±1,1	28,5±0,9	34 120±738	27,0±0,6	24,9±0,5
3	38 060±673	26,4±0,5	27,8±1.5	30 380±164	26,8±0,6	24,9±0,5
4	37 900±797	25,0±0,7	29,9±2,4	30 140±167	26,2±0,8	24,5±0,4
5	35 480±249	25,0±0,7	29,4±2,8	30 100±122	25,1±0,7	24,3±0,7
6	12 922±272	6,4±0,5	7,2±0,2	10 038±229	6,2±0,3	6,7±0,1
7	33 760±602	21,2±1,1	23,1±1,3	29 560±305	21,1±1,1	18,4±0,3
8	19 763±388	8,8±0,8	11,2±1,3	26 148±778	16,4±0,9	14,5±0,3
9	98,34± 0,66	0,0±0,0	0,24±0,04	372,30±0,71	0,0±0,0	0,13±0,02
10	10 240±115	5,8±0,3	4,9±0,1	13 104±75	7,7±0,5	8,9±0,1

In order to corroborate and present the results in a didactic way, it is possible to observe Figure 2. It can be seen that the farther away from the mouth of the Itiberê River the lower the electrical conductivity values of the samples will be. The highest concentration is in the continental waters and the lowest is in the ocean waters.

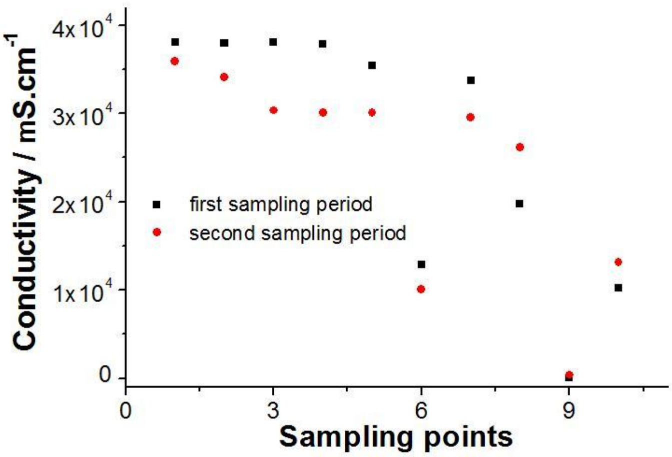

Figure 2. Graphical representation of the electrical conductivity values of the samples taken in the first and second sampling periods.

One of the most worrying results was the phosphorus element in the form of phosphate ion. According to Resolution 357/2005 of CONAMA [1] the element phosphorus concentrations should not exceed 0,150 mg L^{-1} in lotic environments. But on Table 6 is observed that the smallest value is greater than 3 times the maximum amount permitted by this standard. Already the highest value is more than 37 times of the allowed value.

Table 6. Results obtained from the element phosphorus, in the form of the phosphate ion, in the samples collected in April and July 2016 respectively.

Sampling point	*First sampling / mg.L^{-1}*	*Second sampling / mg L^{-1}*
1	0,46±0,02	1,34±0,15
2	0,60±0,04	1,24±0,09
3	0,48±0,07	1,60±0,14
4	0,90±0,02	1,59±0,15
5	1,41±0,13	2,37±0,27
6	4,87±0,23	5,65±0,25
7	1,43±0,05	2,91±0,11
8	1,52±0,18	1,61±0,12
9	2,94±0,38	2,60±0,09
10	1,94±0,26	2,09±0,13

IV. Conclusion

By evaluating all the analyzed parameters, the element phosphorus is the most worrying due to its concentrations that exceed more than 37 times the maximum value of this element in lotic water resources, according to the values recommended by Resolution 357/2005 of CONAMA [1]. With these results it is stated that these waters have a strong eutrophic factor.

By punctually evaluating, the most affected points by the anthropic impact are the sampling points 6 and 9. Beside the sample point 6 there is a single sewer system, and periodically the sludge of this system is removed by trucks, but the liquid portion, when in excess, can overflow and reach Itiberê River and deposit a considerable concentration of urea, ammonium and phosphate. The sample point 9 is located where the sewer system does not exist and for this reason the local population builds illegal connections of sewage that flow directly into the Village River bed providing high concentrations of ammonium and phosphate ion.

The results related to the concentration of the ammonium ion are directly related to the pH values obtained in the evaluated samples, since the higher the concentration of this ion, the lower the pH values observed in these waters. These results corroborate the concepts about the hydrolysis of weak bases cations, that is, those weak bases cations that show low values of ionization constant.

Another factor observed was the values of electrical conductivity that decreased as samples were withdrawn farther and farther away from the river mouth. Thus, it is observed that the greater the distance of the river mouth, the lower the values of the electrical conductivity samples, and in turn the lower the concentrations of total solid residue.

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