Physical-Chemical Parameters Evaluation of Pery River Waters in Pontal do Paraná, PR

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Abstract: This study presents the results of chemical and physical determinations carried out on samples taken from the waters of the Pery River, one of the tributaries of the Guaraguaçu River. This body of water is located on the coast of Paraná, nearby the "Dumping Ground" of the city of Pontal do Paraná. The concentrations of phosphate and nitrogenous nutrients present at the site were determined, as well as other physico-chemical characteristics such as pH, turbidity and dissolved solid residue. The methodology used for the quantification of phosphorus was molybdenum blue. Yet, for the quantification of the nitrogen in the form of the ammonium ion, the indophenol blue method was used. For the determination of the nitrogen in the form of the nitrate ion the Griess method was used, then the reduction of nitrate to nitrite. The evaluation of the results were performed based on the values established by the Brazilian legislation, through Resolution 357/2005 of CONAMA, where it was noticed that the phosphorus concentration exceeded more than sixty times the maximum amount recommended by this resolution. In the case of dissolved solid waste, the international standard for inland waters is 500 mg L⁻¹ and three samples from the first sampling cycle exceeded this value. Therefore it is perceived that the said river is suffering with this anthropic activity.

Key words: Potentiometry, gravimetry, spectrophotometry, anthropic contamination.

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I. Introduction

The aquatic ecosystems are environmental compartments that more incorporate substances coming from natural causes, in other words, without any human contribution. Even if those substances come in low concentrations, they alter the chemical behavior of the water body and their more important uses [Reis; Cavallet; Rocha, 2014]. That interference produces serious problems in the water quality used in different needs for human consumption. So, investigations and investments are necessary for the recovery of that water resource reached [Rocha; Rosa; Cardoso, 2009].

Thus, in the rivers and streams close to the occupation process and to the use of the soil by man, the process of water eutrophication occurs. This happens mainly due to the high introduction of macronutrients, specially phosphorus, nitrogen and potassium, during soil maintenance [Cunha; Rocha, 2015]. In the margins of this water resource is easily perceived the eutrophic process, since there is flowering excess on the banks, as well as their silting process. In this way, the eutrophying process decreases the penetration power of sunlight in the deeper waters, as well as the amount of dissolved oxygen in this region. In turn, the diversity of aquatic species in this environment decreases, whether they belong to fauna or flora aquatic [Branco, 1986]. For all these factors, it is too relevant to evaluate the level of ions, components of these macronutrients, in the continental water reserves.

Nitrogen and phosphorus are the chemical elements that most trigger the eutrophication process of these surface waters, specially when they occur in the most soluble anionic form [France; Moraes; Rocha, 2017]. These chemical elements are among the major nutrients that limit grains primary productivity in agriculture. So, in the water resources close to the agricultural production, they also influence the variety and abundance of aquatic organisms [Marguti; Ferreira Filho; Piveli, 2008].

Nitrogen is introduced into aquatic environments through three ways. The first is the solubilization of gaseous species in rainwater. In this case, sites with strong anthropogenic predominance have higher concentrations of NOx compounds and higher amounts of soluble compounds of the chemical element. The second form is the biological fixation where specific bacteria can transform the nitrogen gas in one of the soluble nitrogen compounds. And the third way is by the allochthonous origin, that is, deposits formed in the

region where the element was not found, but was transported by the water resource to that place. The concentration levels of their forms dissolved in water resource can be influenced by the type of vegetation and its activities. The main forms that nitrogen is found in aquatic systems are ammonia (NH_3), ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), besides organic forms dissolved and particulate in their environment [Spiro; Stigliani, 2009].

The nitrogen element occupies a prominent position among the elements essential to the development of plants [Reis et al, 2015], besides being directly connected to different vital processes that are linked to plants and living beings development.

The most stable form of a chemical element is the one which presents the highest number of oxidation. In the case of the nitrogen element, in an aerobic aquatic resource, the nitrate ion prevails [Baird, 2008]. During the natural process of ammonium ion nitrification and its weak ammonia base, they are oxidized by nitrosomonas bacteria forming nitrite. When it undergoes by bacterial nitrobacter attack, nitrate is directly formed [Branco, 1986]. This natural process is facilitated by the presence of oxidizing chemical species, which are normally intentionally added to the environment. In both cases, the ionization of weak acids and weak bases constants, allied to the Châtelier Principle, facilitate and promote this oxidative process [Brown; LeMay; Bursten, 2007].

Phosphorus is a scarce chemical element in the biosphere, but it is essential for living organisms working and growth. This element occurs in low concentrations naturally. This is why it is considered, in aquatic ecosystems, the main limiting factor of productivity and therefore, it is pointed out as one of the major responsible for eutrophication processes [Cassol et al, 2012].

The quantification of these macronutrients is very important to visualize their availability in water resources, since the lack or excess of them is harmful. There are several techniques available to quantify them. The main factors for the use of one technique or another depend mainly on the availability of the appropriate equipment as well as the limit of quantification desired.

In this study, the concentrations of nitrogen and phosphatic nutrients present in the waters of the Pery River by spectrophotometric technique were evaluated. Other physico-chemical parameters such as pH, turbidity and total dissolved solids were also evaluated in two distinct periods, called high and low season. This river is the only tributary of the Guaraguaçú River, which is located on the left bank of the river. The Guaraguaçú River is considered one of the most important rivers in the Paraná coast due to the volume of water and fishing activities in it [Sato; Angulo, 2002]. The importance of evaluating the physic-chemical characteristics of the Pery River waters is because both Guaraguaçú River and its tributary cross the Argus Thá Heyn Highway (PR-407). This is one of the highways where the tourists go across the Paranaense state and other Brazilian states to travel to this coast besides laying on different rural properties in the coastal region. Also located alongside the Pery River is the "garbage" deposit of the city of Pontal do Paraná, where the waste produced in this municipality is disposed daily. In this way, the Pery River receives part of the "slurry" produced by the decomposition of this waste, as well as the particulate materials that are transported by the air due to the action of the winds. And so, these environmental contaminants are transported to the Guaraguaçu River.

Experimental method

a) Study field and sampling points:

The Pery River is the only affluent of Guaraguaçú River, located on the left shore of the same. The junction from these two rivers occurs in the Pontal do Paraná county showing coordinates of Latitude 25°41'48'' S and Longitude 48°31'07'' W. The same is located about 2Km of distance from the town hall of Pontal do Paraná county, PR. Concerning the fauna and flora, the river region is composed by a riparian forest, among others species of aquatic plants that cover the surface of some points on route of the hydrous body. It is possible to observe the presence of various fauna species that overfly the local like Black-faced Vulture (*Coragypsatratus*), in addition to other animals that are also found in the county, as dogs and cats.

The surface samples of water resource were collected in eight geographic points, distributed over the route of Pery River. The choice of these geographic points occurred by observing the access to the same. So, it was possible to identify the changes in the local water quality and a possible interference through the pollutants activities located near the river, like the "Dumping Ground" that receives discard materials from the Pontal do Paraná city, PR. The sample points are located in the geographic coordinates, according to Table1.

Points	Geographic Coordinates
1	-25.697405, -48.502193
2	-25.697409, -48.501961
3	-25.697109, -48.501926
4	-25.696712, -48.501781
5	-25.687590, -48.490334
6	-25.687660, -48.490341
7	-25.687445, -48.490204
8	-25.687334, -48.490189

Table 1 Geographic coordinates of Pery River collection points.

The samplings were realized during two consecutive years, from December 2015 to May 2017. During the first year, called Stage 1, samples were collected in two specific periods, in December and May. The first sampling was in full high season, in other words, season of the year that results in a greater flow of tourists in the county. The second sampling happened in the denominated low season, therefore with low frequency of tourists. During the second year, called Stage 2, four samplings were realized in 2016 and 2017. Two of these samplings happened in the period of high season and the two others in the low season, over the months of September, December, March and May respectively. In each one of these sample points the sample collect was made with the assistance of a handling polyethylene collector. Then, these samples were stored in plastic bottles and brought to the Environmental Impact Evaluation Lab (LAVIMA) located in State University of Paraná - *Campus* Paranaguá to carry out analytical determinations. Each sample's analytical assay was made five times and then, the average values given. It's done to minimize the possible operational mistakes.

b) Materials and reagents

All the solutions were prepared with distilled water and analytic degree reagents. The experimental measures were realized in laboratory with a temperature of $25\pm2^{\circ}$ C.

The spectrophotometer essays were realized with a support of spectrophotometer U2M Quimis, where all the tests were preceded by the blank determination. Therefore, it was possible to determinate the concentration of ammonium, nitrate and phosphate ions using the Lambert and Beer Law. In the potentiometric essays, a portable pHmeter mpa-210P MS TENOPON model was used. Yet, samples definitions were measured in the portable digital turbidimeter TU430 AKSO after its calibration with solution varying from 0 NTU to 800 NTU.

The following equipments were used to carry out the gravimetric essays: Heating plate DB-IVAC model from Biomixer, a Kiln A1SH model from DeLeo and a Balance FA2101 da Bioprecisa. In a second moment, both the conductimetric essays and the gravimetrics ones used a conductivity meter Mca150 MS TECNOPON. Finally, It was used a portable meter DO-5519 from Lutron to quantify the dissolved oxygen in the water.

c) Analytical methodologies:

The quantity of total dissolved solids present in each sample was determined using a bioprecision balance FA2101. Afterwards, the mass of each empty recipient used in this essay was determined in the kiln DeLeo and in the desiccator to reach the room temperature. Then, around 30 ml were added in the recipients of the water sample from Pery River and verified the exact liquid mass used in each essay. From each sampled point five essays were reproduced. So, these recipients with the sample volumes were carried to the heating plate until all evaporation of the liquid in the recipient. The recipients were put in the kiln for two hours. Finally, the mass was determined after reaching the room temperature in the dissector and done the calculations for the quantification of dissolved sediments.

For the second study, the quantity of total dissolved solids was given using a conductivity technique. At this moment, the conductivity meter mCA150 MS TECNOPON was used. After the calibration in Potassium Chloride solution with conductivity 146,9 μ S cm⁻¹, five essays for each sampling point were carried out to reduce the error rate of the obtained results.

The nitrogen spectrophotometric results were done evaluating two ions, the ammonium and the nitrate.

The concentration quantification of ammonium ion was given according to the methodology of Indophenol depleted in Standard Methods [RICE et al, 2012] using the phenolic acid solution, Sodium nitroprusside, Sodium Hydroxide and Sodium Hypochlorite. After 30 minutes of reactive solution addiction in recipients, the reading of intake values of each recipient was concluded in the spectrophotometer wave-length of 630 nm with the formation of indophenol blue coloration [SILVA et al, 2006].

The ion nitrate determination by the Griess method [GREEN et al, 1982] was initially reduced the same as for nitrite using metal zinc powder. The reduction reactive process from nitrate to nitrite occurs by the sum of equations (1, 2, 3 and 4), as shown by Reis et.al (2015).

$NO_{3(aq)}^{-} + 4H_{(aq)}^{+} + 3_{e}^{-} \leftrightarrow NO_{(g)} + 2H_{2}O_{(l)}$	$E^{\circ} = +0,96 V$	(1)
$Zn_{(s)} \leftrightarrow Zn_{(aq)}^{+2} + 2_e^{-}$	$E^{\circ} = +0,763 V$	(2)
$NO_{(g)} + H_2O_{(l)} \leftrightarrow NO_2^-(aq) + 2H_{(aq)}^+ + e^-$	$E^{\circ} = -1,00 V$	(3)
		-
$NO_{3(aq)}^{-} + 2H_{(aq)}^{+} + Zn_{(s)} \leftrightarrow Zn_{(aq)}^{+2} + H_2O_{(l)} + h_2O_{(l)}$	$NO_{2(aq)}^{-} E^{\circ} = +0,723 V$	(4)

After the necessary time for the reduction process without shaking, the reducing agent was filtered and separated from the samples [CORRÊA, ZACHARIAS, ROCHA, 2016]. In the filtered ones, sulfanilamide solution with naphthyl-1-ethylenediamine bichlorohydrate in mid acid was added. After 15 minutes, the absorbance in the spectrophotometer U2M Quimis in the wavelength 545 nm was calculated.

For the phosphate concentration determination, the blue molybdenum methodology was applied, as described in the Standard Methods [RICE *et al*, 2012], which means the application of ammonium molybdate, nitric acid, ascorbic acid and glycerin solutions. After the solution addiction, the recipients remained 15 minutes for a reaction time. At last, the lectures were performed in each flask in the spectrophotometer in wavelength of 660 nm [MASINI, 2008].

II. Results and Discussion

The sample and air temperature determination values, in its environment, are a good sign to verify if some chemistry process is occurring in the water resource. Mainly when the difference between two values of temperature is excessive and the essay is carried out *in loco*. On table 2 these values are observed and verified that the same happens very close one from another in all the sampling periods except in the month of May on Stage 1 and 2. These samplings show that the values difference between the two temperatures are higher in the sample points closer to the "Dumping Ground", in relation to the other periods, indicating a possible superior addiction of "slurry", and in this way, the addiction of substances that cause this temperature difference.

Stage 1						Stage 2						
	First sampling Second sampling			First sampling Second sampling		pling	Third sampling		Fourth sampling			
	Decem	ber	May		September		December		March		May	
Sample	Water °C	Air °C	Water ^o C	Air °C	Water °C	Air °C	Water °C	Air°C	Water °C	Air °C	Water °C	Air °C
1	23,0	24,0	24,0	21,0	19,0	22,0	24,0	21,0	28,0	28,0	21,0	15,0
2	22,0	22,5	23,0	21,0	20,0	21,0	23,0	21,0	26,0	25,0	20,0	15,0
3	23,0	23,5	23,0	21,0	20,0	22,0	23,0	21,0	27,0	26,0	21,0	14,0
4	22.5	23,0	23,0	20,5	20,0	22,0	23,0	20,5	26,0	26,0	21,0	14,0
5	20,0	20,0	21,0	20,5	18,5	19,0	21,0	20,5	24,0	23,0	17,0	16,0
6	21,0	21,5	21,0	20,5	18,0	19,0	21,0	20,5	24,0	23,0	17,0	14,0
7	20,5	20,5	21,0	20,5	18,5	19,0	21,0	20,5	25,0	24,0	17,0	15,0
8	20,0	20,0	20,5	20,0	18,5	18,5	20,5	20,0	24,0	24,0	17,0	14,0

 Table 2-Temperature values of water and air obtained from the eight sampling points.

Evaluating the pH values obtained during the analytical determinations, no situation was established above the considered normal values, according to specific norms. These values have remained in two sampling periods, between the maximum and minimum limits recommended by the Resolution N° 357/2005 do CONAMA for continental waters, where the values varied between 6,45 and 7,20 in the two samplings periods, except for the point 8, which showed low pH values in the last periods of sampling, meaning more acidic characteristics than the other sample points (Figure 1).

It is also observed in this point the biggest variations result of pH values, although it's a water spring that flows out in Pery River beside Engenheiro Argus TháHeyn Highway (PR-407) which is more susceptible to external influences. During the period of intense rainfall the soil may leach and thus solubilize substances with acidic characteristics which are taken to the river course.



Figure 1 –pH average values obtained from the results of essay realized in the samples removed from eight geographic points of Pery River – a) Stage 1; b) Stage 2.

From the second sampling of Stage 2 it was possible to carry on the water turbidity essays (Table 3). All the obtained results, in this physical essay, were lower than those established by CONAMA (<40NTU). Even so, a high value variation is observed, and also external sources make one region shows larger values than other ones. In the second sampling is observed that the 5, 6 and 7 points closer to the Engenheiro Argus Thá Heyn Highway (PR-407) showed larger turbidity values, denoting some anthropic effect close to the Highway related. Yet, in the fourth sampling, points 1, 2, 3 and 4, which are closer to Pontal do Paraná "Dumping Ground", showed larger turbidity values, demonstrating that substances deposited in the Dumping Ground were moved to Pery River waters and interfered in this specific essay results.

Table 3 – Representation of turbidity values measured in NTU (Nephelometric Turbidity Unit), in the eight
sample points, from 2 nd to 4 th collection period of Stage 2.

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	Second sampling	Third sampling	Fourth sampling
Samples	December	March	May
1	7,75±1,25	2,03±0,43	15,90±0,78
2	8,03±0,98	2,13±0,07	17,02±0,23
3	7,98±0,77	2,11±0,84	17,66±0,60
4	8,93±1,18	2,37±0,27	$18,74{\pm}1,08$
5	8,75±1,01	0,16±0,11	6,47±0,47
6	9,33±0,86	0,81±0,49	6,14±0,41
7	8,26±1,27	0,30±0,10	8,05±1,16
8	1,74±0,39	0,11±0,07	3,15±1,30

It was possible to obtain physic essays of electric conductivity, from the first sampling of the Stage 2. The obtained values from Pery River waters showed values that varied between 54,87 and 245,1 μ S cm⁻¹ (Table 4). Even there being no parameter that establishes the maximum value for this physic essay in the resolution N° 357/2005 of CONAMA, it is noticed that in comparison with others studies carried out in nearby regions [Staszczak; Rocha, 2016], the obtained values are appropriate to continental surface waters. For this kind of sample, the present ion level is relatively low. Yet, in the sample regions where they have significant influence from the cycle of the seas, the presented values are larger than those observed. It's still denoted that the anthropic process, near to Engenheiro Argus Thá Heyn Highway (PR-407), is relevant when the results from the samples taken in September and December/2016 in the points 5,6 and 7 are verified.

 Table 4 – Representation of figures for the electric conductivity in the waters of Pery River, in the eight sample points, between the four collect periods of Stage 2

Samples	First sampling September	Second sampling December	Third sampling March	Fourth sampling May
1	114,0±0,7	152,8±2,3	109,7±2,0	151,2±0,4
2	216,2±1,1	153,3±0,3	109,0±0,3	144,7±0,2
3	193,0±0,8	151,4±0,5	117,0±0,5	146,7±0,4
4	194,7±0,8	152,0±0,4	114,3±1,6	148,6±0,4
5	285,7±3,5	244,3±1,3	119,8±0,5	100,6±0,7
6	204,3±1,7	245,1±0,4	123,2±0,6	101,5±0,6
7	223,1±2,0	201,9±1,6	114,7±0,4	106,5±0,7
8	121,6±0,7	80,2±0,3	158,4±1,7	54,9±1,4

Other important parameter to evaluate the presence of fauna and flora from water resource is the presence of oxygen gas dissolved in the waters. This parameter was evaluated from Stage 2 on and some dissolved oxygen values (O_2) in the evaluated water samples were considered low. Based on CONAMA resolution, values less than 6mg L⁻¹ can represent serious risks to the aquatic ecosystem, because it provokes a reduction in the population of species living in these waters such as fish, because they need the dissolved oxygen to survive. The values found varied from 4,18 to 9,60 mg L⁻¹ in the different sample points (Figure 2).



Figure 2– Representation of dissolved oxygen in the Pery River Waters, referring to eight sample points, among the four sample periods of Stage 2.

The results from the samples that evaluated the total dissolved solid concentrations are showed on Table 5. The first sample values from Stage 1 are worrying because the values varied between 140 ± 94 to 851 ± 43 mg L⁻¹. Therefore, some obtained results were more than 500 mg L⁻¹, which is the maximum limit recommended by CONAMA for continental waters. On the second sampling, the obtained values were below the maximum value indicated by CONAMA. Therefore, these values vary between 82 ± 23 and 201 ± 22 mg L⁻¹. These high values from the second sampling occurred in a strong wind day. Thus, probably, significant quantities of dust were transported to the river and possibly solubilized in these waters. This way, when performing essays, it was observed that these values were higher than the established standard. In the obtained results during the essays from second stage of this study it's noticed that no value exceed the recommended limits by the resolution.

referents to the samplings observed in the eight sampling points. Values expressed in the L.								
	St	age 1		Stage 2				
	First sampling	Second sampling	First sampling Second sampling Third sampling Fourth			Fourth sampling		
Sample	December	May	September	December	March	May		
1	140±9	153±2	65±4	78±3	56±14	78±5		
2	360±2	82±2	65±1	77±1	56±3	76±7		
3	241±8	135±1	66±6	76±2	60±2	77±2		
4	851±4	177±2	67±6	76±2	58±4	77±8		
5	286±1	201±2	105±14	122±5	62±3	52±1		
6	597±6	183±3	106±3	123±4	63±2	53±3		
7	448±1	168±2	107±6	101±7	59±4	56±8		
8	542±6	123±2	36±2	40±2	81±13	28±4		

 Table 5–Representation of analytic results of solid waste dissolved and their respective standard deviation, referents to the samplings observeb in the eight sampling points. Values expressed in mg L^{-1} .

To quantify the nitrogen as nitrate ion in these spectrophotometric essays, samples were conducted with standard solution 0,1; 0,5; 1,0; 3,0 e 5,0 mg L⁻¹ with each of the sampling periods. From the average values of absorbance obtained in each of these standard solutions the standard curve of Stage 1 was outlined (Figure 3a), specifically in may, 2016, when the Straight Equation was obtained. (Abs = 0,06239 + 0,32969 [N]), and the coefficient of linear correlation R² = 0,99735. On Figure 3b is showed the standard curve of Stage 2, specifically in march, 2017, when the Straight Equation (Abs = 0,28517 + 0,28085 [N]) and the coefficient of

the linear correlation $R^2 = 0.99735$ was obtained. By applying the absorbance values obtained from the eight sample points, the concentration values of N-NO₃⁻ points were determined. Afterwards, the average value and standard deviation were determined for each measure of all samples. The obtained values from N-NO₃⁻ concentrations in the two sampling stages are represented on Figure 3c and 3d, where it's noticed that the values are below the maximum limit recommended by the CONAMA, which is 10mg L⁻¹. It is still observed that the 8th sample point values are smaller in relation to other points, because this local is a spring head that flows out in the Pery River and therefore, the current anthropic influence isn't for the nitrate presence (SILVA, ROCHA, 2016).



Figure 3 – Representation of the nitrogen deviation curve in nitrate form, obtained by the Griess method after the nitrate reduction of nitrate to nitrite using zinc powder, in 545 nm – a) Stage 1; b) Stage 2. Graphic representation of the nitrogen concentration values, in nitrate form, obtained in the eight sample points – c) Stage 1; d) Stage 2.

The Determination of the nitrogen element in the form of ammonium ion was done based on its standard solutions 10, 50, 100, 200, 300 μ g L⁻¹ in the Stage 1, 10, 25, 50, 100 and 150 μ g L⁻¹ in the Stage 2 (STANDEN; TALIAARD, 1997). From the average values of absorbance obtained in each of these standard solutions, the standard curve of the Stage 1 (Figure 4a) was outlined, from where the Straight Equation (Abs = 0,17574 + 0,00776 [N]), and the linear coefficient correlation R² = 0,99985 were obtained.

Figure 4b shows Stage 2 deviation curve, from where the Straight Equation (Abs = $0,07543 + 6,97123 \times 10^{-4}$ [N]) and the linear correlation coefficient $\mathbf{R}^2 = 0,99597$ were obtained. The values of concentrations points of N-NH₄⁺ were determined by applying the obtained absorbance values in the eight sample points. Afterwards, the average value and standard deviation of each measure of all samples were obtained.



Figure 4 - Representation of the nitrogen standard curve in ammonium form taken from Indophenol, in 630 nm -a) Stage 1; b) Stage 2. Graphic representation of nitrogen concentration values, in ammonium form, obtained in the eight sample points -c) Stage 1; d) Stage 2.

According to the CONAMA, it's observed that the ammoniacal nitrogen values were most preponderant in the Stage 2, which suggests a strong anthropic activity in the region where it appears in high concentrations. Although a fluctuation of concentration occurs in the eight sample points, it's observed that all the points increased significantly in relation to the previous samples. Point eight is their only one with no significant values, in other words, the headwater near Engenheiro Argus Thá Heyn Highway (PR-407). The quantification of the phosphor macronutrient was measured determining the phosphate ion by the molybdenum blue method from standards solutions 0,15; 0,30; 0,60; 0,90; 1,20; and 1,50 mg L⁻¹ of P. Stage 1 standard curve (Figure 5a) was traced by using these average values of absorbance, from where the Straight Equation (Abs = 0,05178 + 0,1777 [P]), and the linear correlation coefficient $\mathbf{R}^2 = 0,99567$ were obtained. Figure 5b represents Stage 2 standard curve, from where the Straight Equation (Abs = 0,05625 + 0,18909 [P]) and the linear correlation coefficient $\mathbf{R}^2 = 0,99567$ were obtained. Figure 5b represents were obtained curve, from where the Straight Equation (Abs = 0,05625 + 0,18909 [P]) and the linear correlation coefficient $\mathbf{R}^2 = 0,99567$ were obtained. Figure 5b represents stage 2 standard curve, from where the Straight Equation (Abs = 0,05625 + 0,18909 [P]) and the linear correlation coefficient $\mathbf{R}^2 = 0,99567$ were obtained. Figure 5b represents stage 2 standard curve, from where the Straight Equation (Abs = 0,05625 + 0,18909 [P]) and the linear correlation coefficient $\mathbf{R}^2 = 0,99567$ were obtained. Figure 5b represents stage 2 standard curve, from where the Straight Equation (Abs = 0,05625 + 0,18909 [P]) and the linear correlation coefficient $\mathbf{R}^2 = 0,99898$ were obtained. The concentrations values of P-PO₄³⁻ for all the samples were obtained by applying the average absorbance values in the eight sample points.



Figure 5 - Representation of deviation curve of the phosphor element, in phosphate form, obtained by the molybdenum blue method in 660 nm – a) Stage 1; b) Stage 2. Graphic representation of the phosphor concentration, in phosphate form, obtained in the eight sample points – c) Stage 1; d) Stage 2.

By evaluating the results of $P-PO_4^{3^-}$, it is observed that these concentrations are far above the maximum concentration recommended by the CONAMA for continental waters, which is 0,150 mg L⁻¹. At the points 5, 6 and 7 of the first sampling of Stage 2, these values are over 60 times the maximum allowed. The main hypothesis about the fact is related to the cycle of the seas and also Paranaguá and Antonina Seaport, where fertilizers in bulk are transported, but the seaport management is inappropriate, so a large number of them is stored in Paranaguá Bay These material pollutes all the rivers around because of the cycle of the seas in a larger or lesser intensity. But the contamination process through the "Dumping Ground", located next to Pery River, must not be forgotten.

III. Conclusions

The obtained analytic results in these sampling periods related to the difference of temperature between the water and air, the dissolved solid wastes and the phosphate concentrations show this water resource is suffering the first impacts due to the "Dumping Ground" presence in Pontal do Paraná. Some values from the total solid residues of the first Stage are considered high and three of them exceed the CONAMA maximum values. This fact probably happened because the samples were taken in a period of year with high temperature and great movement of the air, so pushing a greater amount of waste to the water reservoir. As to the air and water temperature differences, that is probably this is because of the addition of chemical substances from the "Dumping Ground" and the presence of the sewage from housing on the river banks. Yet, the phosphate concentration follows other values of the coastal region because of the fertilizers transportation process around this region. The appearance of the Black-faced Vulture (*Coragypsatratus*) may be associated to the disposal of dead animals in the "Dumping Ground", as well as the presence of organic waste from houses and general commerce. Studies point out that these birds take advantage of the hot airstreams, which are formed during the day and rise towards the upper layers of the atmosphere, to save energy and travel long distances with their wings open (SILVEIRA, 2012).

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