

Physicochemical characterization of Water Quality - Lagoa dos Índios in Macapá-AP-Brazil

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Authors' contributions

This investigation was performed in collaboration with all authors. Authors JSC, SSMSA, RSR and CBR designed the study, wrote the protocol, involved in writing the first draft, participated in experiments and data collection. Authors FSB, DCB and ACC managed the literature search, analyses of the study and manuscript preparation. Author JSC, ACC and CBRS performed the statistical analysis and also aided in data interpretation and was actively involved in reading the manuscript. All authors read and approved the final manuscript.

ABSTRACT

Aims: To characterize relevant physicochemical parameters of water quality in an Amazonian tropical lake and compare them with values predicted by the Brazilian Resolution CONAMA 357/2005 and those recommended by the similar US-EPA law. In addition, statistically correlating the parameters in different two climatic periods.

Study design: The sampling procedures occurred in five sites of a tropical lagoon (Lagoa dos Índios) in Macapá-AP-Brazil. The investigation occurred during the rainy season (November / 2010) and dry season (March / 2011). Seventeen physical and chemical parameters were analyzed according to APHA (1998). The metal ions were determined by atomic absorption spectrometry, with a Shimadzu device (AAS model 6300). The pH was determined *in situ* with the portable pH-meter, mark ORION, Model 3 STARS THERMO.

Place and Duration of Study/Methodology: The physicochemical analyzes were performed at the Laboratory of Chemistry, Sanitation and Environmental Systems Modeling Laboratory, and the General Laboratory and Analytical Chemistry of the Federal University of Amapá (UNIFAP). The period was from November 2010 to March 2011. Data were analysed using the BioStat 5.0 software to elaborate a Correlation Matrix (Spearman Method and non-parametric test).

Results: Alkalinity presented values outside the EPA standards, unlike hardness, that presented accordingly. Some general values observed could be considered normal when compared to other as the nearby waters of the Amazon River. The results for biochemical oxygen demand (BOD), dissolved aluminum, ammonia nitrogen, total dissolved solids (TDS), nitrate, chloride and turbidity measurement showed in accordance with the reference values of CONAMA and US-EPA. Then a nonparametric test (Kruskal Wallis) showed significant differences in water quality between both seasonal periods as among at the five sampling sites. Kruskal Wallis test showed also significant differences space-seasonal in the

water quality. So, the Spearman correlation showed good fitness with some physicochemical parameters: a positive correlation between pH and alkalinity, EC and pH, alkalinity, TDS, and negative correlation between DO and BOD.

Conclusion: We concluded that the Spearman correlation matrix describes reasonably well the behavior of the heterogeneous quality of the Lagoa dos Índios to the different sampling sites, both in the dry season and in the rainy season. The water quality is yet within legal standards expected to CONAMA Resolution 357/2005 and EPA-USA. However, there is evidence of imbalances of some parameters of water quality resulting from likely effects of urban pollution on the water quality of the lagoon.

Keywords: *Correlation Matrix, spatial-seasonal variation, CONAMA nº357/2005 resolution, EPA, spectrophotometry.*

1. INTRODUCTION

In the Brazilian urban context the excessive growth of aggregate population to new patterns of production and consumption, results in huge amounts of organic and toxic waste pollutants with disastrous effects on biodiversity. The lack of planning is a serious problem which promotes large population concentration in a small area, increasing the occupation of the peripheric and risk areas [1]. The situation arises particularly dramatic in urban and metropolitan areas, especially in areas where housing conditions, sanitation and access to leisure and recreations are increasingly precarious. The low sanitation conditions generate problems such as: pollution of rivers, lakes, coastal zones and bays. This has caused continuous environmental degradation by dumping of increasing volumes of organic and inorganic residues. The release of untreated sewage into the Lagoon of the Indians has increased significantly in recent decades, with severe impacts on fauna, flora and human beings [2].

In Amapá State the cities of Macapá and Santana have a high level population improper of the areas of "undertow". The term "undertow" is used regionally to denominate the various lakes in existing floodplains in the state of Amapá. These lakes occur during the wet period (winter) which extends from December to June. Rain water feeds rivers and igarapes inundating these areas. During the dry season (summer), the waters are mainly concentrated in the channels of rivers and the water levels of the hangovers reduce significantly. The term is also used to define the areas which behave as natural water reservoirs, which are characterized by a complex and distinct ecosystem, under the influence of tides and rainfall [3].

Areas of hangovers are predominant in almost all the urban perimeter of Macapá. Decharacterization of some of these areas due to human occupation, is already evident, even without formal diagnosis. The occupation of hangovers turns out to influence these ecosystems due to lack of minimum housing conditions (such as sanitation, for example) resulting in indiscriminate waste disposal from livestock rearing and recreation that eventually degrade and disfigure the nature of these environments. The Lagoon of Indians located in the city of Macapá-AP is an area of hangover that in recent years has suffered from various environmental problems as a result of over-population and siting of unplanned settlements [4, 5].

Main objective of this investigation is to study the principal parameters of the water quality of a tropical lagoon named Lagoa dos Índios (Indians Lagoon). The specific objective is to analyses the more usual physicochemical parameters predicted by Brazilian Laws such as the using statistical hypothesis tests. The references laws used to compare observed and analyzed are the CONAMA Resolution 357/2005 [6] and regulations of the U.S. Environmental Protection Agency-EPA [7], both with respect to urbanization and industrialization around this water body.

2. MATERIAL AND METHODS

2.1 Localization of the Lagoa dos Índios (Indians Lagoon), sample sites and method of analysis

Samples procedures occurred in two periods: Dry Season (November, 2010) and Wet Season (March/2011), at five sites inside of the Indians Lagoon (Figure 1) defined by Garmin GPS device. The depth of the lagoon presents, on average, 1.5m in the dry season and 3m deep in the wet season.

Collection and preservation of samples were carried out in accordance with the Manual of Procedures and Laboratory Techniques aimed at Analysis of Water and Sanitary Sewage and Industrial of University of São Paulo-Brazil (USP/Brazil) [8].



Fig. 1. Satellite image of Lagoa dos Índios, Macapá-AP-Brazil.
Source: Google, 2014

Laboratory analyzes were performed in triplicate (by sample) at the Laboratory of Chemistry, Sanitation and Modeling of Environmental Systems of Federal University of Amapá. The determination of chloride, alkalinity, nitrates, ammonium nitrogen were performed according to Standard Methods recommended by - APHA [9]. Analyses of Biochemical Oxygen Demand (BOD) were performed using the Winkler method. The analysis relating to determinations of metals (aluminum, iron and manganese) were conducted using Atomic Absorption Spectrometry AAS Model 6300 Shimadzu at the Laboratory of Atomic Absorption and Bioprospecting (LAAB). The determination of the parameters total hardness, color, total suspended solids (TSS) and total dissolved solids (TDS) were performed with model DR2800 spectrophotometer HACH trademark and turbidity determinations were obtained from the American Home turbidimeter AP2000. The physical parameters such as (temperature, pH, conductivity and dissolved oxygen - DO) were taken in-situ by the use of probe YSI multiparameter model 556MPS trademark and ORION pHmeter Model 3 STAR, portable pH, trademark THERMO. Statistical tests of the correlation of Spearman, Kruskal-Wallis test and t-test, were conducted with BioEstat 5.0 software.

In Brazil the law which serves as reference standard to compare changes in freshwaters is the CONAMA Resolution 357/2005. This resolution is original from a National Council on the Environment (Portuguese acronym for the Conselho Nacional do Meio Ambiente - CONAMA), agency subordinated to the Ministry of the Environment. In the United States this function is performed by the U.S. Environmental Protection Agency - EPA.

Table 1 shows the limit values available by CONAMA Resolution 357/2005 and by the EPA.

Table 1. Limit values for the physicochemical parameters.

Parameter	Limit values	
	Brazil	USA
Temperature	—	—
pH	between 6 and 9	Between 6.5 and 9
Alkalinity	—	Min 20 mg/l
Electrical Conductivity (EC)	—	—
DO	Max 5 mg/l	Max 4 mg/l
BOD	Max 5 mg/l	4 mg/l
Hardness (mg/l Ca or Mg CaCO ₃)	—	0 - 75 soft 75 - 150 moderately hard 150 - 300 Hard 300 and up - very hard
Iron dissolved	Max 0.3 mg/l	Max 0.1 mg/l
Aluminium dissolved	Max 0.1 mg/l	Max 0.087 mg/l
Manganese dissolved	Max 0.1 mg/l	Max 0.1 mg/l
Ammonia nitrogen (mg/l NH ₃ -N)	3.0 mg/l N, to pH ≤ 7.566 2.0 mg/l N, to 7.5 < pH ≤ 8.0 1.0 mg/l N, to 8.0 < pH ≤ 8.5 0.5 mg/l N, to pH > 8.5	3.48 mg/l N, to pH ≤ 6.5 3.0 mg/l N, to 6.5 < pH ≤ 7.0 1.0 mg/l N, to 7.0 < pH ≤ 8.0 0.25 mg/l N, to pH > 8.0
Colour	Max 75 mg/l PtCo	Max 75 mg/l PtCo
TSS	—	—
TDS	Max 500 mg/l	Max 500 mg/l
Nitrate	Max 10 mg/l NO ₃ - N	Max 10 mg/l NO ₃ - N
Chloride	Max 250 mg/l Cl	Max 250 mg/l Cl
Turbidity	Max 100 NTU	—

The electrical conductivity (EC) and total suspended solids (TSS) parameters are not regulated by CONAMA Resolution 357/2005 and by EPA, but we analyzed to support a better characterization of water body studied. This procedure was carried out because these parameters were strongly correlated with other parameters in aquatic environments.

3. RESULTS E DISCUSSION

3.1 Seasonal variability of physico-chemical parameters and comparison with CONAMA and EPA references

Table 2 shows the results obtained for the parameters analyzed in five sampling sites and their differences. Kruskal-Wallis tests were performed to compare both observed and laws values. It was possible to verify that at least three sample sites three tests resulted in significant differences between the mean values. The results are presented in the table 2 and compared to the values normalized by CONAMA and EPA.

Table 2. Mean values of the parameters studied at the Lagoa dos Índios in Macapá-AP-Brazil during the dry and wet seasons.

Parameter	Period	Site 1	Site 2	Site 3	Site 4	Site 5
Temperature (°C)	dry	25.90 ^{A,B}	28.21 ^A	26.83 ^C	28.97 ^{B,C}	27.84
	wet	26.98	25.99 ^A	25.98 ^{B,C}	28.16 ^{A,B}	27.18 ^C
pH	dry	4.726 ^{A,C}	5.486 ^B	5.791 ^A	5.625	6.101 ^{B,C}
	wet	5.635	5.585 ^{A,B}	6.445 ^{A,C}	5.872 ^B	5.611 ^C
Alkalinity (mg/l CaCO ₃)	dry	10.0	8.0 ^{A,B}	34.0 ^{A,C}	18.0 ^{B,D}	8.0 ^{C,D}
	wet	6.0	6.0 ^A	32.0 ^{A,B}	14.0	6.0 ^B
Electrical conductivity (µS/cm)	dry	58 ^{A,C}	160	165 ^A	76 ^B	232 ^{B,C}
	wet	19 ^A	14 ^{B,C}	83 ^{A,B}	29 ^C	27
DO (mg/l)	dry	1.31 ^{A,B}	4.24 ^{A,C}	1.49	2.14 ^B	1.47 ^C
	wet	1.55	4.22 ^{A,B}	1.14 ^A	1.03 ^{B,C}	2.21 ^C
BOD (mg/l)	dry	1.71 ^{A,B}	4.53 ^{A,C}	1.79 ^C	1.97 ^B	1.84
	wet	1.52 ^{A,B}	1.42 ^C	0.9 ^A	0.46 ^B	1.38 ^C
Hardness Mg CaCO ₃ (mg/l)	dry	0.57 ^A	2.67 ^{A,B}	2.12	0.56 ^{B,C}	2.33 ^C
	wet	0.43	0.25 ^{A,B}	0.83 ^{A,C}	0.30 ^C	0.57 ^B
Hardness Ca CaCO ₃ (mg/L)	dry	0.85 ^A	0.15 ^{A,B}	0.81	1.03 ^{B,C}	0.77 ^C
	wet	0.99 ^A	1.02 ^{B,C}	0.98	0.66 ^B	0.65 ^{A,C}
Iron dissolved (mg/l Fe)	dry	4.51 ^A	3.38 ^B	2.66 ^{A,C}	4.00	5.73 ^{B,C}
	wet	1.76 ^A	2.56 ^{B,C}	0.90 ^B	0.88 ^{A,C}	1.16
Aluminium dissolved (mg/l Al)	dry	0.030 ^{A,B}	0.051 ^A	0.039 ^C	0.05	0.091 ^{B,C}
	wet	0.020 ^A	0.059 ^{A,B}	0.002 ^{B,C}	0.022	0.033 ^C
Manganese dissolved (mg/l Mn)	dry	0.055 ^{A,B}	0.105 ^A	0.070 ^C	0.100	0.219 ^{B,C}
	wet	0.049 ^A	0.075 ^{A,B}	0.062 ^C	0.033 ^{B,C}	0.054
Ammonia nitrogen (mg/l NH ₃ -N)	dry	0.26 ^{A,B}	0.53 ^{A,C}	0.53 ^{B,D}	0.37 ^{C,D}	0.51
	wet	0.13	0.04 ^{A,B}	0.69 ^{A,C}	0.07 ^C	0.14 ^B
Nitrate (mg/l NO ₃ -N)	dry	1.70	0.80 ^A	0.70 ^{B,C}	1.80 ^B	2.50 ^{A,C}
	wet	1.30 ^{A,B}	0.80 ^A	1.00	0.80 ^B	1.00
Colour (mg/l PtCo)	dry	207 ^A	185 ^B	144 ^{A,C}	189	368 ^{B,C}
	wet	111	164 ^{A,B}	120 ^C	72 ^{A,C}	107 ^B
TSS (mg/l)	dry	16,0 ^{A,B}	21,0 ^C	22,0 ^A	26,0 ^{B,C,D}	21,0 ^D
	wet	9,0 ^A	39,0 ^{A,B}	12,0	8,0 ^{B,C}	21,0 ^C
TDS (mg/l)	dry	0.028 ^{A,B}	0.075	0.08 ^A	0.035 ^C	0.11 ^{B,C}
	wet	0.009 ^A	0.007 ^{B,C,D}	0.041 ^{A,B}	0.013 ^C	0.013 ^D
Chloride (mg/l Cl)	dry	62.98 ^{A,B}	54.56 ^C	21.88 ^A	24.65	17.48 ^{B,C}
	wet	59.98 ^{A,B}	53.98 ^C	18.95	18.69 ^A	17.52 ^{B,C}
Turbidity (NTU)	dry	10.6 ^A	6.6 ^{A,B}	7.44 ^C	9.3	14.8 ^{B,C}
	wet	3.13 ^A	30 ^{A,B}	7.48 ^C	1.21 ^{B,C}	5.02

Means followed by the same indices in the horizontal differ significantly (Kruskal-Wallis p<0.05).

Parameters whose values were in non-compliance with Brazilian legislation are pH, DO, Fe, Mn and color. The pH values showed results according to the standards in sampling point 5 in the dry period (pH = 6.101) and sampling point 3 in the wet period (pH = 6.445). Even presenting values less than the legal standards, values were considered normal for Amazonian waters, which are slightly acidic [10], and are in agreement with results presented in studies conducted with waters of the Brazilian Amazon region [11,12,13,14]. The natural acidity characteristic of these waters may be related to the presence of potentially acidic substances, derived from various natural sources, which are carried from the soil to the waters of rivers and lakes [13, 14, 15].

The DO values were below the allowed for all the points in both the dry and wet period (highest value = 4.24 mg/l). The low DO concentration is due to the oxygen consumption caused by the decomposition of organic matter (oxidation) by microorganisms, material possibly originated from wastewater disposed in the natural water bodies [16,17, 18].

Very high values of dissolved iron were observed at all points in both the dry and in the wet period (lower value = 0.90 mg/l and highest value = 5.73 mg/l) and the values of dissolved manganese were above the permitted only in points 2 and 5 in the dry period (point 2 = 0.105 mg/l and 5 point = 0.219 mg/l). All concentration values of dissolved iron were above the values allowed by law. The causes can be naturally related to the geological and soil characteristics which are subjected to erosion [19]. Thus, elevated iron dissolved concentration can be attributed to sewage as a result of anthropogenic influence and it can cause serious damage to public health, animals and aquatic plants [20, 21, 22].

The color parameter values presented in accordance with legal standard only at sampling point 4 in the wet period (72 mg/l PtCo). Substances dissolved in the water can elevate their intensity of color, and some of these substances may be originate from organic sources, such as plankton, plant and animal, and inorganic origin, such as Fe and Mn ions [23].

The hardness has no values standardized by the Brazilian environmental legislation, but presents standard values regulated by EPA. Values less than 3 mg/l for Ca^{+} and Mg^{+} in both dry and wet periods were characterized as soft waters for all sampling points. The hardness is the ability of water to react soap and is described as the sum of polyvalent cations such as iron, barium, strontium, magnesium, calcium. These cations react with soap to form precipitates or react with anions forming crusts [24]. According to EPA, water with hardness values up to 75 mg/l are considered soft.

The EC has not values normalized by CONAMA and EPA. Significant differences were observed for values of EC in both dry (higher values) and wet (lower values) periods. Elevates Electrical conductivity in the dry period and low values during the wet period were determined in study conducted in Ribeirão Salgadinho in Xavantina-MT-Brazil [25]. The low values in the wet period may be related to a reduction in the concentration of electrolytic substances due to the increased volume of water.

The values of the parameters BOD, dissolved aluminum, ammonia nitrogen, STD, nitrate, chloride and Turbidity were all in agreement with both the CONAMA Resolution 357/2005 and with the values normalized by the EPA. The BOD parameter value presented (4.53 mg/l), close to the reference values only at sampling point 2 in the dry period. The value closer of limit can be related to the creation of buffalo cattle near this point.

Aluminum concentration (0.091 mg / L) in sampling point 3 during dry period was observed close to the legal standard. The presence of dissolved aluminum in the soil can be extremely toxic to vegetation, especially in the wet period when the metal can react with acids precipitated with the rains, when it also be leached to water bodies [22]. Urban expansion near the sampling point 3 (Figure 1), represents a potential source of waste disposal for Aluminum and other metals.

Ammonia Nitrogen and nitrate presented low concentrations (highest value 0.69 mg/l for $\text{NH}_3\text{-N}$ and 2.5 mg/l $\text{NO}_3\text{-N}$) for all sampling points in both the dry and wet periods.

Organic nitrogen is converted to ammonia by ammonification, ammonia is converted into nitrite by nitrification, and finally nitrite is converted to nitrate by denitrification. The existence of ammonia nitrogen (mainly in large concentrations) indicates recent dumping of waste of animal and vegetable origin, therefore not yet occurred nitrification and denitrification [18, 26, 27]. The nitrate is final product of nitrogenous organic matter mineralization. Trace amounts of nitrate are present in natural waters and its increase indicate potential waste disposal or bad use of fertilizers in agricultural activities near rivers and lakes [28]. Low concentration of $\text{NH}_3\text{-N}$ indicate two possibilities: either there is low levels of waste of animal and vegetable origin, or ammonia would have been converted to nitrate (with higher values).

Measurements of TDS were observed with lower values in the dry period (higher value 0.110 mg/l) and in the wet period (higher value 0.041). Inorganic salts are the main constituents of dissolved solids, but may also contain dissolved gases and small amounts of organic [28]. Low concentrations for TDS were also determined in research with the waters of the Rio Araguari, Amapá-Brazil [29].

The alkalinity reported high value only in sampling point 3, with the dry period 32 mg/l CaCO_3 and wet period 34mg/l CaCO_3 . Physicochemical analyzes performed with water streams in Manaus-AM-Brazil [16], showed low levels of alkalinity in preserved areas. This may mean that the waters in sampling point 3 may be in the early stages of change for this parameter. And the values provided by the EPA for alkalinity cannot considerable for Amazonian waters.

Chloride parameter showed low values compared to the reference values (maximum of 62.98 mg/l in the dry period and maximum of 59.98 mg/l in the wet period). In natural waters Cl^- ions originates from leaching of soil and rocks composed of chlorine salts. Their values can be increased by the influence of waste disposal of urban areas, industries and agricultural activities [23, 30]. Low concentration can be attributed to the absence of agricultural activities near the sampling sites. And naturally absence of rocky soils near the Lagoa dos Índios (Indians Lagoon) [23].

Turbidity presented a higher value in sampling point 2 in the wet period (30 NTU). The turbidity is related to the presence of organic and inorganic materials finely divided, microscopic organisms, as well clay and silica in water. Its increase may be caused naturally by soil leaching and by anthropogenic influence from the dumping of waste and depend on tidal effect of Amazon River [18, 28]. The turbidity parameter is in conformity with the legal standard for Lagoa dos Índios (Indians Lagoon). The increase in turbidity at sampling point 2 in relation to the other can be related to the presence of urban expansion closer (see Figure 1), which can present origin in the sewage sources.

The TSS (Total Suspended Solids) parameter are not regulated by CONAMA and neither by EPA. The values are below 40 mg/l for the dry and wet period. But the suspended solids may contain toxic components inside of the solid particulates such as heavy metals and pesticides and other micropollutants originating from industrial waste, fertilizer, drainage of roads, drains, and soil erosion [31].

3.2 Temporal variability and heterogeneity of the Water Quality Parameters

Table 3 shows the results for t-test, where only the alkalinity, dissolved iron, electrical conductivity and TDS parameters were significantly different relative temporal variability. Trend of these parameters, in general, is to present higher values in the dry season and lower in the wet period. These results allow us to infer that rainfall significantly interfere in the flow of the effluents into the lagoon reducing the concentration of existing chemical constituents due volumetric dilution of water in the wet period. Similar results were determined in research conducted in the waters of the basins of hangovers Igarapé of Fortaleza and Rio Curiaú in Macapá-Amapá-Brazil [4]. But often the reverse can occur due to the inverse load compensation of pollutants through the process of leaching the soil by rainfall [18].

Data results are showed in Table 3 for both seasonal periods. Mean and Coefficient of Variation (CV) were didactically considered the more important statistic parameters for the present analysis. In details, Table 3 indicate heterogeneity or high CV values, which amplitude ranged from 3,40% (Temperature - Homeostasis due dry climate conditions) to 125% (Turbidity and Ammonia-Nitrogen - Amazon River Intrusion by semidiurnal tidal effect) [18]. Other factors can be considered such as different types of interactions with vegetation communities, cattle existence and intense human occupation near this ecosystem which can be the causes for the large variations of the CV for most of parameters.

Table 3. Variation in parameters values analyzed for the Lagoa dos Índios (Indians Lagoon) in Macapá-AP-Brazil in Dry and Wet period.

Parameters	Dry period			Wet period		
	Mean $\pm$ se	Range	CV (%)	Mean $\pm$ se	Range	CV (%)
Temperature (°C)	27.55 $\pm$ 0.53	25.90-28.97	4.36	26.85 $\pm$ 0.41	25.98-28.16	3.40
pH ^{ns}	5.54 $\pm$ 0.23	4.72-6.10	9.28	5.83 $\pm$ 0.16	5.58-6.44	6.22
Alkalinity** (mg/l CaCO ₃)	15.6 $\pm$ 4.95	8-34	71.04	12.8 $\pm$ 5.04	6-32	88.11
Electrical conductivity* (μS/cm)	138.2 $\pm$ 31.8	58-232	51.54	34.4 $\pm$ 12.44	14-83	80.92
DO ^{ns} (mg/l)	2.13 $\pm$ 0.54	1.31-4.24	57.35	2.03 $\pm$ 0.58	1.03-4.22	64.47
BOD ^{ns} (mg/l)	2.38 $\pm$ 0.56	1.71-4.63	52.63	1.13 $\pm$ 0.2	0.46-1.52	39.38
Hardness MgCaCO ₃ ^{ns} (mg/l)	1.65 $\pm$ 0.45	0.56-2.57	60.97	0.47 $\pm$ 0.10	0.25-0.83	49.08
Hardness ^{ns} Ca CaCO ₃ (mg/l)	0.72 $\pm$ 0.14	0.15-1.03	46.40	0.86 $\pm$ 0.08	0.65-1.02	21.83
Iron dissolved** (mg/l Fe)	4.05 $\pm$ 0.52	2.66-5.73	28.69	1.45 $\pm$ 0.31	0.88-2.56	41.12
Aluminium dissolved ^{ns} (mg/l Al)	0.052 $\pm$ 0.01	0.03-0.091	66.01	0.027 $\pm$ 0.009	0.002-0.059	41.12
Nitrate ^{ns} (mg/l NO ₃ - N)	1.50 $\pm$ 0.33	0.70-2.50	50.11	0.98 $\pm$ 0.09	0.80-1.30	20.91
Manganese dissolved ^{ns} (mg/l Mn)	0.11 $\pm$ 0.03	0.05-0.219	58.73	0.05 $\pm$ 0.007	0.033-0.075	28.51
Ammonia nitrogen ^{ns} (mg/l NH ₃ -N)	0.44 $\pm$ 0.05	0.26-0.53	27.46	0.21 $\pm$ 0.12	0.04-0.69	125.85
Colour ^{ns} (mg/l PtCo)	218.6 $\pm$ 38.7	144-368	39.63	114.8 $\pm$ 14.75	72-164	28,74
TSS ^{ns} (mg/l)	21.2 $\pm$ 1.6	16-26	16.81	17,8 $\pm$ 5.8	8-39	72.54
TDS* (mg/l)	0.065 $\pm$ 0.015	0.02-0.11	51.79	0.016 $\pm$ 0.006	0.007-0.04	83.65
Chloride ^{ns} (mg/l Cl)	36.31 $\pm$ 9.33	17.4-62.98	57.49	33.82 $\pm$ 9.50	17.52-59.98	64.57
Turbidity ^{ns} (NTU)	9.75 $\pm$ 1.44	6.60-14.80	33.12	9.36 $\pm$ 5.26	1.21-30.0	125.71

(T-test) ns = Non significant, p<0.05, * = Significant, at 0.05, ** = Significant at 0.01

243 **3.3 Correlation between physicochemical parameters**

244 **Non-Parametric Spearman** correlation analyzes were performed individually for the
245 dry period and the wet period and their values are shown in Table 4.

246 The pH and alkalinity showed a strong positive correlation in the wet period. The pH
247 can be described as the measurement of the concentration of free water protons. The
248 constituents of natural waters that influence pH are solid and dissolved gases, originated
249 from the dissolution of **clayey soil**, oxidation of organic matter, photosynthetic interactions
250 **and effluents due anthropogenic influence [32]**.

251 Table 4: Spearman correlation coefficients (**r**) among eighteen physicochemical parameters of water quality (Lagoa dos Índios-Macapá-AP-
 252 Brazil) for two seasonal period (Wet - dark color, and Dry - bright color).

Parameter	Temperature	pH	Alkalinity	EC	DO	BOD	Hardness Mg CaCO ₃	Hardness Ca CaCO ₃	Iron dissolved	Al dissolved	Mn dissolved	Ammonia nitrogen	Nitrate	Colour	TSS	TDS	Chloride	Turbidity
Temperature	–	-0.28	-0.30	-0.35	-0.50	-0.48	-0.37	-0.81	-0.48	-0.14	-0.93	-0.49	-0.06	-0.87	-0.55	-0.39	-0.33	-0.66
pH	0.57	–	0.99	0.97	-0.56	-0.57	0.74	0.17	-0.60	-0.76	0.005	0.92	-0.06	-0.17	-0.43	0.96	-0.50	-0.26
Alkalinity	-0.14	0.24	–	0.97	-0.52	-0.57	0.73	0.17	-0.58	-0.73	0.02	0.92	-0.09	-0.13	-0.39	-0.96	-0.50	-0.22
EC	0.19	0.80	-0.02	–	-0.52	-0.42	0.87	0.15	-0.61	-0.76	-0.08	0.97	0.02	-0.10	-0.38	0.99	-0.54	-0.27
DO	0.51	0.009	-0.33	0.09	–	0.58	-0.48	0.34	0.88	0.92	0.76	-0.44	-0.35	0.84	0.97	-0.49	0.50	0.93
BOD	0.37	-0.02	-0.37	0.17	-0.98	–	-0.05	0.44	0.68	0.45	0.58	-0.23	0.52	0.64	0.49	-0.39	0.64	0.40
Hardness Mg CaCO ₃	0.15	0.57	0.001	0.86	0.48	0.57	–	0.09	-0.57	-0.73	0.13	0.91	0.34	-0.07	-0.36	0.88	-0.49	-0.37
Hardness Ca CaCO ₃	-0.16	0.03	0.48	-0.32	-0.86	-0.94	-0.68	–	0.60	0.06	0.67	0.31	0.30	0.73	0.29	0.18	0.71	0.53
Iron dissolved	0.03	0.10	-0.69	0.21	-0.35	-0.32	-0.17	0.15	–	0.80	0.65	-0.49	-0.02	0.81	0.77	-0.58	0.85	0.83
Al dissolved	0.47	0.76	-0.39	0.77	-0.01	-0.007	0.44	-0.10	0.68	–	0.46	-0.73	-0.43	0.59	0.88	-0.74	0.44	0.78
Mn dissolved	0.43	0.72	-0.43	0.76	-0.03	-0.01	0.42	-0.10	0.72	0.99	–	0.21	-0.11	0.97	0.80	0.12	0.36	0.84
Ammonia nitrogen	0.36	0.79	0.23	0.86	0.39	0.42	0.92	-0.45	-0.26	0.49	0.45	–	0.17	0.02	-0.32	0.98	-0.39	-0.20
Nitrate	0.13	0.16	-0.52	0.10	-0.48	-0.50	-0.35	0.40	0.95	0.88	0.67	-0.33	–	-0.08	-0.46	0.03	0.38	-0.45
Colour	0.12	0.41	-0.58	0.56	-0.26	-0.21	0.18	0.01	0.92	0.64	0.91	0.11	0.84	–	0.84	-0.07	0.56	0.90
TSS	0.85	0.64	0.36	0.11	0.20	0.03	0.03	0.21	-0.23	0.26	0.20	0.37	-0.02	-0.13	–	-0.35	0.33	0.93
TDS	0.16	0.80	-0.04	0.99	0.07	0.15	0.85	-0.31	0.20	0.76	0.75	0.86	0.09	0.55	0.10	–	-0.52	-0.24
Chloride	-0.43	-0.88	-0.47	-0.53	0.37	0.44	-0.18	-0.49	-0.11	-0.57	-0.54	-0.49	-0.29	-0.31	-0.69	-0.53	–	0.47
Turbidity	-0.06	0.25	-0.43	0.32	-0.58	-0.54	-0.14	0.35	0.94	0.70	0.74	-0.16	-0.19	0.92	0.94	0.32	-0.33	–

253 - Highlighted values **r (r > 0,70)** are significant for **Spearman** correlation with $p < 0.05$.

Alkalinity is described as a measure of capacity of water to neutralize acids. In natural waters it is constituted mainly of salts of acids and weak bases or strong bases, such as phosphates, silicates, bromates, carbonates and bicarbonates [9,32]. For pH below 4.3 the water has strong mineral acidity, pH values between 4.3 and 8.3 is related to water that presents bicarbonates and some weak acids [33, 34, 35]

In the wet period EC displayed positive correlations with pH and alkalinity, whereas in the dry period it was negatively correlated with ammonia, TDS and hardness. The EC expresses the ability of a liquid to conduct electrical current, and can be influenced by the type, amount, concentration, mobility and valence of the ionic species in dispersal beyond the temperature of the solution [9, 28]. Existence of ions, also in the cited parameters, such as the presence of ions which influence the pH (H^+ or OH^-), alkalinity (CO_3^{2-}), the Nitrogen ammonia (NH_4^+) and TDS, which presents dissolved materials [33, 36]. This also justifies the positive correlations presented in the wet period by TDS versus pH ($r = 0.96$), alkalinity versus Ammonia Nitrogen ($r = -0.92$), and EC versus Ammonia Nitrogen ($r = 0.92$), since the inorganic salts are major constituents of dissolved solids, but they may also contain ions, dissolved gases and small quantities of organic material [37].

Also was observed positive correlation among DO versus dissolved iron ($r = 0.88$) and dissolved aluminum ($r = 0.92$), which, may be related to increased dissolution of iron and aluminum compounds, especially the oxides of these metals, which release oxygen in water increases the concentration of dissolved oxygen [38]. Negative correlations are observed in the dry period for hardness $Ca\ CaCO_3$ versus DO ($r = -0.86$) and $Ca\ CaCO_3$ versus BOD ($r = -0.94$). The consumption of dissolved oxygen in reactions of formation of carbonates explain the inverse relationship demonstrated by the correlation [39]. The strong negative correlation between DO versus BOD in the dry season, can be explained biogeochemical processes such as respiration of aerobic microorganisms [40]. The BOD represents the potential of biodegradable organic matter in aquatic environments. Corresponds to the amount of dissolved oxygen removed from the water by respiration by microorganisms. The greater the amount of biodegradable organic matter present in the body of water means that there is higher BOD concentration corresponding to greater demand for oxygen [41]. High concentration OD indicates better capacity water body to promote depuration of organic materials. The OD can be influenced by temperature, atmospheric pressure, photosynthesis, respiration of aquatic plants and oxygen demands by some microorganisms [41]. Relatively low values r ($r = -0.58$) for DO versus BOD in the rainy period, may be related to the reduction of the concentration of chemical constituents, due to the variation of dilution capacity of water because the rains in this period [25].

Turbidity was positively correlated with the color and TSS ($r = 0.94$) in the dry season and the wet period. These parameters presented direct proportional relationship with the turbidity. So, the greater the amount of TSS means higher turbidity and lower water clarity. This effect difficult the light absorption and reduces the photosynthetic rate of aquatic algal and plants. Furthermore, it prejudice pasture for food by aquatic animals [20, 42]. Positive correlations among color versus turbidity and color versus TSS were also evident in a similar study conducted in a basin of high Acaraú, CE, Brazil [43].

Positive correlations occurred among color versus dissolved iron ($r = 0.92$) and color versus dissolved manganese ($r = 0.91$) in wet season. The salts of Fe and Mn have similar characteristics in their interactions with natural waters. These ions are easily oxidized to form insoluble hydroxides. Waters with these metals have low turbidity and high color level [26, 44]. Iron and manganese dissolved ions, added to organic matter result directly in increased values of color [23].

4. CONCLUSION

Field and laboratorial analyzes showed that five parameters presented values outside of the legal standards. pH parameter presented peculiar characteristics, since water Estuarine Amazonian Waters present normally tendency to acidity and even with values

below allowed by CONAMA Resolution 357/2005 and EPA. So, these yet can be considered normal. The results for DO, dissolved iron, dissolved manganese and colour show that these parameters are in the initial state of change in Lagoa dos Índios (Indians Lagoon). Decontrolled waste disposal generated by urban expansion added to industrial and commercial activity around the lagoon may be the principal cause of variations ranges of the water quality parameters.

Water quality parameters in non-compliance with the legislation CONAMA and EPA yet can be considered normal compared to other existing results in the literature for Amazonian waters.

Regarding the temporal variability, water quality parameter values were lower in the wet period and higher in the dry season. These results could be attributed to decreased concentration of some physicochemical constituents, especially due to the elevated variation of the volume of water from the rains.

Seasonal variability data: Kruskal-Wallis non-parametric test for mean and CV significance comparisons, also the t-test (Tables 1, 2 and 3) show that the Lagoa dos Índios presents a high degree of spatial heterogeneity to majority parameters. The relatively large area of the lagoon and the different characteristics of the vegetation and occupation of soil can be influence in the pollution level of the water, both combined with natural variations characteristic of water basin.

Correlation analysis also showed values expected for the dynamics of the water body compared to existing studies on the interrelation of physicochemical parameters as in the case of positive correlation of the pH versus alkalinity ($r = 0.99$) and EC versus alkalinity ($r = 0.92$), EC versus alkalinity ($r = 0.97$), TDS versus alkalinity ($r = -0.96$), negative correlation between DO versus BOD ($r = 0.86$) due to consumption of DO and increased demand for this gas (BOD). But other significant relationships ($r > 0.70$) also appear in the matrix.

CONSENT

Not Applicable

COMPETING INTERESTS

Authors hereby declare that there are no competing interests.

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