PANAMJAS
Pan-American Journal of Aquatic Sciences

Characterization of dissolved inorganic carbon and dissolved oxygen in two impacted Amazonian lakes

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Abstract. Six surface water campaigns were carried out in lakes Bolonha-LB and Água Preta-LAP (Brazil) during 2018 - 2019. Temporal and spatial variations of temperature, pH, electrical conductivity, dissolved oxygen (DO), total alkalinity (TA), turbidity, dissolved carbon dioxide (CO_{2aq}), and partial pressure of CO_2 (pCO_2) were analyzed and estimated. High levels of CO_{2aq} were observed during the study (104 - 998 µmol l^{-1}), while CO_{2eq} in equilibrium with the atmosphere ranged between 11.5 and 12.3 µmol l^{-1}. The pCO_2 values ranged from 3,400 to 23,600 µatm. DO ranged from 1.0 - 8.5 mg l^{-1} and showed significant spatial differences ($p < 0.05$) between the lakes studied. Apparent oxygen utilization (AOU) showed positive values in 98.5% of the samples collected, indicative of heterotrophic processes (respiration > production). The analysis of the relationships between AOU and excess CO_2 indicated that about 65% of the carbon mineralization in the lakes is anaerobic, indicating the predominance of the respiration process in the systems studied. A comparative analysis with other 117 tropical lakes showed that LAP and LB are part of the 78% of lakes with CO_2 supersaturation. This work showed that: the heterotrophic processes identified during this study are mainly a product of the inorganic contributions of organic matter from the adjacent urban region.

Keywords: carbonate system, DIC, dissolved carbon, AOU, tropical lakes.

Caracterização do carbono inorgânico dissolvido e oxigênio dissolvido em dois lagos impactados na Amazônia. Resumo: Seis campanhas em águas superficiais foram realizadas nos lagos Bolonha e Água Preta (Brasil) durante 2018 - 2019. Variações temporais e espaciais de temperatura, pH, condutividade elétrica, oxigênio dissolvido (DO), alcalinidade total (TA), turbidez, dióxido de carbono dissolvido (CO_{2aq}) e pressão parcial de CO_2 (pCO_2) foram analisadas e estimadas. Altos níveis de CO_{2aq} foram observados durante o estudo (104 - 998 µmol l^{-1}), enquanto o CO_{2eq} em equilíbrio com a atmosfera variou entre 11,5 e 12,3 µmol l^{-1}. Os valores de pCO_2 variaram de 3.400 a 23.600 µatm. DO variou entre 1,0 - 8,5 mg l^{-1} e apresentou diferenças espaciais significativas ($p < 0,05$) entre os lagos estudados. A utilização aparente de oxigênio (AOU) mostrou valores positivos em 98,5% das amostras coletadas, indicativo de processos heterotróficos (respiração>produção). A análise das relações entre AOU e excesso de CO_2 indicaram que cerca de 65% da mineralização de carbono nos lagos é anaeróbia, indicando a predominância do processo de respiração nos sistemas estudados. Uma análise comparativa com outros 117 lagos tropicais mostrou que, LAP e LB fazem parte do 78% de lagos com supersaturação de CO_2. Este trabalho mostrou que: os processos heterotróficos identificados durante este estudo são principalmente um produto das contribuições de matéria orgânica da região urbana adjacente.

Palavras-chave: sistema carbonático, DIC, carbono dissolvido, AOU, lagos tropicais.

Introduction

Dissolved CO_2 (CO_{2aq}) is a master variable in aqueous chemistry. It is the most dynamic constituent of dissolved inorganic carbon and is usually the major acid in inland waters that have not been impacted by acid rain (Cole & Praire, 2009). Unlike in seawater, the concentrations of dissolved inorganic carbon (DIC), total alkalinity (TA), and CO_{2aq} in inland waters vary greatly, because of the widely varying impacts of local geology, water cycle, watershed vegetation, climate on inland waters, and anthropic pressure.

The annual cycle in most freshwaters involves changes in the pH, dissolved oxygen (DO), and CO_{2aq}. Those of pH are again most generally linked with net consumption and production of CO_{2aq}; elevated pH may be correlated with a lower rate of photosynthesis per unit biomass (Talling et al. 2010), whereas, low pH values may be associated with high respiration rates. Additionally, dissolved oxygen (DO) can indicate organic consumption rates through estimates. Thus, CO_{2aq} and DO can indicate the trophic state of an aquatic system through the consumption/production of these gases. Consequently, these estimates allow us to characterize the regulatory factors of the aquatic metabolism of the lakes and identify the possible foreign contributions from the study region.

This study represents the first records of CO_{2aq} levels and other parameters associated with the carbonate system in the Bolonha (LB) and Água Preta (LAP) lakes in the Amazon region. This information will be of technical and scientific usefulness to cover the demand for information related to the regional and global geographic coverage of the parameters associated with the carbon cycle, mainly in the bodies of tropical waters.

The main objective of this work was to characterize the contents of CO_{2aq} and DO and its parameters associated in two Amazonian lakes with strong anthropic pressure.

Material and Methods

Study area and sampling campaigns: Lakes LB (577,000 m^2) and LAP (3,116,000 m^2) correspond to the Utinga watershed in the city of Belem in Brazil (Sodre, 2007). These two lakes are water reservoirs for the public supply of the city of Belem (~2 million people) and other adjacent municipalities. The water from these reservoirs is supplied by the Guamá River through an adductor channel (~7 m^3 s^{-1}).

The Guamá River is a typical Amazonian River, classified as a clear water river according to Junk et al. (2011); their waters have near-neutral pH (6.0 - 8.5), relatively high concentrations of dissolved solids, and turbid waters. The soils of the LAP and LB lakes watershed are mainly latosols in 85% of the region (Junk et al. 2011).

The climate in the region is characterized as hot and humid (Afi; Koppen classification), with high rainfall (~2,800 mm yr^{-1}) mainly during the months of February-March.

From October 2018 to March 2019, six consecutive campaigns were carried out, including the dry period (October and November), the transition period (December and January), and the rainy period (February and March; Fig. 1) in the Agua Preta and Bologna lakes. Additionally, water samples were collected from the Guamá River at a station near the entrance to the channel that connects the river to the lakes (Fig. 1).

In each campaign in the lakes (4 stations) and the river (1 station), surface water samples were obtained at 5 points through Niskin bottles (2L), for the determination of TA and salinity. In situ, water temperature, electrical conductivity (µS cm^{-1}) were measured. CO_2 concentrations and dissolved inorganic carbon concentrations (DIC) were calculated from pH and alkalinity measurements after correction for temperature, altitude, and ionic strength following Cole et al. (1994) and Weiss (1974). pH was measured with a precision of 0.01 pH units using a calibrated pH meter, mark Analion®, model PM 608, and TA by Gran's titration (APHA, 1992). The partial pressure of CO_2 (pCO_2) of the water, was calculated using Henry's law, as the ratio between the CO_2 concentration and Henry's constant for this gas at a given temperature and salinity. The surface water temperature was obtained using a digital thermometer (Kestrel®; precision: ±0.1 ºC). Salinity was obtained by comparison with chlorinity and determined by titration with $AgNO_3$ (Grasshoff, et al. 1983) with an

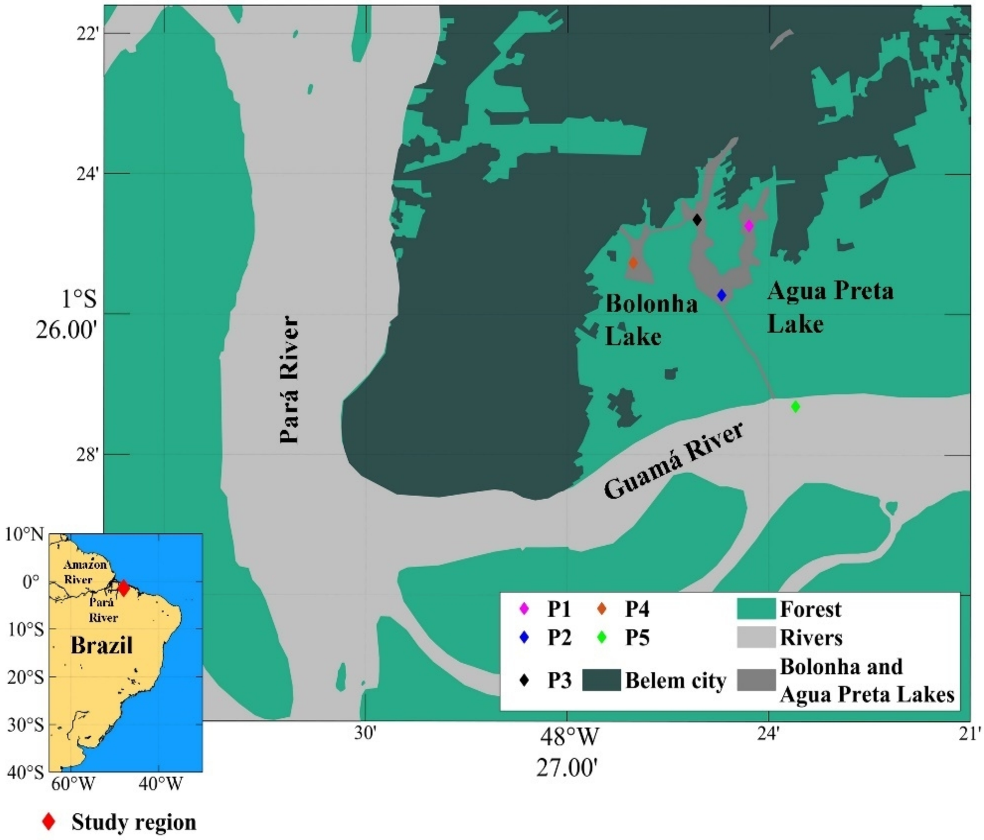

Figure 1. Location of the study area in the LB and LAP lakes and Guamá River. The dots indicate the sampling stations (5).

accuracy of 0.1 g kg^{-1}. The samples for the other parameters (turbidity, DO, biochemical oxygen demand (BOD) and, TA were preserved as described in APHA (1992) and transported to the Environmental Chemistry Laboratory, of the Federal Rural University of the Amazonia.

The turbidity data were obtained through a turbidimeter, HACH 2100 P ®, with an accuracy of ±2%.

DO was determined using the modified Winkler method Strickland & Parsons (1972), with an accuracy of ±1.3 μmol l^{-1}. Apparent Oxygen Utilization (AOU) represents one estimate of the O_2 utilized due to biochemical processes relative to a preformed value. AOU (μmol l^{-1}) was calculated as the difference between the O_2 gas solubility (O_2*) and the measured O_2 concentrations and expressed as:

$$AOU = (O_2^*) - (O_2) \quad (1)$$

where (O_2*) is calculated as a function of in situ temperature and salinity, and one atmosphere of total pressure. The (O_2*) values were calculated using the equation of Garcia & Gordon (1992) based on the (O_2*) values of Benson & Krause (1984); and (O_2) is the measured O_2 concentration (μmol l^{-1}). BOD_5 was determined according to the method described in Standard Methods for the Examination of Water and Wastewater (APHA, 1992) over a period of 5 days at 20 °C.

Data on rainfall were obtained from the national meteorology institute (INMET) for Belem city.

Groundwater HCO_3^- data were obtained from good records adjacent to lakes LAP and LB, performed by Rosa et al. (2013). Soil runoff estimates were performed according to the coefficients used by Noriega & Araujo (2009) for latosols.

Estimates of carbonate system parameters and statistical analysis: The DIC, CO_{2aq}, KCO_2 (CO_2 solubility coefficient), and bicarbonate (HCO_3^-) were estimated using the CO2sys software (Lewis & Wallace, 1998), using pH and TA measurements, with the dissociation constants given by Cai and Wang (1998) for waters with 0 - 40 salinity. PH values <5.8 were taken from this estimate according to the recommendation of Raymond et al. (2012).

Low pH values can propagate a significant error in estimating carbonate system parameters.

The excess of CO_2 (CO_{2aq}; μmol l^{-1}) is defined as the amount of DIC that is transferred as CO_2 to the atmosphere after attaining air-water equilibrium. The excess of CO_2 was calculated according to the equation from (Zhai et al. 2005), as follows:

$$\text{Excess } CO_2 = CO_{2aq} - KCO_2 \times pCO_{2\ air} \quad (2)$$

The partial pressure of atmospheric CO_2 (pCO_{2air}) was obtained through the following equation:

$$pCO_{2air} = XCO_2 \times (P_{atm} - pH_2O) \quad (3)$$

where P_{atm} = barometric pressure, obtained from the local meteorological data (atm); XCO_2 = mole fraction of atmospheric CO_2, obtained from NOAA (http://esrl.noaa.gov) (ppm); and pH_2O = water vapor pressure (μatm), obtained from (Weiss, 1980).

The results obtained were statistically analyzed using descriptive statistics (mean, standard deviation, minimum value, maximum value, coefficient of variation-CV), and non-parametric tests (Mann-Whitney and Kruskal-Wallis; used to identify differences between 2 and > 2 series of data, respectively). Additionally, Pearson's correlation test (identification of correlation between parameters) was used. All analyses were performed using the free software Past2017®.

Results

In the fluvial waters of the LB and LAP lakes during the 2018 - 2019 period, rainfall, evaporation, winds, and air temperature, corresponding to historical data in the region (Mann-Whitney test; $p > 0.05$; $\alpha = 0.05$). The freshwater budget (precipitation - evaporation) was positive during the study period (average: 340 mm). The intensity of the winds showed a range of 0.6 to 1.5 m s^{-1} (average: 0.9 ± 0.3 m s^{-1}), with greater intensities in the months of October and November (dry period; Fig. 2).

The thermal variation of the water showed a range of 28.0 to 30.4 °C (average = 29.2 ± 0.7 °C), with higher values in the months corresponding to the dry period (Fig. 2 and Fig. 3A). According to the temporal analysis, the water temperature showed significant differences between the months studied (Kruskal-Wallis test; $p = 0.04$; $\alpha = 0.05$); whereas, the Dunn test identified these significant differences between the months of March (wet period) and October (dry period; $p = 0.005$), and between March (wet period) and November (dry period; $p = 0.02$), respectively. The spatial analysis showed no statistically significant differences between the 4

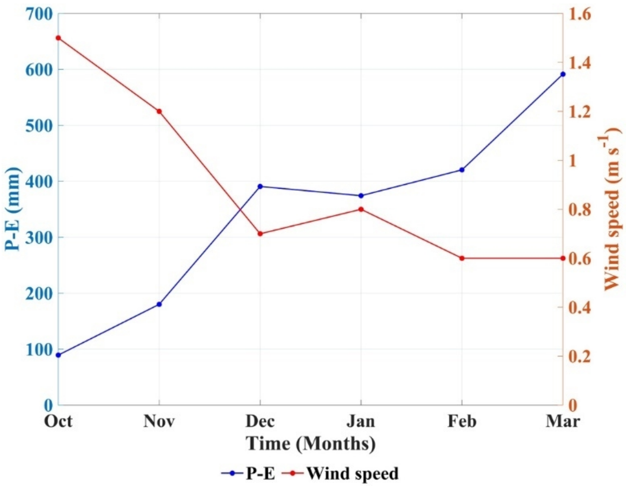

Figure 2. Temporal distribution of hydric balance (P-E; blue color) and wind intensity (red color) in the study region of the LB and LAP lakes.

collection points (Kruskal-Wallis test; $p = 0.18$; $\alpha = 0.05$), nor between the LB and LAP lakes (Mann Whitney test; $p = 0.57$; $\alpha = 0.05$; Table I).

Significant differences were observed between water temperature and air temperature (Mann Whitney; $p = 0.005$; $\alpha = 0.05$), with higher values on the aquatic surface.

Low values of electrical conductivity in LB and LAP were observed during this study (range: 34.0 - 103.0 μS cm^{-1}), consequently, the salinity also showed low values (< 0.05; Fig. 3B), indicating a low concentration of dissolved salts. The temporal analysis showed significant differences between the months of the study (Kruskal-Wallis test; $p = 0.0007$; $\alpha = 0.05$). these differences were observed between March and the months of November and December (Dunn test; $p = 0.001$, $p = 0.04$; $\alpha = 0.05$, respectively). The spatial analysis showed no significant differences (Table I).

The pH fluctuated in the range of 5.8 to 6.7, with an average pH of 6.2 ± 0.2 units for the study period (Fig. 3C). According to the current legislation, the pH values in freshwaters must oscillate between 6-9 (CONAMA, 2005). The pH measured in the LB and LAP lakes did not show significant differences between the months of study (Kruskal-Wallis test; $p = 0.62$; $\alpha = 0.05$); however, the spatial analysis showed significant differences between the collection points (Kruskal-Wallis test; $p = 0.002$; $\alpha = 0.05$). According to the Dunn test, point 4 (LB) differs from the other 3 (LAP; Dunn test; $p < 0.05$; $\alpha = 0.05$), consequently, the lakes also differ statistically (LB vs LAP; Mann Whitney test; $p = 0.0001$; $\alpha = 0.05$; Table I). In the river, the values

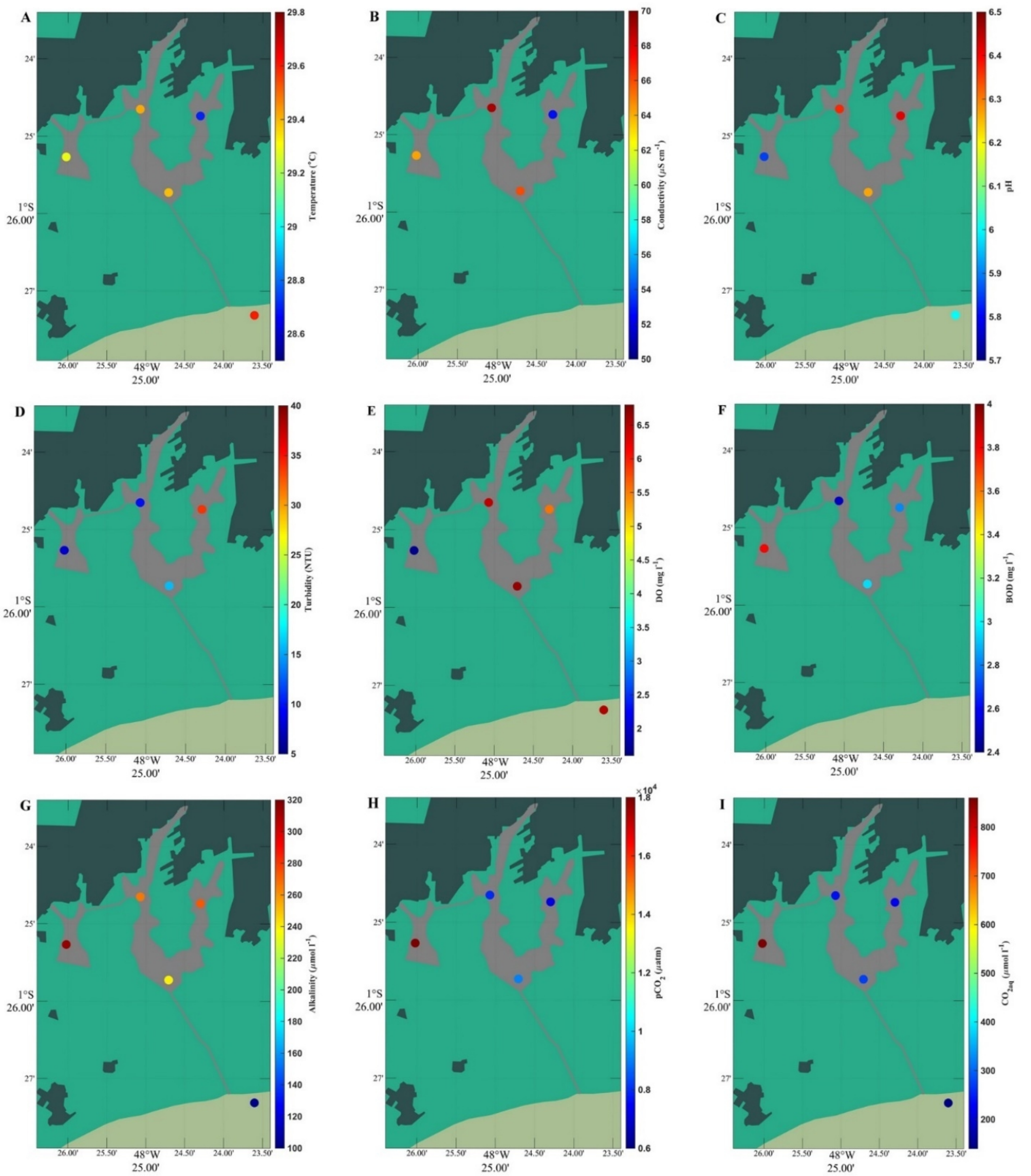

Figure 3. Spatial distribution of: water temperature (A); Electric conductivity (B); pH (C); Turbidity (D); DO (E); BOD (F); TA (G); *p*CO_2 (H); CO_{2aq} (I).

recorded (average = 6.0) were lower than LAP but more alkaline than those observed in LB.

Similar to electrical conductivity, turbidity and pH showed low values in this study (average = 17 ± 15 NTU), indicating a low number of particles in suspension (Fig. 3D). According to environmental regulation, the maximum limit allowed is 40 NTU for freshwater (CONAMA, 2005). The temporal analysis did not show significant differences between the months studied (Kruskal-Wallis test; p = 0.72; α = 0.05). However, the spatial analysis showed significant differences between the

Table I. Temporal and spatial statistics in LB and LAP lakes. KW: Kruskal-Wallis test; MW: Mann-Whitney test. p <0.05 indicates significant differences for α = 0.05. In bold, significant p-values. M indicates the month in numerical order. p indicates the sampling points. LB indicates Bologna Lake and LAP indicates Agua Preta Lake.

Parameter\tests	KW test (months)	Dunn test (months)	KW test (points)	Dunn test (points)	MW test (Lakes – LB; LAP)
		Observations			
Water temperature (°C)	**p=0.04**	M3-M10 **p=0.005** M3-M11 **p=0.02**	p=0.18	-	p=0.57
EC (µS cm^{-1})	**p=0.0007**	M3-M11 **p=0.001** M3-M12 **p=0.04**	p=0.80	-	p=0.60
Turbidity (NTU)	p=0.72	-	**p=0.006**	P1-P4 **p=0.005**	**p=0.004**
pH	p=0.62	-	**p=0.002**	P1-P4 **p=0.004** P2-P4 **p=0.02** P3-P4 **p=0.01**	**p=0.0001**
DO (mg l^{-1})	p=0.77	-	**p=0.001**	P2-P4 **p=0.003** P3-P4 **p=0.008**	**p=0.0001**
BOD_5 (mg l^{-1})	p=0.53	-	p=0.22	-	p=0.052
TA (µmol l^{-1})	**p=0.005**	M3-M12 **p=0.008** M2-M3 **p=0.04**	p=0.3 2	-	p=0.10

campaign points (Kruskal-Wallis test; p = 0.006; α = 0.05). These differences were observed between points 1 and 4 (Dunn test; p = 0.005; α = 0.05). These differences were reflected in the spatial analysis between the lakes (LB and LAP; Mann-Whitney test; p = 0.004; α = 0.05).

Variations in DO (1.0 - 8.5 mg l^{-1}) indicated a wide range of values, with an average value of 5.1 ± 2.2 mg l^{-1} (Fig. 3E). This value is in accordance with the minimum limit required by the environmental legislation of 5.0 mg l^{-1} for freshwater bodies (CONAMA, 2005).

The temporal analysis for DO did not show significant differences between the months of study (Kruskal-Wallis test; p = 0.77; α = 0.05). However, the spatial analysis showed significant statistical differences between the collection points (Kruskal-Wallis test; p = 0.001; α = 0.05). According to the Dunn test, these differences were between point 4 and point 3 and also between point 4 and point 2 (Dunn test; p = 0.003 and p = 0.008; α = 0.05, respectively). Additionally, LAP and LB showed significant differences (Mann-Whitney test; p = 0.0001; α = 0.05; Table I). The concentrations obtained in the river were close to the values recorded in LAP (Fig. 3E).

BOD concentrations showed values below the maximum limit required by environmental legislation (< 5.0 mg l^{-1}). During the study period, concentrations ranged from 1.3 to 4.8 mg l^{-1} (average = 3.0 ± 0.9 mg l^{-1}; Fig. 3F). The temporal statistical analysis did not show significant differences between the months (Kruskal-Wallis test; p = 0.53; α = 0.05). Similarly, the spatial analysis showed no significant differences between the campaign points (Kruskal-Wallis test; p = 0.22; α = 0.05), and between the lakes (Mann-Whitney test; $p = 0.052$; $\alpha = 0.05$; Table I).

The TA varied between 160 and 400 µmol l^{-1} (average = 273.0 ± 65 µmol l^{-1}), during the study period (Fig. 3G). Significant differences were observed between the months (Kruskal-Wallis test; $p = 0.005$; $\alpha = 0.05$). According to the Dunn test, the month of March differs significantly from the months of December and February (Dunn test; $p = 0.008$; $p = 0.04$; $\alpha = 0.05$, respectively). The spatial statistical analysis of TA did not show significant differences between the collection points or between the studied lakes (Kruskal-Wallis test; $p = 0.32$; $\alpha = 0.05$ and Mann-Whitney test; $p = 0.10$; $\alpha = 0.05$; Table I). The concentrations recorded in the Guamá River were lower than those recorded in Lakes LAP and LB (Figure 3G)

pCO_2 values ranged from 3,400 to 23,600 µatm, indicating supersaturation in partial CO_2 pressure when compared to atmospheric values (~ 400 µatm). The pCO_2 values did not show significant differences between the studied periods (Kruskal-Wallis test; $p = 0.70$; $\alpha = 0.05$; Fig. 3H).

High levels of CO_{2aq} were observed during the study (104.0 - 998.0 µmol l^{-1}), whereas, CO_2 in equilibrium with the atmosphere (CO_{2eq}) varied between 11.5 and 12.3 µmol l^{-1} (Fig. 3I).

Discussion

According to the historical climatological records and the study period, precipitation, evaporation, air temperature and wind intensity did not show significant differences from normal climatological conditions. According to the Beaufort empirical scale, the wind intensities recorded in the period are called Breeze (1.0 - 3.0 m s^{-1}) and do not cause agitation on the aquatic surface. The observed differences between water and air temperature are common in many lotic systems. This is mainly because, the air temperature changes faster than the water temperature (thermal inertia); therefore, the times when the values on both interfaces are exactly the same are very rare. Bodies of water, such as lakes, ponds, and rivers, are much slower to cool down than land areas. Statistical amplitude between the two climatic periods was 0.7 ºC. This variation was lower than that observed in 2006 (1.0ºC) by Sodré (2007) for the same months in the systems studied.

The low levels of electrical conductivity are indicative of low content of dissolved salts. Natural waters have values between 10 - 100 µS cm^{-1} (FNS, 2014) and are generally recommended for human consumption because they have low concentrations of dissolved salts.

Similar to conductivity, turbidity also showed low values. The spatial differences observed in this study (point 1 and point 4) may be due to the fact that point 1 (average = 34.0 NTU) corresponds to a station close to the margin in the LAP, surrounded by neighborhoods with high population density and clandestine sources of domestic sewage, while point 4 (average = 8.0 NTU) corresponds to the LB near the water treatment plant (Fig. 3D).

The pH also showed low values, with 100% of the samples with values < 7. The pH observations in the LB and LAP lakes indicated a lower pH in LB. These values are similar to those observed by other authors in the study region (Brito et al. 2020; Vasconcelos & Souza, 2011; Sodré, 2007). The low pH values observed in these systems can have high concentrations of dissolved organic acids of allochthonous and indigenous origin. Generally, in low pH conditions, high concentrations of sulfuric, nitric, oxalic acid, in addition to carbonic acid, formed mainly by the metabolic activity of aquatic microorganisms, can be found. These pH variations in the aquatic environment are directly related to the carbon and oxygen cycles.

According to the estimates of the parameters of the carbonate system, the pH showed a strong positive correlation with DO and negative with CO_{2aq} ($r^2 = 0.82$ and $r^2 = -0.93$, respectively; Table II). The range of observed values is also in agreement with the values observed by other authors (Brito et al. 2020; Vasconcelos & Souza 2011; Silva et al. 2020). The work of Vasconcelos & Souza (2011), carried out between 2007 and 2009 showed average values in the range of 1.5 to 4.5 mg l^{-1} in the lakes.

According to Brito et al. (2020) DO concentrations in these systems are higher during the rainy season; however, our results showed that the highest values were in the months associated with the dry period (average = 5.3 m l^{-1}), while the lowest values were observed in the rainy period (average = 4.9 mg l^{-1}).

Based on table II, the DO exhibited a high correlation with pCO_2 ($r^2 = -0.7$); additionally, DO showed a strong negative correlation with CO_{2aq} ($r^2 = -0.86$), indicating that wastewaters of domestic and industrial origin increased during this period, thus increasing the decomposition of organic matter and decreasing the pH (pH vs DO; $r^2 = 0.82$; Table II). Additionally, AOU was positively correlated with the excess of CO_{2aq} ($r^2 = 0.85$; Table II). These

Table II. Pearson correlations between the lake systems-linked variables in the 2018-2019 data series of pH, water temperature T(°C), CO_{2aq}, $HCO3^-$, pCO2, DIC, salinity, CO_2 excess, rainfall, DO and AOU. In bold, significant p-values described in the discussion section.

Parameters	**pH**	**T (°C)**	**CO_{2aq}**	**HCO_3**	**pCO_2**	**DIC**	**Salinity**	**CO_2 Excess**	**Rainfall**	**DO**	**AOU**
pH		0.007	**-0.933**	-0.372	-0.888	-0.888	-0.203	-0.933	-0.006	**0.819**	-0.814
T°C	0.007		-0.028	-0.132	-0.055	-0.050	0.273	-0.027	-0.638	0.151	-0.190
CO_{2aq}	0.933	-0.028		0.586	0.932	0.987	0.198	1,000	0.020	0.857	0.852
HCO_3	0.372	-0.132	0.586		0.647	0.705	0.010	0.586	0.214	0.453	0.455
pCO_2	-0.888	-0.055	0.932	0.647		0.940	0.280	0.932	0.014	0.694	0.691
DIC	0.888	-0.050	0.987	0.705	0.940		0.175	0.987	0.059	0.837	0.833
Salinity	0.203	0.273	0.198	0.010	0.280	0.175		0.198	0.690	0.007	0.018
CO_2 Excess	0.933	0.027	1,000	0.586	0.932	0.987	0.198		0.020	0.857	0.852
Rainfall	0.006	0.638	0.020	0.214	0.014	0.059	-0.690	0.020		0.116	0.141
DO	0.819	0.151	**-0.857**	-0.453	**-0.694**	-0.837	0.007	-0.857	-0.116		-0.999
AOU	0.814	0.190	**0.852**	0.455	0.691	0.833	-0.018	0.852	0.141	0.999	

results indicate that the organic load that enters the LB and LAP lakes has a significant impact on the microbial processes associated with the carbon cycle.

Generally, an aquatic ecosystem goes through phases of liquid production of organic matter, when production exceeds mineralization and phases of liquid respiration when the opposite occurs. Thus, these systems can show changes in the other parameters of the carbonate system such as TA, DIC, and HCO_3^- through the annual cycle.

TA and DIC showed a low correlation between them (r^2 = 0.5). The processes that partition dissolved CO_{2aq}, pCO_2, and DIC in fluvial environments are complex and influenced by a combination of sources and natural processes, such as the types of rock and soil in the hydrographic basin, water-atmosphere interaction sand oxidation/reduction reactions of anthropogenic inputs (Araujo et al. 2013; Mortatti et al. 2006). When analyzing whether the type of rock/soil influenced the water CO_2 content, no correlation between rainfall/fluvial runoff and pCO_2/HCO_3^- was observed (r^2 = 0.01 and r^2 = 0.2, respectively), suggesting that the transport processes via fluvial runoff are not the main factors that are responsible for the high concentrations of CO_{2aq} found in the studied lakes.

The TA contribution from the Guamá River was lower than the values recorded in the lakes. We can assume that river inputs add inorganic carbon to lakes, but they are not the main source of carbonate load.

The average distribution of the main compounds of the DIC were: HCO_3^- = 45.2%; CO_3^{2-} = 0.01% and CO_{2aq} = 54.7%. Of these 3 compounds, CO_{2aq} was the parameter that had the highest variation coefficient - CV (CV = 0.71) and directly influenced the variations in the concentrations of DIC and TA. According to Niel et al. (1998) and Araujo et al. (2013), under conditions of high CO_{2aq} values, which result from bacterial respiration, carbonic acid is produced and decreases the river water pH. If the characteristics of the body of water are such that the CO_2 concentration in the aqueous media is close to equilibrium with atmospheric CO_2, strong correlations between alkalinity, pCO_2, and pH would be expected. However, the complex set of processes that lead to the production or consumption of CO_{2aq} and the production or removal of carbonic acid (HCO_3^-) prevent the establishment of a correlation between alkalinity, pH, and pCO_2 (r^2 = 0.42 at TA vs pCO_2 and r^2 = 0.14 TA vs pH, respectively).

Similar to CO_{2aq}, pCO_2 showed a high CV (CV = 0.6), indicating strong variations across the studied period, indicating a low buffer capacity of the system, probably due to the anthropic impact adjacent to the lakes. Some studies have indicated that a sanitary landfill (Aurá dump) could be contributing through underground migration; however, a study by Bahia et al. (2004) indicated that the variations in conductivity detected were better correlated with lithological variations than with leachate.

These high pCO_2 values are higher than those reported in other Amazonian lakes (average = 7,956 µatm; range = 3,033 - 11,346 µatm; Pinho et al. 2016).

The Amazonian lakes sampled here were characterized by a prevalence of CO_2 supersaturation, consistent with general trends previously reported for global lakes (Raymond et al. 2013; Cole et al. 2007; Fig. 4A).

The very high pCO_2 levels observed here, with an average of 11,207 ± 6,200 µatm for Amazon Lake waters, are consistent with those reported previously for the Amazon floodplain lakes (3000 - 4898 µatm; Rudorff et al. 2012), Pantanal lakes and wetlands (2732 - 10620 µatm; Hamilton et al. 1995), and coastal lakes (768 - 9866 µatm; Kosten et al. 2010; 361-20,037 µatm; Marotta et al. 2010) and for global values for tropical lakes (1255 - 35,278 µatm; Marotta et al. 2009), reservoirs (1,840 µatm; Aufdenkampe et al. 2011) and wetlands (3,080 - 6,170 µatm; Aufdenkampe et al. 2011).

According to the pCO_2 values and high concentrations of CO_{2aq} in the LB and LAP lakes, we can indicate that these systems are sources of CO_2 into the atmosphere through the annual cycle (Fig. 4A and Fig. 4B). The biological processes associated with the carbonate system indicate that respiratory processes prevail over productive processes (Respiration > Production) making the system heterotrophic.

The high organic load included in these systems may be associated with the accumulation of organic matter at the bottom of the lakes. Additionally, it is possible that the most significant concentrations of organic matter in the studied systems have both natural and anthropic origin.

Significant levels of organic matter in low energy environments are common, with a predominance of fine sediments, since these are typical sedimentation sites. In a way, the low energy in these environments causes the accumulation of large amounts of organic matter and fine particles in the sedimentary environment. The amount of carbon and organic matter in sediments depends on two main factors: deposition and decomposition. The deposition is directly associated with biological production, however it is limited by geomorphological aspects, such as: depth, local hydrodynamics and particle diameter, among others. Decomposition, on the other hand, depends on the available dissolved oxygen content, the presence of decomposing organisms and the nature of the inorganic material.

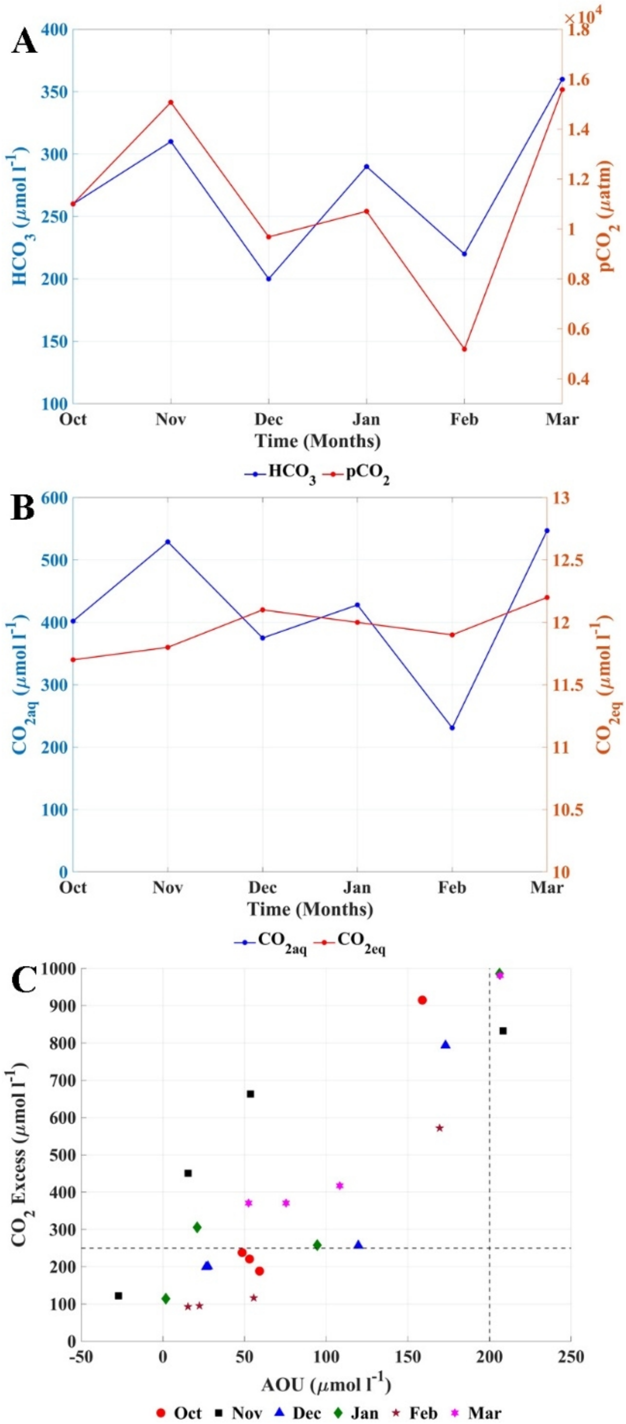

Figure 4. Temporal variation (months) of: (A) HCO_3^- (blue axis) and pCO_2 (red axis); (B) CO_{2aq} (blue axis) and CO_{2eq} (red axis) and rate of (C) CO_2 excess vs AOU during 2018 and 2019 in the LB and LAP lakes.

All stations in this study showed excess CO_2 when compared to CO_2 at equilibrium in water bodies. Conversely, the observed DO showed low concentrations in 38% of the samples (< 5 mg l^{-1}) and consequently positive AOU values. According to Fig. 4C, for estimated positive AOU values in 98.5% of collected samples, indicating heterotrophic processes (respiration) in aquatic systems. Aerobic waters are characterized by excessive concentrations of CO_{2aq} and AOU below 250 and 200 µmol l^{-1}, respectively, while anaerobic waters have higher values. Anoxia corresponds to an AOU of ~250 µmol l^{-1}. Fig. 4C indicated that, to a greater extent, the organic matter in the systems studied is being decomposed under anaerobic conditions.

The results obtained from these campaigns will indicate that heterotrophic processes dominate the river systems studied. To associated organic matter, natural and anthropic pathways seem to be the main factors that induce these strong oscillations of dissolved CO_{2aq} and DO.

The values obtained of pCO_2 and CO_{2aq} in this study were compared latitudinally with other lakes in the tropical and subtropical range obtained from Marotta et al. (2009). The results showed that 78% of the pCO_2 values observed in tropical and subtropical lakes exceed the average atmospheric pCO_2 value (observed period average = 396 µatm; Fig. 5A), indicating a supersaturation concerning atmospheric pCO_2, including the LAP and LB systems of this study (Fig. 5A). According to figure 5B, the CO_{2aq} values showed CO_2 supersaturation, above the equilibrium value (CO_{2eq}; Fig. 5C), while the CO_2 excess (Fig. 5D) indicated that the LAP and LB lakes exceed > 100% of average CO_2 excess of tropical and subtropical lakes. The comparative

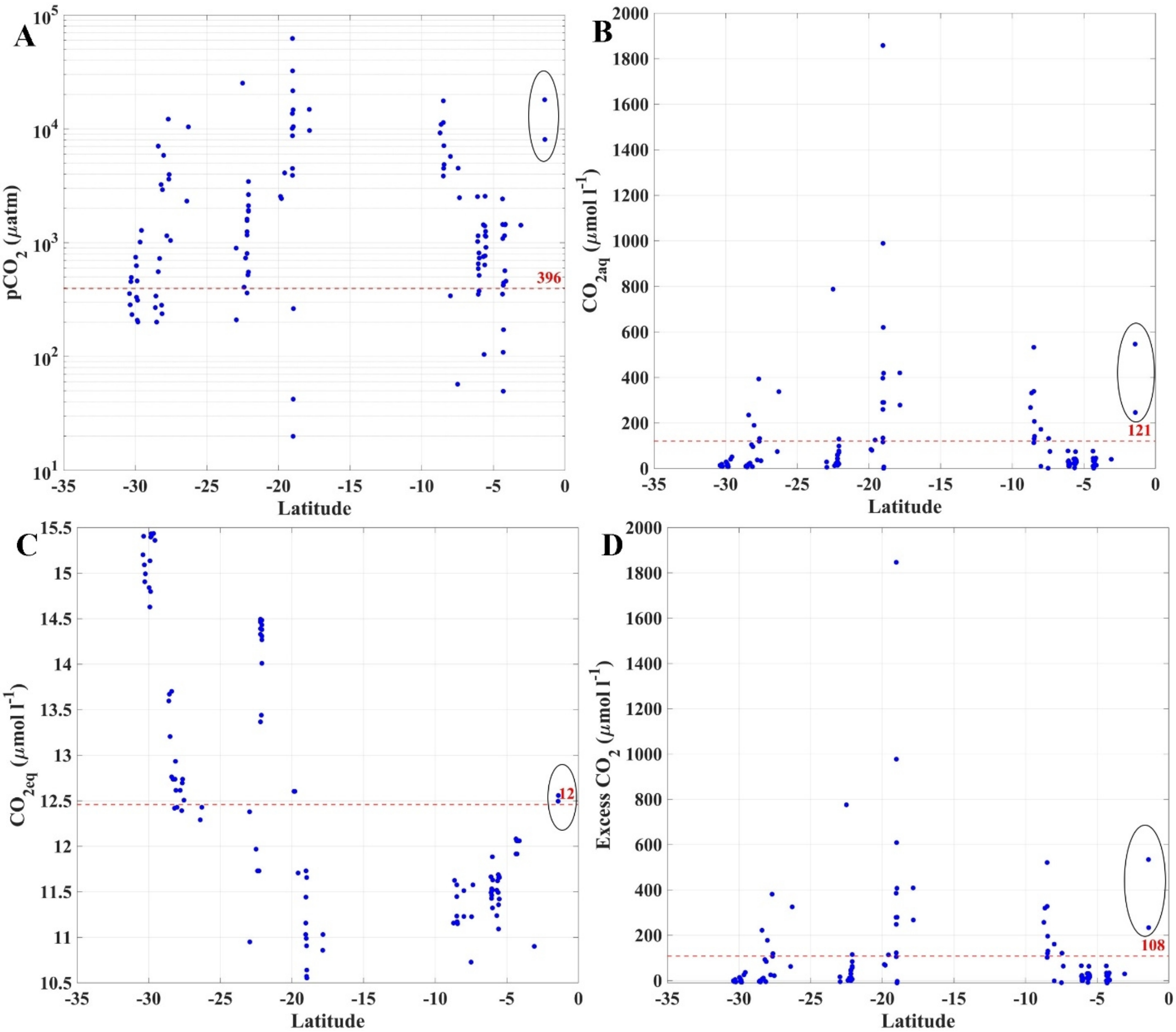

Figure 5. Latitudinal variations of pCO_2 (A); CO_{2aq} (B); CO_{2eq} (C); excess CO_2 (D). The red line in the graphs represents the average value. Lakes LAP and LB are indicated with an ellipse.

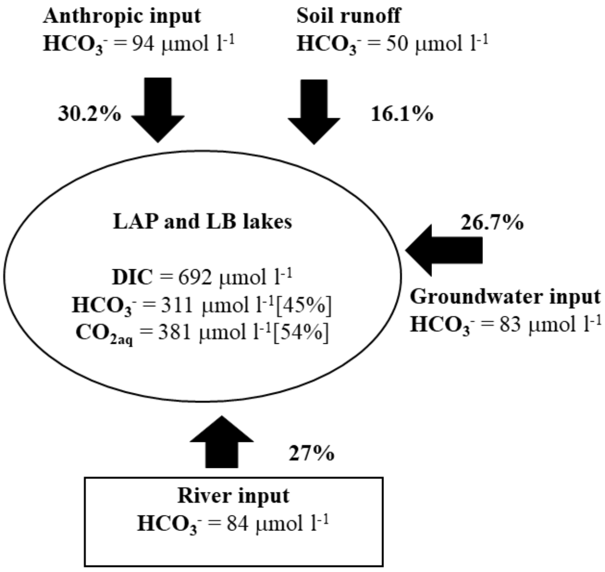

Figure 6. DIC balance in the LAP and LB lakes basin, in Belem city for the studied period, considering the anthropic inputs, soil runoff, groundwater input and Guamá River input (values in µmol l^{-1}).

analysis described above showed that the LAP and LB systems are supersaturated concerning atmospheric pCO$_2$ similar to other tropical and subtropical systems. Additionally, the excess of dissolved inorganic CO_2 demonstrates the anthropic input, mainly from domestic and industrial sewage from the region adjacent to the lakes. This is supported by the balance of the main carbonate species from the data obtained in the lakes, in the adjacent river, in the groundwater and, from the contribution of the soil. The balance showed that 30% of the dissolved inorganic carbon (HCO_3^- = 311 µmol l^{-1} of DIC = 692 µmol l^{-1}) in the lakes is of anthropic origin (Fig. 6). As indicated above, HCO_3^- represented 45% of DIC, while the remainder corresponds to CO_{2aq}. The natural contribution of HCO_3^- represented ~16% of the total DIC in the lakes; however, we must consider that other natural sources can be included in this balance (example: atmospheric deposition). The river supplies 27% of the HCO_3^- present in the lakes, similar to the groundwater input (26.7%). Both inputs contribute significantly to DIC concentrations in lakes LAP and LB.

The anthropic contributions in this balance are also evidenced by the results obtained in figure 3F (BOD), where it is possible to observe that the stations close to the urban region in lakes LAP and LB showed higher values of DO consumption (high BOD), indicative of the inputs of organic matter through diffuse sources of the adjacent urban region. The results shown above allow us to have a first estimate of the trophic state of these lakes about carbon and oxygen.

This study allowed to characterize the parameters associated to the carbonate system of 2 tropical lakes in the Amazon region. The values obtained from CO_{2aq} and DO will show that these systems have high pollution indices associated principally with anthropic processes.

Conclusions

The six campaigns carried out in LAP and LB lakes during 2018 - 2019 showed that: high levels of CO_{2aq} were observed during the study, indicating supersaturation of CO_2, while the DO showed significant variations between the lakes studied. These variations in the oxygenation of the lake waters showed positive values of AOU in 98.5% of the samples collected, indicative of heterotrophic processes (respiration > production) in the aquatic systems studied.

The pCO$_2$ and CO_{2aq} results observed in LAP and LB were compared to 117 other tropical and subtropical lakes, which indicated a CO_2 supersaturation in 78% of the total lake systems. This excess of CO_2 in the LAP and LB systems showed that the anthropic factor is the main contributor (30%) of DIC in the lakes. The values obtained from CO_{2aq} and DO will show that these systems have high pollution indices associated principally with anthropic processes.

The characterization of the trophic state in lakes LAP and LB through dissolved inorganic carbon and oxygen showed that: the heterotrophic processes identified during this study are mainly a product of the contributions of organic matter from the adjacent urban region.

This adjacent urban region is increasing and sanitation is minimal, key factors for an increase in organic matter inputs in lakes LAP and LB.

Acknowledgments

We thank the Brazilian National Institute of Meteorology (INMET) for the database used in this study (rainfall). Moacyr Araujo thank the support of the Brazilian Research Network on Global Climate Change FINEP/Rede CLIMA (grants 01.13.0353-00). Humberto L. Varona thanks to the TRIATLAS project, which has received funding from the European Union's

Horizon 2020 Research and Innovation Program under grant agreement no. 817578 and acknowledge to the International Joint Laboratory TAPIOCA (IRD-UFPE-UFRPE). Moacyr Araujo thanks the Brazilian Research Network on Global Climate Change - *Rede CLIMA* (FINEP-CNPq 437167/2016-0).

References

APHA. 1992. **Standard Methods for the Examination of Water and Wastewater**. 18th Edition. A.E Greenberg; L.S. Clesceri; A.D. Eaton (Eds). American Public Health Association, Washington, 1100p.

Araujo, M., Noriega, C., Veleda, D. & Lefèvre, N. 2013. Nutrient input and CO_2 flux of a tropical coastal fluvial system with high population density in the Northeast region of Brazil. **Journal of Water Resource and Protection**, 5:362-375. doi:10.4236/jwarp.2013.53A037.

Aufdenkampe, A., Mayorga, E., Raymond, P., Melack, J. & Doney, S. 2011. Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. **Frontiers in Ecology and the Environmental**, 9, 53–60.

Bahia, V. E., Gouvea, J. L. & Fenz, N. 2004. Influência do depósito sanitário metropolitano de Belém (Aurá) sobre as águas subterrâneas da área. **Revista Águas Subterrâneas**, 18:89-101. doi: 10.14295/ras.v18i1.1339.

Benson, B. B. & Krause, D. 1984. The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. **Limnology and Oceanography**, 29: 620–632. doi.org/10.4319/lo.1984.29.3.0620.

Brito, F. S. L. Pimentel, B.A., Vilhena, J.C., Rosário, K.K.L., Morais, M.S., Cruz, R.H. R. & Correa, V.L.S. 2020. Behavior of physicochemical variables of water Bolonha-Belém-PA. **Brazilian Journal of Development**, 6(1): 1738-1757. doi:10.34117/bjdv6n1-120.

Cai, W-J. & Wang, Y. 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha rivers, Georgia. **Limnology and Oceanography**, 43:657-668.

Cole, J. J., Caraco, N. F., Kling, G. W. & Kratz, T. K. 1994. Carbon dioxide supersaturation in the surface waters of lakes. **Science**, 265:1568-1570.

Cole, J. J. & Prairie, Y. T. 2009. Dissolved CO_2. Pp. 30-34. In: Likens, G.E. (Ed). **Encyclopedia of Inland Waters**. V. 2. Elsevier, Oxford, 2250 p.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J. & Striegl, R. G. 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. **Ecosystems**, 10, 172-185. doi: 10.1007/s10021-006-9013-8.

CONAMA-Conselho Nacional do Meio Ambiente. 2005. Resolução 357(in portuguese) - Classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, 27 pp. Conselho Nacional do Meio Ambiente, Brasil. http://www2.mma.gov.br/port/conama/legiabre.cfm?codlegi=484.

Garcia, F. H. & Gordon, I. I. 1992. Oxygen solubility in seawater: better fitting equations. **Limnology and Oceanography**, 37: 1307–1312. doi.org/10.4319/lo.1992.37.6.1307.

Grasshoff, K., Ehrhardt, M. & Koroleff, K. 1983. **Methods of seawater analysis**, 2nd ed. Wiley-Verlag, Weinheim, Germany, 419 p.

Hamilton, S. K., Sippel, S. J. & Melack, J. M. 1995. Oxygen depletion and carbon dioxide and methane production in waters of the Pantanal wetland of Brazil. **Biogeochemistry**, 30, 115–141.

Junk, W. J., Piedade, M. T. F. & Schöngart, J. 2011. A Classification of Major Naturally-Occurring Amazonian Lowland Wetlands. **Wetlands**, 31, 623–640. doi:10.1007/s13157-011-0190-7.

Kosten, S., Roland, F., Da Motta Marques, D., Van Nes, E., Mazzeo, N., Sternberg, L., Scheffer, M. & Cole, J. 2010. Climate dependent CO_2 emissions from lakes. **Global Biogeochemical Cycles**. 24, GB2007. doi:10.1029/2009GB003618.

Lewis, E. & Wallace, D. 1998. (Eds.). **Program developed for CO_2 system calculations**. National Laboratory Environmental Sciences Division, Oak Ridge, Tennessee, USA, v. 4735. doi:10.15485/1464255. World Wide Web electronic publication, accessible at http://www.cdiac.ess-dive.lbl.gov/ftp/co2sys/. (Accessed 12/01/2021).

Marotta, H., Duarte, C. M., Sobek, S. & Enrich-Prast, A. 2009. Large CO_2 disequilibria in tropical lakes. **Global Biogeochemical Cycles**, 23, GB4022. doi:10.1029/2008GB003434.

Marotta, H., Duarte, C. M., Pinho, L. & Enrich-Prast, A. 2010. Rainfall leads to increased pCO_2 in Brazilian coastal lakes. **Biogeosciences**, 7, 1607-1614. doi:10.5194/bg-7-1607-2010.

Mortatti, J., Probst, J. L., Oliveira, H., Bibian, J. P. R. & Fernandes, A. M. 2006. Fluxo de carbono inorgânico dissolvido no Rio Piracicaba (São Paulo): partição e reações de equilíbrio do sistema carbonato. **Geociências**, 25(4): 429-436.

Neal, C., House, W., Jarvie, H. & Eatherall, H. 1998. The significance of dissolved carbon dioxide in major lowland rivers entering the North Sea. **Science of the Total Environment**, 210-211: 187-203. doi:10.1016/S0048-9697(98)00012-6.

NOAA- National Oceanic and Atmospheric Administration - Earth System Research Laboratories (ESRL), 2021. **Trends in Atmospheric Carbon Dioxide**. World Wide Web electronic publication, accessible at http://esrl.noaa.gov/. (Accessed 12/01/2021).

Noriega, C. & Araujo, M. 2009. Nitrogen and phosphorus loading in coastal watersheds in northeastern Brazil. **Journal of Coastal Research**, SI56, 871-875.

Pinho, L., Duarte, C. M., Marotta, H. & Enrich-Prast, A. 2016. Temperature dependence of the relationship between pCO_2 and dissolved organic carbon in lakes. **Biogeosciences**, 13, 865–871. doi: 10.5194/bg-13-865-2016.

Raymond, P., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C. & Hoover, M. 2013. Global carbon dioxide emissions from inland waters. **Nature**, 503:355-359. doi:10.1038/nature12760.

Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P., Laursen, A.E., Mc Dowell, W. H. & Newbold, D. 2012. Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. **Limnology and Oceanography**, 2:41-53. doi: 10.1215/21573689-1597669.

Rosa, L. L., Melo, M. & Santana, H. 2013. Avaliação paralela da qualidade da água do lago água preta, de águas subterrâneas de áreas próximas e a água para abastecimento. **Saneamento Ambiental e Águas Urbanas (XX SBRH - Simpósio Brasileiro de Recursos Hídricos).** Associação brasileira de Recursos Hídricos, Bento Gonçalves-RS, SBRH2013__PAP013171.

Rudorff, C. M., Melack, J. M., MacIntyre, S., Barbosa, C. C. F. & Novo, E. M. L. M. 2012. Seasonal and spatial variability of CO_2 emission from a large floodplain lake in the lower Amazon. **Journal of Geophysical Research**, 117, G01002. doi:10.1029/2011JG001699>.

Silva J. P., Mesquita, K. F. C., Pereira, J. A. R., Sousa, R. R., Varela, A. W. P., Sousa, P. H. C. & Santos, M. L. S. 2020. Índices de qualidade da água no sistema de captação de água da região amazônica (Brasil). **Scientia Plena**, 15: 1- 9. doi: 10.14808/sci.plena.2019.124301.

Sodré, S. S. V. 2007. Hidroquímica dos lagos Bolonha e Água preta, mananciais de Belém-Pará (in Portuguese). PhD. Thesis. Federal University of Pará, Belem, Brazil, 115 p.

Strickland., J. D. H. & Parsons, T. R. 1972. A practical handbook of seawater analysis. 2 ed. **Fisheries research board of Canada bulletin**, Ottawa, 167: 207-211.

Talling, J. F. 2010. pH, the CO_2 system and freshwater science. **Freshwater Reviews**, 3(2):133-146. doi: 10.1608/FRJ-3.2.156.

Vasconcelos, V. M. M. & Souza, C. F. 2011. Caracterização dos parâmetros de qualidade da água do manancial Utinga, Belém, PA. *Brasil.* **Revista Ambiente & Água**, 6(2): 305-324. doi.org/10.4136/ambi-agua.202.

Weiss, R. F. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. **Marine Chemistry**, 2:203-215. doi: 10.1016/0304-4203(74)90015-2.

Weiss R. F. & Price, B. A. 1980. Nitrous oxide solubility in water and seawater. **Marine Chemistry**, 8: 347–359. doi:10.1016/0304-4203(80)90024-9.

Zhai, W., Dai, M., Cai, W-J., Wang, Y. & Wang, Z. 2005. High partial pressure of CO_2 and its maintaining mechanism in a subtropical estuary: the Pearl River estuary, China. **Marine Chemistry**, 93:21-32. doi:10.1016/j.marchem.2004.07.003.

Received: March 2022
Accepted: April 2022
Published: August 2022