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The physical-chemical characteristics of surface waters in the management of quality in clearwater rivers in the Brazilian Amazon

Christiane do Nascimento Monte[a,*], Edinelson Correa Saldanha[b], Igor Costa[c], Thiago Shinaigger Rocha do Nascimento[d], Mateus Santos Pereira[a], Louisiane Farias Batista[d] and Danilo Costa Pinheiro[a]

[a] Department of Geology, Federal University of Western Pará, Av. Vera Paz, s/n. Salé, Santarém, PA, CEP 68035-110, Brazil
[b] Post-Graduation Program in Society, Nature and Development (SND-Ufopa), Federal University of Western Pará, Av Mendonça Furtado, 2946, Santarém ,PA, CEP 68040-070, Brazil
[c] Bachelor in Earth Sciences Federal University of Western Pará, Av. Vera Paz, s/n. Salé, Santarém, PA, CEP 68035-110, Brazil
[d] Bachelor of Science and Water Technology, Federal University of Western Pará, Av Mendonça Furtado, 2946, Santarém ,PA, CEP 68040-070, Brazil
*Corresponding author. E-mail: christiane.monte@yahoo.com.br

ABSTRACT

The study of water quality in the Amazon region is important for understanding the functioning of ecological mechanisms. The standard that governs water quality in Brazil, including the Amazon, is Resolution CONAMA 357/05, which uses criteria inspired by standards from other countries. However, this resolution does not consider characteristics of Amazonian aquatic ecosystems, and this can lead to incorrect interpretation of the data. Furthermore, there are few studies on the physical-chemical characteristics of clearwater rivers in the Amazon and the influence of the forest-water interface. Therefore, water samples were collected from four clearwater tributary watersheds of the Amazonas and Tapajós Rivers during the dry season in the city of Santarém, Pará. Most of the points were collected in pristine areas in order to capture the natural physicochemical characteristics of clearwater rivers, as well as to show the importance of ecoregional aspects in water quality management. All samples were below pH 6.0, which represents non-compliance with the CONAMA resolution. Statistical tests yielded negative correlations between pH and conductivity ($r = -0.87$, $p < 0.05$), Therefore, the rivers of lower ionic load are influenced by the type of surrounding vegetation, which are characteristics that have been widely reported for blackwater rivers.

Key words: Amazon, Clearwater river, Forest-water interface, Micro-basin, Water quality

HIGHLIGHTS

- The forest-water interface directly influences physicochemical factors in clearwater rivers.
- Rivers with lower ionic load are influenced by dissolved colloidal substances.
- Conductivity can be used as an indicator of organic matter in clearwater rivers.
- Parameters in natural conditions do not comply with the CONAMA standards.
- The standards require adaptation to the characteristics of Amazonian rivers.

INTRODUCTION

Water quality is important for economic development, public health policies, and maintaining a balanced environment (Lu *et al.*, 2015; Shi *et al.*, 2017; Xu *et al.*, 2019). Water quality degradation is related to pollution from diffuse sources, which makes monitoring complex (Xu *et al.*, 2019; Peluso *et al.*, 2020). Brazil is a country

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that has many water resources; however, a portion of these resources are currently degraded, mainly due to urban expansion of several large cities.

Unplanned urban expansion has increased the input of domestic and industrial effluents into rivers and estuaries, and agricultural waste has significantly increased the input of nutrients into water resources (Peluso *et al.*, 2020). To manage water quality, the Brazilian environmental agency created a resolution in 2005.

In the CONAMA Resolution 357/05, waters were divided into three types: fresh, brackish, and saltwater, with freshwater divided into five classes (special, 1, 2, 3, and 4). The criteria used for the classification were physical-chemical, hydrobiological, nutrients, and organic and inorganic pollutants (Pizella & Souza, 2007; Silva *et al.*, 2013). The current legislation has limits established according to stricter norms of other countries, mainly those whose economic and social realities are similar, like South Africa (Pizella & Souza, 2007). However, Brazilian legislation presents inconsistencies related to regional characteristics (Silva *et al.*, 2013).

The legislation does not take into consideration ecoregional aspects, as in the case of Amazonian rivers, which present unique characteristics compared to the rest of the country (Silva *et al.*, 2013). The lack of recognition of these characteristics may lead to poor management of water resources in the region, which holds the largest reserve of non-frozen freshwater on the planet (Trancoso *et al.*, 2007; Ríos-Villamizar *et al.*, 2020).

According to Costa & Persechini (2012), the main existing or potential pressures on water quality in the Amazon Basin are: domestic sewage, urban solid waste, industrial activities (mainly in the Manaus Free Trade Zone and in the Tapajós River basin with industries focused on slaughtering cattle, pigs and poultry), mines, deforestation, inadequate soil management, hydroelectric plants, navigation, and drought effects, which cause the drastic reduction of oxygen levels in streams and lakes due to the low rate of renewal of their waters and the reduction in the dilution capacity of polluting loads.

In the Amazon, factors such as geology, soil, vegetation, and forest-water interaction give rise to rivers with different concentrations of particulate and dissolved compounds, which are directly reflected in the three main classifications of rivers, known as black, white, and clear water rivers (Costa *et al.*, 2013). In general, Amazonian rivers are known to have large amounts of dissolved organic matter (Schmidt, 1982; Monteiro *et al.*, 2014; Wasserman *et al.*, 2019), which directly impacts pH, conductivity, and dissolved oxygen, especially, blackwater rivers (Monteiro *et al.*, 2014). Clearwater rivers (Sioli, 1968; Schmidt, 1982), are characterized by low ion concentrations, and lower concentration of humic substances compared to white- and blackwater rivers (Schmidt, 1982). In addition, they drain areas of ancient, highly eroded shields, which are covered by deep and weathered soils, such as latosols, resulting few suspended solids in the water, which is therefore poor in nutrients (Devol & Hedges, 2001; Costa *et al.*, 2013).

The Tapajós River is a tributary of the Amazon River on the right bank. It is a clearwater river, which is originated from the confluence of the rivers Teles Pires and Juruena, in Central Brazil (state of Mato Grosso) (Sousa Júnior, 2014) in the Brazilian Cerrado region (Trancoso *et al.*, 2007). Most of the basin is located on a crystalline base and drains Cretaceous sedimentary rocks (Silva *et al.*, 2013; Sousa Júnior, 2014), which influence the more acidic pH of the river and the micro-basins that make up the distribution system of tributaries.

The concept of the micro-basin is part of several watershed subdivisions described in the literature, and hydrological and ecological characteristics can be adopted as criteria for units of measurement (Teodoro *et al.*, 2007). Regarding the unit of measurement criteria, Cecílio & Reis (2006) define the micro-basin as a restricted area sub-basin with extensions ranging from 0.1 km^2 to 200 km^2, from a hydrological point of view.

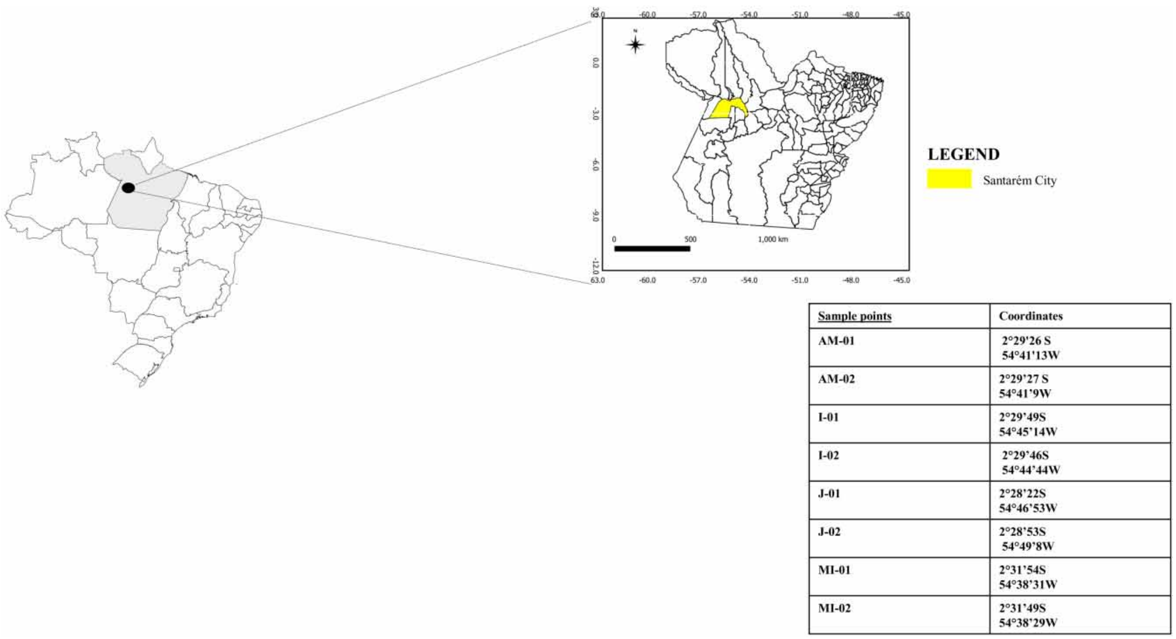
According to Zeidemann (2001), in small Amazon streams (igarapés) different types of water with chemical composition and transparency similar to the large rivers can also be observed. However, the variations in the streams occur in a more intense and rapidly changing way, with changes from one type of water to another being possible in a matter of a few days, or even hours because of the mixture between rivers that drain different regions or of seasonal variations determined by larger or smaller amounts of rain (Zeidemann, 2001). Therefore, the study of water quality in Amazonian streams is important because of their higher sensitivity to environmental variations.

Water quality can vary according to local lithology and environmental conditions (Sahoo *et al.*, 2019), and vegetation physiology directly influences water cycles at local, regional and global scales (Khan & Zaheer, 2018). The Amazon is a region that has unique characteristics that make its waters different from those of the rest of the Brazilian territory, and there are few studies in the literature which address the physicochemical characteristics of clearwater rivers and the effects of land management on water quality. Most of the studies concentrate on the Amazon River, a whitewater river, or on the blackwater rivers, such as the Negro River. Studies done on clearwater rivers concentrate mainly on the contamination of mercury in the Tapajós river basin, however, there are no studies on the physical-chemical characteristics of this type of Amazonian river with comparisons with the CONAMA standards currently in use in Brazil.

The current Brazilian environmental standards are equivalent for rivers in the Brazilian territory with different natural characteristics, which can cause a misinterpretation in the management of water quality in the Amazon region. Therefore, this study aims to investigate whether there is a relationship between the physical-chemical characteristics of clear water streams in pristine areas in the city of Santarém, Pará-Brazil, and the Brazilian standards in CONAMA 357/05 using statistical data. The goal of this analysis is to provide the basis for a possible modification of the CONAMA standards to be more aligned with the characteristics of Amazonian environments, consequently improving the management of water quality in a strategic region of growth and development of the country.

MATERIALS AND METHODS

The sampling campaigns were divided between the years 2018, 2019, and 2020 in the dry season in the watersheds of Irurá (I-01 and I-02), Miritituba (MI-01 and MI-02), Mararu (AM-01 and AM-02), and Juá (J-01 and J-02), all in Santarém – Pará (Figure 1). The Irurá and Juá watersheds flow into the Tapajós River,



Sample points	Coordinates
AM-01	2°29'26 S 54°41'13W
AM-02	2°29'27 S 54°41'9W
I-01	2°29'49S 54°45'14W
I-02	2°29'46S 54°44'44W
J-01	2°28'22S 54°46'53W
J-02	2°28'53S 54°49'8W
MI-01	2°31'54S 54°38'31W
MI-02	2°31'49S 54°38'29W

Fig. 1 | Study area and sample points.

and the Mararu and Miritituba watersheds flow into the Amazon River. The reason for choosing this season is because there is less influence of precipitation, which is associated with characteristics such as a lower dilution factor and a lower contribution of continental drainage, which directly interferes with physicochemical parameters such as pH and conductivity (Pinheiro *et al.*, 2019).

Pinheiro *et al.* (2019), performed a study on the Trophic State Index (TSI) in the Irurá watershed in two Amazonian seasons (dry and wet) and showed that in the wet season the pH decreases due to the greater contribution of organic matter, resulting from the forest-water interface, and the electrical conductivity also increases due to greater availability of salts, which are carried with the rain. Because of this, the authors chose the dry season for this study as a way to validate the methodology for clearwater rivers, which up to now have been tested only in blackwater rivers.

The Amazon watershed is the largest hydrographic drainage system in the world in length, crossing the South American subcontinent from west to east (Eva & Huber, 2005; Val *et al.*, 2017); however, it is different from the Amazon Hydrographic Region, in which the watershed is part of and limited to the Brazilian state (Val *et al.*, 2017). The main factors that remodeled and recomposed the structure of occupation of the Brazilian Amazon region were the variations economic activities and population changes, which, at the beginning of the 21st century, generated complex urban behaviors and patterns in the middle of the rainforest (Becker, 1995). According to Becker (2010), one of the biggest and worst environmental problems in the Amazon is the living conditions in cities and urban settlements, given that population growth was not accompanied by the implementation of adequate development mechanisms to provide minimum conditions of health, education, and salaries combined with a lack of urban infrastructure.

Physical-chemical parameters such as temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) were determined *in situ* with the aid of the AKSO AK87 multiparameter probe. In the laboratory turbidity analyses were performed using a PoliControl AP 2000 turbidimeter and total dissolved solids (TDS; mg/L) with the multiparameter probe.

The analysis of total phosphorus (mg/L) was performed using the method of Reduction with Ascorbic Acid with spectrophotometer readings as described in APHA (2005).

Statistical analysis was performed using STATISTICA 7.0 software. The Principal Component Analysis (PCA) test and Spearman correlations ($p < 0.05$) were applied to verify possible relationships between physical-chemical parameters and phosphorus. This is a multivariate analysis which allows for investigations with a large amount of available data (Wu *et al.* 2014, 2020; Li *et al.*, 2019; Silva e Silva *et al.*, 2020).

RESULTS

Physical and chemical parameters

Water temperature showed low variation at the studied points (Table 1) however, Juá showed the lowest values due to the greater integrity of the riparian forest. The pH values, as expected for the Amazon region, were characterized as acidic in all studied streams, indicating the presence of humic and fulvic acids (Rios-Villamizar *et al.*, 2020). The acidic pH in clearwater rivers indicates that the amount of dissolved organic matter is higher than in rivers of different environments in the country. Previously, it was seen in other studies, that only black- and whitewater rivers had higher interference of organic matter on physical-chemical parameters due to the forest-water interface and lithology.

The dissolved oxygen (DO) concentrations were low, except for point J-02, which was the only one within the current standard for rivers. According to CONAMA 357/05, DO concentrations below the recommended value suggest anthropic interference, such as dumping of domestic sewage. However, this study collected most of the

Table 1 | Physical-chemical and total phosphorus parameters in the Irurá, Mararu, Miritituba and Juá micro-basins.

	Dry Season							
	Samples							
	Irurá		Mararu		Miritituba		Juá	
Parameters	I-01	I-02	AM-01	AM-02	MI-01	MI-02	J-01	J-02
Temperature (°C)	27.2	27.2	26.7	27.5	27.2	27.4	23.4	23.5
pH	5.2	5.2	4.6	4.5	5.9	5.6	5.3	5.3
Electrical Conductivity, EC (μS/cm)	15.6	13.6	17.6	22.7	11.9	11.4	–	–
Dissolved Oxygen, DO (mg/L)	3	1.6	4.7	4.5	5	5.3	4.2	6
Total Dissolved Solids, TDS (mg/L)	6.4	8.3	9	9	30.3	42.6	76.8	108.8
Turbidity (NTU)	2.47	2.72	1.7	5.2	3.93	3.58	65.1	169.5
Phosphorus (mg/L)	0.06	0.09	0.1	0.03	0.02	0.02	0.013	0.615

samples in pristine areas to capture the natural characteristics of Amazonian rivers, including clearwater rivers, so this characteristic may be linked to the forest-water interface.

However, only the points of the Juá watershed were above the allowed values for class 1 and class 2 of the standard (60 and 100 NTU, respectively) for turbidity, which may be related to the discharge of sewage at these points, and consequent anthropic interference. This can be confirmed using total phosphorus (TP), which is another indication of domestic effluent discharge, although only point J-02 was above the allowed value for the class 1 standard.

The electrical conductivity was low in all points, which is agreement with values for rivers in the region, as studied by Wasserman *et al.* (2019) who found values between 0 and 140 μS/cm. Monteiro *et al.* (2014) in their study in blackwater rivers, found there is a correlation between electrical conductivity (EC) and dissolved organic matter. Wasserman *et al.* (2019) state that higher concentrations of organic carbon can attribute higher conductivity values in rivers with low concentrations of ions, such as clearwater rivers.

The PCA plot (Figure 2) showed the influence of two factors, which together were responsible for more than 70% of the analysis. Conductivity was negatively correlated with pH (Spearman $r = -0.87$; $p < 0.05$), indicating that there is a direct relationship between the two parameters in clearwater rivers, not necessarily only in rivers with higher ionic loads, as discussed in other studies in the region.

TDS were positively correlated with DO and with turbidity (Spearman $r = 0.73$; $r = 0.77$ $p < 0.05$, respectively), and Pinheiro *et al.* (2019) state that this type of correlation is found in mesotrophic environments. Although total phosphorus did not show any statistically significant results, it is an important tool in water quality management in aquatic environments.

DISCUSSION

The negative correlation found between EC and pH is in agreement with results reported by Monteiro *et al.* (2014) and Wasserman *et al.* (2019); however, this type of correlation was also found in blackwater rivers, such as the Negro River. According to Monteiro *et al.* (2014), electrical conductivity can be related to the amount of dissolved organic matter, and in blackwater rivers the organic load is higher compared to other types of Amazonian rivers, due to the forest-water interface. Consequently, the increase in the concentration of dissolved organic matter is directly linked to higher electrical conductivity.

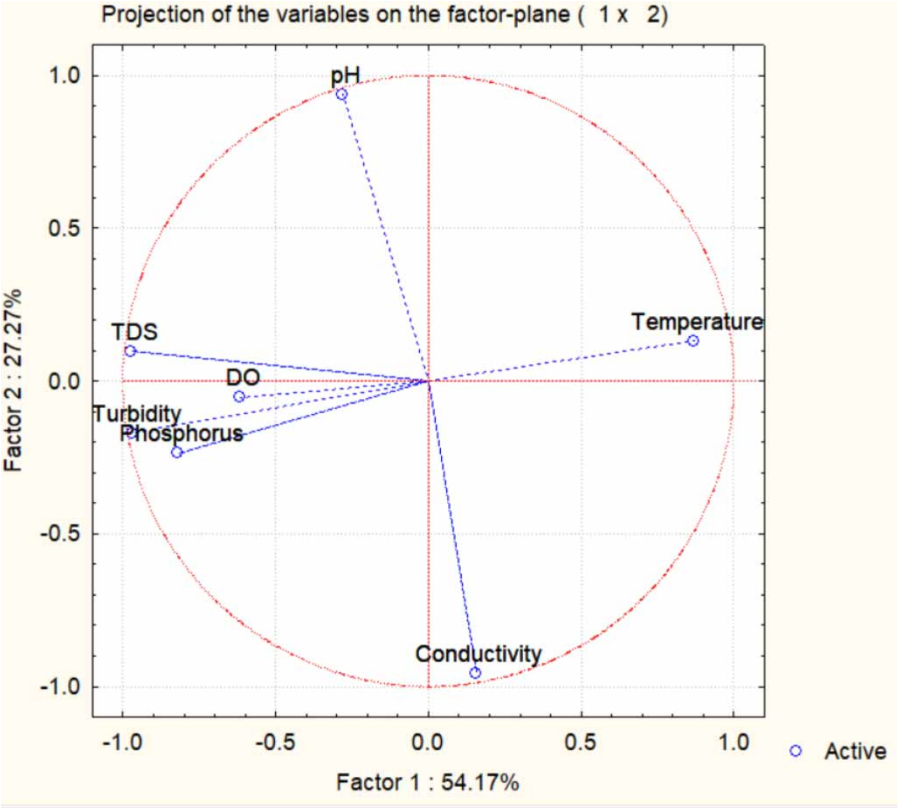


Fig. 2 | The plot of PCA test.

However, the decomposition of OM leads to the formation of humic and fulvic acids (Sioli & Klinge, 1962; Pinheiro *et al*., 2019; Silva & Silva *et al*., 2020), and the presence of these acids in water makes the pH more acidic, being found mainly in blackwater rivers. In the present study, a negative correlation between EC and pH was found in clearwater rivers, which are characterized by lower concentrations of ions, compared to blackwater rivers. On the other hand, vegetation also influences the different types of Amazon rivers (Stefanelli-Silva *et al*., 2019), wherein clearwater and blackwater rivers are surrounded by the flood forest type called igapó, while whitewater rivers are surrounded by várzea vegetation (Junk, 1984; Sioli, 1984; Stefanelli-Silva *et al*., 2019).

The igapó vegetation is composed of plant species that are specialists with respect to surviving prolonged periods of inundation, and these characteristics are directly linked to the higher concentrations of dissolved organic carbon (DOC), and consequently of humic acids, which in blackwater rivers present higher concentrations and molecular mass compared to the other two types of Amazonian rivers (Küchler *et al*., 1994, 2000; Stefanelli-Silva *et al*., 2019). According to the results in the current study, it can be inferred that the forest-water interface has similar behavior as that of the blackwater rivers, due to the composition of the type of vegetation cover near the rivers, which directly impacts the physicochemical parameters of the clearwater rivers.

TDS directly influences salinity, which in turn is related to the electrical conductivity, and this parameter can indirectly indicate the existence of pollution of the water resource due to high concentrations of ions in effluents (Abreu & Cunha, 2015). However, the positive correlation between TDS and DO found in this study may be related to the number of colloidal particles in the season of collection. In the dry season, oxygen levels tend to decrease due to the increase in water temperature, which decreases the solubility of gases, especially oxygen. Therefore, the greater colloidal contribution in the waters will influence the color of the water body, the darker water body will have a decrease in luminosity, which will consequently make the temperature colder, increasing gas solubility and increasing DO levels (Sawyer & McCarty, 1982).

Increased turbidity may indicate anthropogenic influence, such as erosion, and this consequently decreases primary production, which directly impacts the maintenance of aquatic biota (Abreu & Cunha, 2015). Associating the two parameters, it can be inferred that turbidity and TDS can be related to sediment dynamics, chlorophyll-a production of the aquatic environment, and also to sewage discharge among other anthropic influences (Pinheiro *et al.*, 2019; Silva & Silva *et al.*, 2020). Chlorophyll-a reflects primary productivity in oligotrophic and mesotrophic environments, which can contribute to increased DO due to photosynthetic activity, but not necessarily in eutrophic environments. Primary productivity can contribute to higher oxygen consumption, due to increased respiration in the aquatic environment, which decreases DO concentrations, leading to negative impacts on biota (Pinheiro *et al.*, 2019).

In this study, most samples were collected in pristine areas, suggesting that the positive correlation of turbidity with DO is related to sediment dynamics, except for the Juá samples, which are influenced by domestic sewage dumping and agricultural waste.

Although there were no statistically significant results, TP is important for understanding the degree of eutrophication of the aquatic ecosystem (Pinheiro *et al.*, 2019). Most points showed low concentrations of the nutrient, suggesting that reduced anthropogenic influence, except for samples J-01 and J-02.P, is associated with the trophic state of the water body since P is an essential element for aquatic life (Abreu & Cunha, 2015). Santos *et al.* (2007) found mean concentrations in the euphotic layer of the Amazon River of 0.13 μmol/L, which is in agreement with that found in this study. Dissolved inorganic phosphorus (DIP) is a portion of TP, with DIP being the most bioavailable form to aquatic organisms, and its concentrations are directly linked to the primary production of the environment (Paula Filho *et al.*, 2012).

Abreu & Cunha (2015) performed a study on the Jarí River in Amapá and found low concentrations of P, however, the authors emphasize the need to constantly study this parameter, which is directly associated with the health of the aquatic environment.

Legislation – CONAMA 357/05

The Brazilian legislation is composed of compilations of consolidated environmental norms from other countries, mostly from temperate regions (Pizella & Souza, 2007), which does not represent the diversity of biomes of a tropical country. In the specific case of the Amazonian aquatic ecosystem, the construction of the Brazilian standard is more complex, because this ecosystem is characterized by natural conditions that are different from the rest of the country. The forest-water interface significantly influences Amazonian fluvial dynamics, and this interface directly interferes with the physical and chemical characteristics of rivers. According to Junk *et al.* (2010), biota and soil materials in the Amazon are dependent on the movements and properties of Amazonian waters, which are moved by annual flood pulses.

The CONAMA Resolution 357/05 recommends that the DO concentrations for classes 1 and 2 should not be lower than 6 and 5 mg/L, respectively (BRASIL, 2005). However, according to the results of the present study, in most samples, except samples J-01 and J-02, the DO concentrations were not in accordance with the standard for both classes. The non-compliance of DO in pristine areas, according to the standard, is not related to a eutrophic environment as can be caused by sewage disposal but is a natural condition of the Amazon region due to the particularities of the forest-water interface, which creates a system that is adapted to its flora and fauna (Silva *et al.*, 2013).

Other studies of different types of Amazonian rivers found similar results. Rodrigues-Filho *et al.* (2015) found DO below 5.0 mg/L in some stretches of the Xingu River, as did Silva *et al.* (2019), who found DO concentrations below 6.0 mg/L for the Negro and Trombetas Rivers, and below 5.0 mg/L for the Nhamundá I River. Silva *et al.* (2013) studied several parts of the Amazon River and found DO concentrations below 5.0 mg/L. These concentrations are considered natural due to the ecological characteristics of the Amazon region (Silva *et al.*, 2013).

Similar to the DO, the pH found in the samples of this study did not conform to the standard at any sample point. According to CONAMA 357/05, the pH should range between 6.0 and 9.0. However, all samples presented acidic pH. Acidic pH is typical of Amazonian rivers and is a result of humic substances derived from the decomposition of organic matter of forest origin (Wasserman *et al.*, 2019), and in some places in the Amazon, the lithology also influences the acidity of surface waters (Costa *et al.*, 2020). Wasserman *et al.* (2019) found pH below 6.0 for most Amazonian rivers of different types. Silva *et al.* (2019) found values below 5 in the Urubu River. Rios-Villamizar *et al.* (2020) found pH below 5 in blackwater rivers, and below 6 in clearwater rivers, which were classified as acidic and not in accordance with Resolution 357/05.

However, the characteristics presented in this study and in other studies in different types of Amazonian rivers showed that these are natural characteristics of the ecosystem, due mainly to forest-water interactions, which directly impact the physical-chemical factors of water resources and is important in maintaining the regional ecosystem. However, these natural characteristics are not considered in the application of the regulation, which can distort water quality management in the region. Therefore, it is necessary to adapt the standards to the characteristics of Amazonian rivers.

CONCLUSIONS

The management of water quality is important in the Amazon region, mainly because the region is extensive and undergoes intense anthropogenic processes, such as burning, urban expansion, and agriculture, which directly impact the quality of water resources. However, the existing legislation does not consider the regional ecological processes, which make the Amazonian aquatic ecosystem different from other tropical environments, which can lead to distortion and incorrect interpretation of water quality management in the region.

The present study showed that clearwater rivers have similar physicochemical behavior to blackwater rivers, due to the type of vegetation that is around the floodplains of both rivers. Moreover, clearwater rivers suffer the direct influence of the forest-water interface, even presenting lower ionic loads, and consequently, a lower amount of dissolved humic substances; up to now these characteristics were seen only in blackwater rivers.

This study conducted in Amazonian micro-watersheds is a tool for the understanding of natural mechanisms and their influence on water quality in the region because these sites are more accessible to study, with part of them distributed in Amazonian urban areas, which are now expanding both in the Brazilian Amazon and the International Amazon and which are more susceptible to environmental changes. There is a need to expand studies in the rainy season to compare the physicochemical behavior of clearwater rivers in the two seasons. In addition, it is necessary to expand the studies in clearwater rivers due to the scarcity of bibliographic material and the importance of this type of river for the Amazonian ecosystem.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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