Original Research Article

Water typology in the Amazon: Close correlation with the hydrogeochemistry of river basins

ABSTRACT

A study on the typology of Amazonian waters was developed in the North Geographic Region of Brazil, considering a set of historical data from 1995 to 2022. The objective was to discuss and point out which environmental parameters are considered preponderant within the classification criteria of Amazonian waters. Historical data on temperature, density, pH, conductivity, oxygen, transparency, light attenuation, turbidity, color, total and dissolved solids, hardness, alkalinity, $CaCO_3$, BOD, COD, main cations and anions, iron, C, N and P fractions, silicate, trace elements (Al, Cu, Zn and Mn) and chlorophyll *a* were analyzed. The analysis comprised water samples from the National Hydrometeorological Network (Sub-Basins 10 to 19), with a total of 36 basins, including tributaries, lakes and adjacent streams. The historical series was statistically analyzed through the techniques of Cluster, Principal component analysis (PCA), Piper Diagram and image interpolation by the ordinary kriging method. The results indicated a strong seasonal trend, with an evident distinction between the flood and ebb periods. The typology of white, black and clear waters was also evidenced, this last group being an intermediate class to the others, due to the physical-chemical standards. The PCA highlighted the parameters conductivity, pH, calcium, bicarbonate and Dissolved inorganic

carbon (DIC) (Factor 1), and turbidity and alkalinity (Factor 2) as preponderant in the water classification. The ionic balance demonstrated that the white waters stood out for the highest concentrations of calcium and magnesium. The results suggest a pattern of calcic waters oscillating towards sodic and carbonated waters, with a subgroup in the northern eastern region of seasonally sodic-chlorinated waters, due to the influence of ocean tides. Image interpolation suggested a predominance of white waters in the western southern zone (Western Amazon) and white waters transitioning to clear waters in the eastern zone (Eastern Amazon). The analysis also showed a predominant strip of black and clear waters in the northern zone, and a strip of white waters in the central Amazon.

Keywords: Amazon; electrical conductivity; pH; Sioli's classification; spatial similarity; water typology.

1. INTRODUCTION

The Amazon incorporates the most extensive and complex river-lacustrine system on the planet, with the Northern Geographic Region of Brazil representing 52% of the biome. The inserted rainforest plays an important role in the hydrological cycle, especially in transpiration and precipitation events, ensuring the maintenance of surface and underground aquifers in the region, as well as the thermal balance in a large part of the continent. These are shared events; whose resulting precipitation establishes the balance of the annual water cycle. Meteorological studies suggest that precipitation is a strong indicator of the importance of surface processes and climate in the regional hydrological cycle [1]. Eventually, extratropical events also interfere with this balance, altering and enhancing the times of flood and ebb of Amazonian rivers and lakes. Despite this, as these are non-regular events, they are not considered a priority in determining the environmental variables that act and control seasonal hydrological events.

The hydrological cycle in association with climate patterns regulates the transport and volume of organic and inorganic materials to surface waters. The supply of these components to the aquatic system comes from the geological unit, its basement and pedological characteristics [2-3], as well as from the direct interference of biogeochemical cycles interrelated to forest biomass. From this interaction, a cause-effect relationship is established between the forest and the watershed, with an important flow of macro and micronutrient fractions from the terrestrial to the aquatic environment [3,4] and vice versa. The configuration of limnological processes, such as the load of total suspended solids, water transparency, gas solubility, concentration of organic carbon components, decomposition rate and volume of ionic elements, is a function of the geological origin and rainfall regime different from the drainage basins. The interaction of this complex physical-chemical system with the biological system results in a broad and diversified water typology.

This immense mosaic of fluvial-lacustrine environments is related both to the drainage area and to environmental factors, incorporating relief, pedology, soil and climate to the different types of vegetation present around the rivers, streams and lakes. The result of this interaction is a significant difference in the physical and chemical composition of the waters, which led some pioneers to define different types of water for the region [5-8]. The first classification of Amazonian waters began with Sioli's studies between 1950 and 60 [5,6,9], relating optical behavior and water transparency to the physical-chemical characteristics of river systems. This classification was practical and functional, such that it continues to this day in limnological studies. The purpose of this study was to discuss and point out which environmental parameters are considered preponderant within the water classification criteria, in order to contribute to the expansion and solidity of the typology of Amazonian aquatic systems. A set of physical, chemical, physical-chemical and biological variables was considered from a series of historical seasonal and annual data from 1995 to 2022, for the wide hydrological region located in the North Region of Brazil.

2. MATERIAL AND METHODS

2.1 Study Area

The Brazilian Amazon covers an area of more than five million km^2, incorporating nine states, seven of which lie within the North geographic region, which represents 45% of the national territory. The region's immense and diverse river-lacustrine system plays an important role in the exchange of energy, moisture and biomass for the ecological system, including the maintenance and regulation of the climate from regional to global. The North Region of Brazil's diversity of aquatic environments is due to the immense drainage area associated with geographic, geomorphological and climatic aspects. The relief is basically divided between the higher terrains, formed mostly by sandy and sandy-silty soils and covered by Dense *Ombrophilous* Forest, which are never flooded and lower lands, which are formed by weathered clay soils and periodically flooded (*Várzea*). The Central Amazon is represented by the floodplain, with a large extension of flooded lands (floodplains and igapós), of Holocene sedimentation with a predominant composition of clayey and silt-clay sediments. These sediments are usually deposited by clogging in lakes and periodically flooded land, and sandy sediments can also be observed in marginal dikes [2,10-12].

Considering the seasonality and the annual mean values of air temperature and precipitation, the predominant climate in the region, according to the Köppen-Geiger classification, is Equatorial (*Af*) hot and humid with influence of the Monsoon climate (*Am*) to the east and Savannah climate with summer rains (*Aw*) to the south. The region's average rainfall oscillates between 2000 and 2400 mm/y, with rains concentrated predominantly between January and May. The hydrological regime of the Amazonian rivers is marked by two distinct periods: Floods and ebbs, separated by a brief moment of relative hydrometric stabilization defined here as *functional shutdown*, which exerts a great influence on the abundance and richness of species of aquatic flora and fauna [2], especially in the floodplain.

2.2 Analytical Procedures

There were a total of 393 sampling sites monitored in the seven states that make up the Northern Region of Brazil from 1995 to 2022 (Fig. 1). Most of the samples followed the seasonal pattern, taking into account the hydrological levels of the respective basins, highlighting the periods of high water (flood) and low water (ebb). The sampling water network comprised rivers, streams and lakes in the basins of the National Hydrometeorological Network (Sub-Basins 10 to 19) [13], including the Acre and Purus rivers – between the states of Acre and Amazonas; Abunã, Madeira, Jamari, Mamoré, Guaporé, Jiparaná, Capivari, Formoso and Machado – in Rondônia; Uraricoera, Mucajaí and Branco – in Roraima; Javari, Japurá, Juruá, Solimões, Badajós, Urucu, Coari, Negro, Mamiá and Manacapuru rivers – in the State of Amazonas; Jarí river between Pará and Amapá; Tapajós, Xingu and Parauapebas rivers – in Pará; Aurá, Guamá, Acará, Mojú, Capim, Gurupi and Piriá – strictly on the N-NE axis of the State of Pará; and the Tocantins River south of Araguaina in Tocantins.

The measured and compared limnological parameters were subsurface water temperature (T ºC); pH; electrical conductivity (EC μS_{25}/cm); dissolved oxygen (DO mg/l) and oxygen saturation (O_2 %); transparency (Sec m); light attenuation coefficient (K 1/m) and euphotic zone limit (Z_{eu} m); turbidity (NTU); color (Col mg/l Pt); total solids (TS mg/l), total dissolved solids (TDS mg/l); hardness (Hard mg/l); alkalinity (Alk mg/l) and total alkalinity (Talk meq/l); $CaCO_3$ (mg/l); biochemical oxygen demand (BOD mg/l); chemical oxygen demand (COD mg/l); total ions Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, HCO_3^- and CO_3^{2-} (mg/l); total (TFe) and dissolved (DFe) iron (mg/l); fractions of PO_4, total phosphorus (TP) and total dissolved phosphorus (TDP), nitrogen forms NO_2^-, NO_3^-, NH_4^+, total organic nitrogen (TON), total nitrogen (TN), dissolved organic (DOC) and inorganic (DIC) carbon, total carbon (TC) all in mg/l; silicate (SiO_2 mg/l); trace elements Al, Cu, Zn and Mn (mg/l); and chlorophyll-*a* (ChL_a µg/l). The content of ionic salts present in the water samples were estimated by the sum of the main ions, and correlated with the electrical conductivity. The collection, storage, transport and analysis procedure followed international recommendations and protocols [14,15].

The organization of data to the normal distribution pattern and homogeneity between variances was previously analyzed using the Shapiro-Wilk and F-Test methods. Hierarchical analyzes were established to identify both seasonal patterns in the water, influenced by periods of drought and rain, and to differentiate groups arising from the classification by the degree of optical behavior. The spatial similarity analysis (Cluster) was applied using the minimum variance method [16]. The theoretical distribution model was adjusted to the historical series, based on probabilistic terms. Principal Component Analysis (PCA) was applied to identify the main variables in the hierarchical classification of waters, in this case, a rotation with the maximum variation (varimax) was adopted, only values greater than |0.7| were considered significant. The typology of Amazonian waters was tested by analyzing the ionic balance, using the geometric triangulation method (Piper Diagram) [17,18] for the seasonal moment. Image interpolation maps, based on the cartographic base, with isovalues were established, using the ordinary kriging method for the data. Statistical analyzes and graphic constructions were elaborated with the help of software ArcMap® 9.3 ©2008; Surfer® 9.11.947 ©2010 Golden Software, Inc.; Qualigraf Beta version Mobüs [19] and Statistica 7.0 © Stat Soft. Inc. 2004.

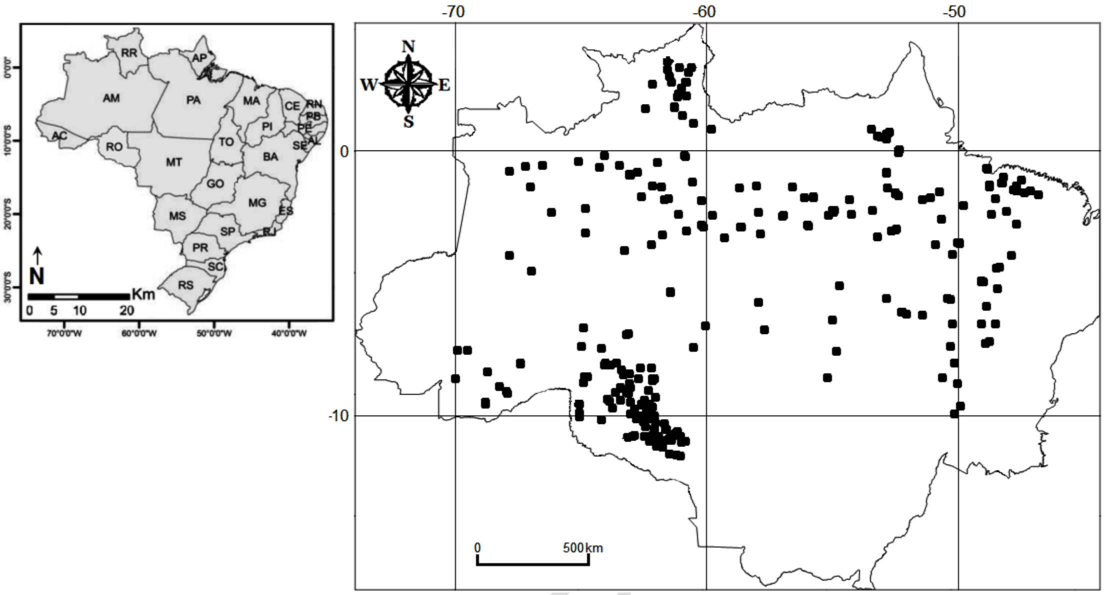

Figure 1: Study area with the respective measurement and sampling points for the historical series from 1995 to 2022.

3. RESULTS AND DISCUSSION

3.1 Similarity between the River Basins

The first step in the discussion of the results was to define whether or not there was a significant separation between the data from high and low water periods. The result suggests a strong seasonality between times of flood and ebb, with a matrix distance greater than 15,000 units between periods (Fig. 2). It was also possible, within the flood and ebb subgroups, to show aggregations of values for the different types of monitored water. During high water periods, the Acre and Purus rivers, classified as white water systems, were isolated from the other water systems. There was also a significant separation between the group formed by black and clear waters from the other white waters, primarily from the Madeira, Solimões and Amazonas river basins. Continuing the interpretative analysis, the period of ebb or low waters had a strong indication of isolation of the lentic and lotic water systems of black waters (Fig. 2), suggesting that the moment of low waters without the interference of other aquatic systems reveals the real 'identity' of black water bodies. This occurred predominantly in lacustrine systems.

The results presented in Fig. 2 suggest that there is seasonality between high and low water moments, as well as an evident separation of water typology, especially during times of ebb. The next step is to seasonally identify how this typological separation occurred, highlighting the main basins monitored throughout the historical series. Thus, the results shown in Fig. 3 represent the spatial similarity dendrogram for the periods of flood to flood pick (Fig. 3A) and ebb to drought (Fig. 3B). The difference between the matrix distances in seasonal moments suggests a slight and better homogeneity of the results in periods of low water, although the difference of ten thousand units may not be as representative. It was possible, in both moments, to evidence smaller groupings between water basins with similar typologies. This was the case of the Acre and Purus river basins, which remained grouped at both times, as well as the Solimões-Amazon System. Analyzing each hydrological moment separately, during periods of high water, usually accompanied by strong and lasting rainfall, it was possible to identify sub-groupings involving the Negro and Urucu rivers (1st sub-group); Solimões – Amazonas System and the Purus river basin (2nd s-g); Amazon, Madeira, Pará and Purus rivers and Guajará Bay (3rd sub-group); and Branco and Negro rivers (4th sub-group). Most of these correlations showed a degree of linkage between 4000 and 1000 units, this in a universe of maximum linkage of 26 thousand units (Fig. 3A), suggesting a moderate to good correlation between the subgroups. A similar pattern was observed during periods of low water (Fig. 3B), but with a smaller Euclidean distance between the components of each subgroup, suggesting a good strong correlation between them. The conclusion so far is that there is significant seasonality and intense differentiation between the types of water monitored, resembling the classification of water originally established by Sioli [5,6] into white, black and clear waters.

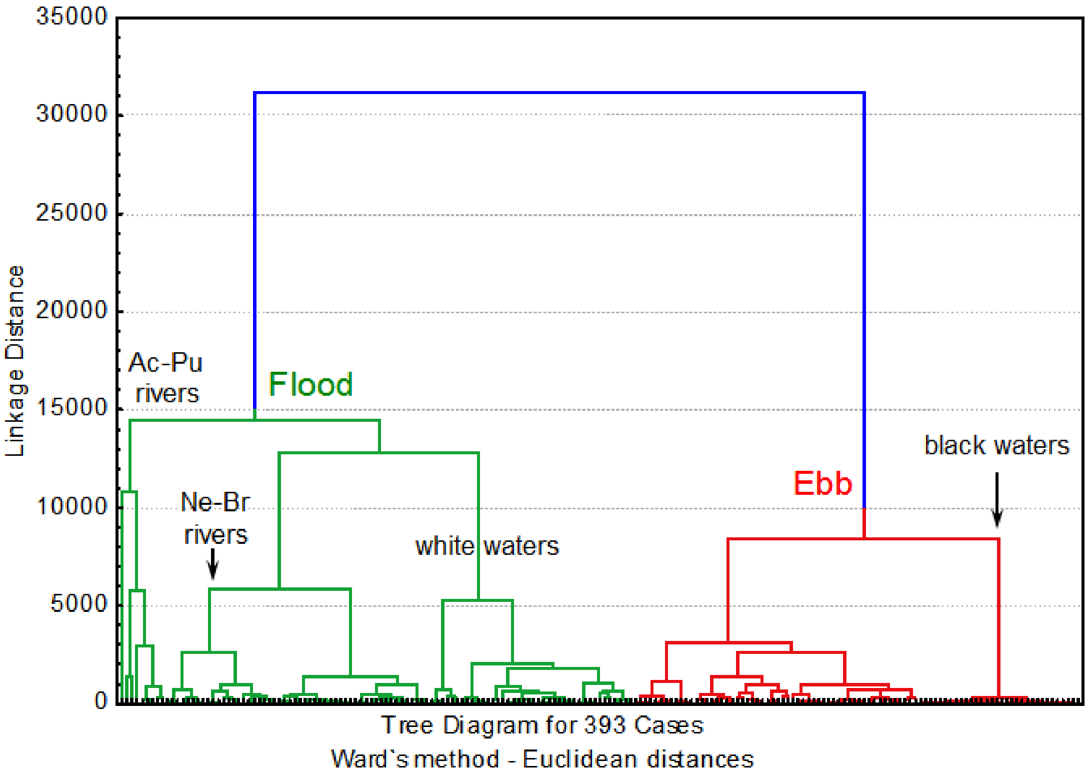

Figure 2. Dendrogram of Spatial Similarity for the water systems monitored in the period from 1995 to 2022, considering the total data for the hydrological year. Caption: Basins of rivers Ac= Acre; Pu= Purus; Ne= Negro; Br= Branco.

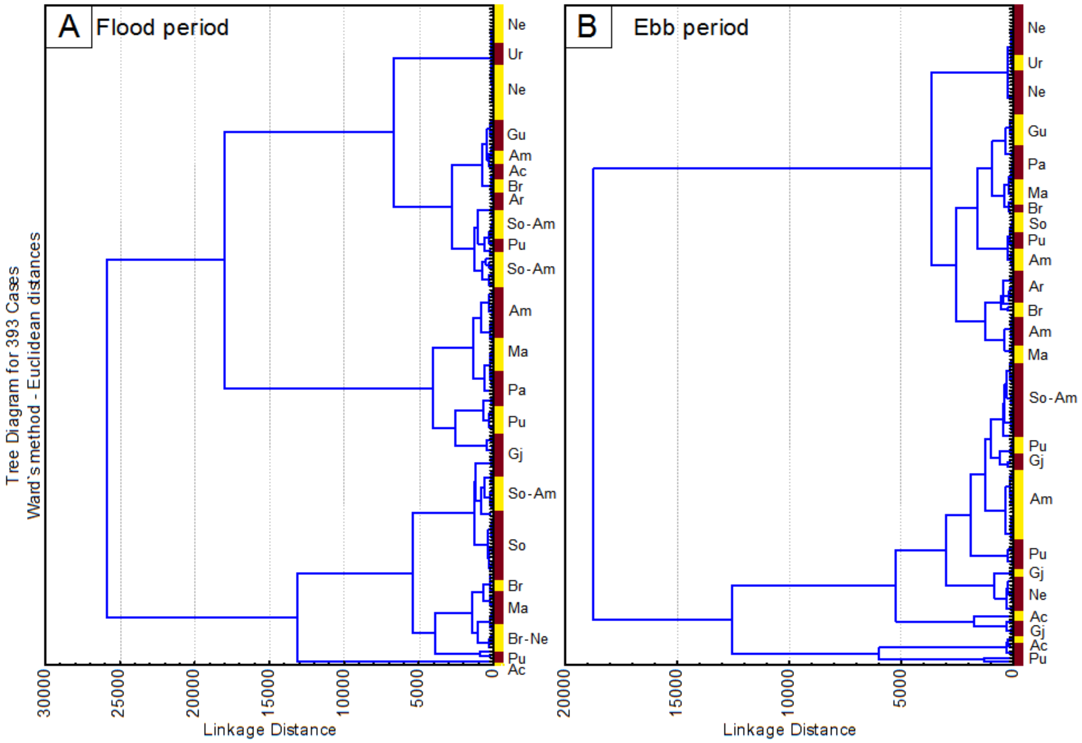

Figure 3. Spatial Similarity Dendrogram for the water systems monitored in the period from 1995 to 2022, considering seasonal data for high (3A) and low (3B) waters. Caption: Basins of rivers Ac= Acre; Am= Amazon; Ar= Araguari; Br= Branco; Gj= Guajará; Gu= Guamá; Ma= Madeira; Ne= Negro; Pa= Pará; Pu= Purus; So= Solimões; Ur = Urucu.

3.2 Main Variables in Water Typology

Next, an attempt was made to identify which environmental variables were predominant in the grouping of classes, which evidenced the classification of waters. For this, criteria and limits were established. The neutral climatic periods, within the monitoring historical series, were considered the rule in the hydrological cycle, as well as the direct influence of rainfall on the water cycle, allowing the seasonal analysis. Ecological subdivisions established as *terra-firme* (upland), which extends from the Pre-Andean zone to the shields of the Guianas and Central Brazil, were also considered to influence the typology of the waters; permanently flooded areas (*igapós*), and floodplain areas [20,21], the latter two in the central zone of the Amazon. The areas of direct marine influence, are also included in the ecological subdivision in the northeastern zone of the North Region, under the control of the tidal cycle. In this region are found the basins of the rivers Guamá, Acará, Mojú, Capim, Gurupi and Piriá. Three subgroups were evidenced with regard to the geological basement and soil typology: One characterized by recent **clayey** sediments, corresponding to the Oxisol environments that dominate the landscape of Central Amazonia; another formed by weathered sandy soils, where Spodosols are found with thick layers of white sand and coarse texture, and between these intermediate surfaces of Argisols [22,23]. Seasonal flood areas based on Oxisols and Argisols are considered extension areas of the Pre-Andean region, as suggested by Fittikau *et al*. [20], due to the fact that these environments are the result of the transport of sediments from higher regions, which end up being deposited in the course of rivers in the plain area.

Once the environmental limits were defined, the result of the principal component analysis proposed eleven variables in Factor 1 and six variables in Factor 2, with significance greater than │0.65│, to explain the behavior trend of Amazonian waters. Factor 1 was responsible for 24.1% and Factor 2 for 14.8% (total 38.9%) of the potential explanation for the water classification pattern in the monitored region (Table 1). The percentage of total variance was 26.8 for Factor 1 and 12.1 for Factor 2 (Table 2). Factor 1 emphasized the components related to electrical conductivity, ionic elements and pH. Correlated to the buffering capacity of the fluvial-lacustrine systems in the region, variables such as calcium, calcium carbonate and bicarbonate also stood out in Component 1. Transparency, measured by the Secchi disc, organic and inorganic forms of carbon and silicon oxide complete the group of variables of Component 1. Factor 2 highlighted turbidity, color, total and dissolved solids, hardness and alkalinity (Table 1). Conductivity was the predominant variable in the analysis, with significant differences both in the seasonal aspect and in terms of water classification. In general, conductivity was higher during periods of low water, due to increased resuspension of bottom sediments. The EC values, on average, were 51.7 and 55.6 μS_{25}/cm for the periods of flood and ebb in the white water basins; 7.8 and 8.5 μS_{25}/cm for black water, and 18.3 and 16.8 μS_{25}/cm in the same periods for clear water. This significant difference contributed to the high EC index obtained in the PCA. The results highlighted in the PCA of this research corroborate with previous studies on the hydrochemistry of the Solimões River [24], which showed through the PCA the variables EC and calcium, magnesium and bicarbonate ions, as indicators of the typology of the waters, differentiating the white waters and black.

Since it is dependent on the ionic composition of the water and influenced by the periods of rain, EC showed a strong correlation with the ions and concentration of total and dissolved sediments (r> 0.88). The decrease in the volume of rainfall during periods of ebb, in most of the monitored region, suggests an increase in ionic concentration and nutrient load in diverse lakes, especially in island lakes, channels and lowlands from Várzea. The exception was observed in the forests streams, which had a reducing in the conductivity in the drought periods. This pattern extended over most of the Northern Region, with the exception of the northern eastern zone, where the influence of the tides, periodically flooding the marginal lands, had greater significance than precipitation. This was notably observed in the Guajará bay and throughout the water network of the Guamá basin and tributaries.

Table 1. Factor Loadings (Varimax raw) with extraction by Principal Components.

Var	Fac 1	Fac 2	Var	Fac 1	Fac 2	Var	Fac 1	Fac 2
T	.03061	-.16890	$CaCO_3$	.79917	.24693	NO_2	-.22647	.53614
pH	.82981	.08766	BOD	.22419	.31154	NO_3	-.23836	.35297
EC	.84051	.25235	COD	.22101	.25316	NH_4	-.32555	.47614
DO	-.19789	.37917	Na	.58053	-.15235	TON	.44180	-.21172
O_2	-.21311	.38960	K	.53625	.16067	TN	-.17580	.15762
Sec	-.75453	.03728	Ca	.81035	.07260	DOC	.78927	-.05863
K	.57805	.22024	Mg	.54640	-.12785	DIC	.79524	.03138
Z_{eu}	-.73332	.23747	SO_4	.55703	-.13645	TC	.68038	.02655
NTU	.23282	.78168	Cl	.57115	-.15263	SiO_2	.66735	.18211
Col	.23901	.74904	HCO_3	.81562	.33358	Al	-.06601	-.33931
TS	.27806	.76753	TFe	.59709	.24409	Pb	.11486	.30202
TDS	.35971	.71137	DFe	.26799	.22218	Sb	.14935	.43959
Hard	-.36980	.76029	PO_4	.39921	.63857	Mn	.13869	.54256

Alk	-.27864	.78988	TDP	.43628	.36121	ChL_a	-.62225	-.31670
TAlk	-.21626	.50712	TP	.53690	.23446			
						Expl.Var	10.89206	6.61426
						Prp.Totl	.24093	.14816

Red marked loadings are >.650000

Table 2. Eigenvalues with extraction by Principal Components.

	Eigenvalue	% Total variance	Cumulative Eigenvalue	Cumulative %
1	12.1254	26.8342	12.1254	26.8342
2	5.3809	12.0751	17.5063	38.9093

3.3 Geological Base and Water Typology

There is an evident influence of the geological foundation (stratigraphic unit) and the lithological formation of the drainage basin on the physical-chemical composition of the water. In the NW-SW axis and limits of the Western Amazon, the Solimões Formation includes an area between the Tabatinga (AM) and Rio Branco (AC) municipalities. In this strip of land, soils of the Dystrophic Red-Yellow Argisols type (PVAd) associated with Orthic Chromic Luvisols (TCo) to Pall Chromic Luvisols (TCp) are formed by clayites, fine sandstone and siltstones, with a mineral composition of quartz, kaolinite, illite and muscovite, and containing SiO_2 and Al_2O_3. The Solimões Formation covers the headwaters of the Solimões, Javari, Juruá, Purus and Acre rivers. There was a predominance of the Içá Formation in the northern west zone, including the imaginary line that connects the municipality of Caracaraí (RR) to the municipalities of Barcelos and Codajás (AM), which extends from upper Solimões river upstream of Manaus.

The sedimentological analysis identified a predominance of Hydromorphic Ferrihumilúvic Spodosols (ESKg) soils associated with Yellow Latosols (LAd) and Dystrophic Red-Yellow Latosols (LVAd) with a sandy texture, containing pink and whitish fluvial clayey sandstones, patches of clay, peat and gravel, and ferruginous reddish-yellow friable siltstones and clay stones. Part of the basins of the Branco, Negro and Solimões rivers are located in the Içá Formation. There is a predominance of the Alter do Chão Formation in the central zone of the State of Amazonas, which extends from near the meeting of the waters of the Negro and Solimões rivers to the vicinity of Macapá (AP). In this range, soils of the LAd type associated with LVAd predominated, with a texture of medium to coarse sandstone, clay and claystones.

The Amazon River, from the meeting of the waters, runs through an extensive floodplain of Quaternary sediments, and receives the waters of the Tapajós and Xingu rivers on the right bank. In the eastern northern zone, towards the continental limits of the Amazon, is the mouth of the Amazon and Pará rivers and the basins established between the Guajará Bay and the Gurupi River. This area is in the transition of the Alter do Chão and Barreiras Formation stratigraphic units, and is influenced by marine erosion processes. The predominant soil in the region is LAd associated with Dystrophic Haplic Plinthosols (FXd) and Haplic Haplic Gleissoils (GX) Dystrophic to Eutrophic soil patches, with sandstones, siltstones, conglomerates and clays, silty-clay and sandy-clay sedimentary fractions. The sub-basins from the western portion of the southern zone follow the same distribution mosaic as in the central zone, with alternations between PVAd and LAd soils, as is the case on the left and right banks of the Madeira River. The mosaic in the eastern portion of the southern zone is much more complex, with varied sediments of granite, volcanic, gneiss, migmatites, granulites, shale and quartz compositions, all on Undifferentiated Fractured basement. It is in this area that the middle and lower stretches of the Parauapébas and Tocantins rivers are found.

This lithological differentiation was fundamental to explain the divergence of the physicochemical variables observed. The concentration of acidic humic substances (humic and fulvic acids), in the Negro river basin and adjacent lake systems, comes from the decomposition of organic matter (OM) of shallow ESKg soils, which once drained, supply the river-lacustrine system place with wine-colored acidic waters. The adsorption of organic compounds is low, because it is predominantly weathered sandy soils, unlike what occurs in clayey sediments from white water basins. Studies linking the colloidal properties with the ability to exchange cations in sediments indicated a strong bond-attraction between clay mineral particles and organic matter [25]. This condition especially explains the acidic pH pattern in the black water drainage basins; and neutral to weakly alkaline in white water. The rate of OM decomposition in sandy *terra-firme* soils is slow, so that incomplete decomposition becomes a continuous source of soluble humic substances. Soil texture and clay content are indicators of the speed and condition of the organic matter decomposition process (complete or incomplete), acting as key-elements for the storage or release of organic compounds in the marginal soils of the basin. Studies regarding DOC behavior in tropical forest soils [26,27] confirmed this distribution pattern.

The geomorphological condition of the basins was another influencing factor for the water classification. The Rio Negro basin, for example, is an old and consolidated basin, with a leached rocky base and the presence of canyons along its stretch, contributing little to the transport of sediments and erosion of the marginal vegetation cover. The white water basins originating in the Pre-Andean region, such as the Solimões-Amazonas System, have a high capacity for soil and plant material loss through weathering, due to the high slope in the upper section (Upper-Middle Solimões River) and large swath of flooding in the Central Amazon plain (*Várzea*). This condition explained the difference in the rates of total solids (TS) and dissolved solids (TDS) between white, black and clear waters. The result was a significant variation in the concentrations of the variables TS, TDS, turbidity (NTU), transparency (Sec) and color, with significant results in the Cluster and PCA analyses. The cause-effect reaction stems from the fact that the high concentration of TS interferes with turbidity and transparency, which in turn interfere with the apparent color of the water. The high concentration of humic substances also influenced color and turbidity.

3.4 Ionic Distribution

The other cause-effect relationship associated conductivity with pH, Ca^{2+} and organic fractions, especially carbon. The process of formation of carbonated fractions begins from DIC and CO_2 solubilization, in a cause and effect relationship with the pH of the aqueous system. There is a decrease in the pH of the system, with the formation of carbonic acid. If there are favorable physical-chemical conditions, dissociation of the acid occurs, forming fractions of bicarbonate and carbonate (Eq. 1). The pH is a determining factor in the speed and direction of the reactions, establishing which steps will occur and what will be the proportion of carbonic species in each portion of the reaction, from that point on, depending on the type of geological basement and mineral composition (Calcite, Magnesite or Dolomite), the metallic ions (Ca^{2+} and Mg^{2+}) start to react with the carbonate ion, forming mineral carbonates, which precipitate to the bottom sediment (Eq. 2). As these reactions are dependent on the dissolved ionic concentration and the pH of the system, a variation in the concentration of the carbonated forms was observed depending on the type of water. Due to the acidic pH, in the black water systems, there was a predominance of free CO_2 formation, estimated from the DIC, and carbonic acid, in addition to low levels of total and dissolved $Fe^{2+/3+}$. Due to the slightly alkaline pH and the high load of transported suspended sediments, in the white waters there was a predominance of formation of bicarbonate and carbonate ions and alkaline and earth metallic elements. The result of this combination was the high rate of formation of precipitated mineral carbonates, confirmed by the geochemical analysis. The levels of mineral carbonates and dissolved carbonate forms oscillated in the clear waters within the previously established range between the black and white waters, varying as a function of the ionic concentration and pH of the medium.

This difference in the proportion of carbon species is due to the unique physico-chemical characteristics of each system. In general, a large part of the CO_2 remains free in solution and a solubilized portion of it reacts with water (Eq. 1), establishing the equilibrium of the system (buffering system). According to Drever [27], such reactions control the pH of most aquatic systems, and when there is a significant variation in pH or oxygen partial pressure, calcium and magnesium ions can abruptly alternate their dissolved and precipitated volumes. This sudden oscillation was observed especially in the eastern northern region, in the areas of direct influence of the tidal zone. In this case, the salinity associated with the temperature and higher density of marine waters may be interfering with the carbonate formation reaction, by altering the respective equilibrium constants. Changes in the concentration of forms of HCO_3^-, CO_3^{2-} and $CaCO_3$ may have occurred due to a sudden change in pH, an increase in the system's alkalinity or even as a result of a decrease in carbonate precipitation, all situations influenced by tidal variation. The basins of the Guamá, Acará, Moju, Gurupi and Capim rivers, in addition to the Guajará bay, in the northern east zone, were all recognized as white water systems, especially considering the variables EC, transparency and volumes of TS and TDS.

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} + H_2O_{(aq)} \leftrightarrow H_2CO_{3(aq)} \leftrightarrow HCO_3^{-}{}_{(aq)} + H^{+}_{(aq)} \leftrightarrow CO_3^{2-}{}_{(aq)} + 2H^{+}_{(aq)} \quad (1)$$

$$[Mg^{2+}]\ Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \leftrightarrow [Mg^{2+}]\ CaCO_{3(aq)} \downarrow \quad (2)$$

The ionic balance constructed from the Piper Diagram (Fig. 4) confirmed the classification of water typology established by Sioli [5,6]. The black waters were strongly grouped, with equidistant vector values for the cation group. Despite this, within the black water group, the lake environments showed slightly different behavior in relation to the waters of the Negro River, especially for alkalis. The white waters stood out for the highest concentrations of calcium and magnesium. The tributaries, especially in the Solimões-Amazonas System, on the right bank stand out for their varied concentration of dissolved calcium and bicarbonate ions. Following the same trend, the Acre and Purus rivers also showed punctual variations of the main cations and anions, highlighting them from the others, as evidenced by the Cluster analysis.

It was also possible to observe, within the white waters of the extreme east of the north, a subgroup influenced by tidal currents, with high levels of sodium and chloride, especially in periods of high water (Fig. 4A). It was observed in general, in clear water low levels of sodium and potassium ions were observed in addition to total iron. Some clear water lake systems tended to present ionic behavior similar to black water lakes, with acidic pH and predominant formation of carbonic acid. This reinforces that clear waters act as an intermediate class to the physical-chemical extremes, depending a lot on the pH and the concentration of dissolved calcium in the water column. The proportionality ratios, based on the ionic balance, were established for the sum of the main anions (Σ^-) and cations (Σ^+) in white, black and clear water. The greatest difference between the proportionality of anions was observed in black water, as for the cations, the greatest variation in relation to the general pattern of distribution was observed in clear waters. The average proportionality ratio for Σ^- was 9:1:5 and for Σ^+ it was 16:4:1, respectively.

The anionic distribution pattern in continental Amazonian waters, based on this study, showed a predominance of bicarbonate over sulfate and chloride ions, regardless of the period of the water cycle (flood or ebb). The established cationic distribution pattern, likewise, suggests the ordering $[Ca^{2+}] > [Mg^{2+}] > [Na^+] > [K^+]$, strongly associated with the water typology. The highest cation proportionality ratio was observed between the waters of the Amazon and Negro rivers, during flood periods with high rainfall. The maximum ratio of proportionality of the cations was $[Ca^{2+}]$ 35:1:6; $[Mg^{2+}]$ 10:1:3; $[Na^+]$ 6:1:2 and $[K^+]$ 3:1:1, for white, black and clear water respectively. The results classify the sampled points as calcic waters oscillating to sodic and carbonated waters.

Eventual differences in the proportionality values calculated in this study, in relation to other works carried out in continental Amazonian waters, can be explained by two factors: The high number of sampling points in white (48%) and clear (37%) waters in relation to black waters (15%); and the inclusion of a significant number of sampling sites in white waters under the influence of marine currents, in this case with a high contribution of sodium and chloride ions at an alkaline pH. The marine influence especially on the continental waters of the northern eastern zone may be interfering with the normal distribution pattern of the ionic charge.

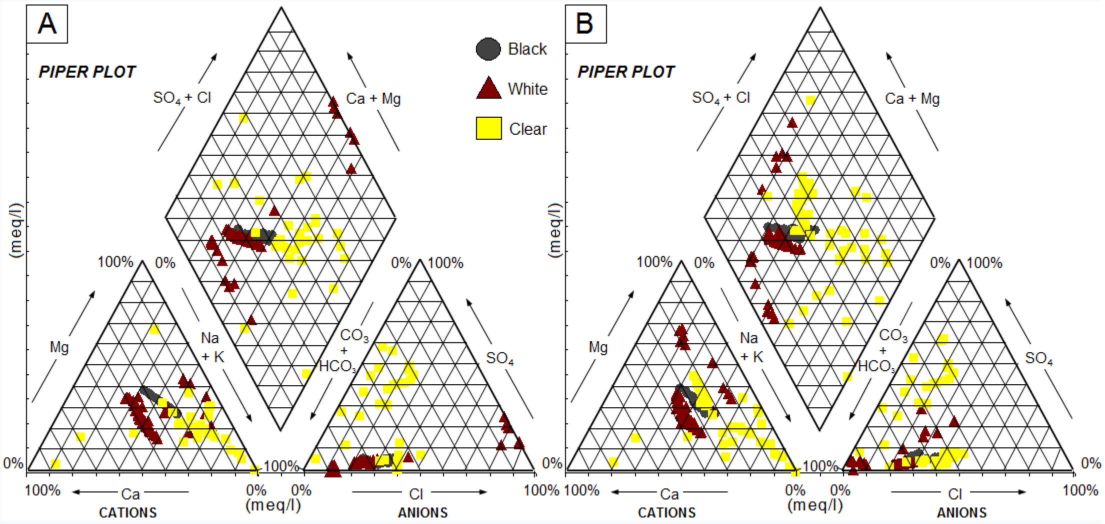

Figure 4. Piper tri-linear diagram for water systems monitored from 1995 to 2022, considering seasonal data for high (A) and low (B) waters in % meq/l.

3.5 Water Framing

The last stage of the study on the typology of Amazonian waters considered the construction of maps, based on the interpolation of images. The first step was the construction of the layers related to each variable that stood out in the PCA analysis (Table 1) for factors 1 and 2, respectively. Layer overlay techniques were applied, highlighting the intersection between the eleven variables evidenced in Factor 1 and the six variables in Factor 2 of the PCA. The results were interpolation maps resulting from the intersection between the variables pH, EC, transparency (Sec), Z_{eu}, $CaCO_3$, Ca^{2+}, HCO_3^-, DOC, DIC, TC, SiO_2 (Fig. 5A) and between the variables turbidity (NTU), Col, TS, TDS , Hard, Alk (Fig. 5B).

In general, a similar distribution behavior was noted between the two figures, highlighting the predominance of black and clear waters in the northern region, due to the direct influence of the Negro and Branco river basins, with their extensive networks of lakes and streams. Another important highlight was the south west zone, between the states of Acre, Amazonas and Rondônia; in this area you can find mainly the headwaters of the Acre, Purus, Juruá, Javari and Madeira rivers, all classified as white water rivers; in this particular range, the difference in water classification was the concentrations of TS and TDS transported by the basins, evidenced by interpolation (Fig. 5B). The intersection of the layers, between the central and southern zones, showed a pattern of classification of waters transiting between white and clear waters; in this extensive range are the basins of the Tapajós, Xingu, Parauapebas and Tocantins rivers and their respective tributaries. This distribution pattern was observed in both maps, either because of the influence of EC (Fig. 5A) or because of the influence of turbidity (NTU) associated with the load of TS and TDS (Fig. 5B).

The greatest oscillations observed in the interpolation analysis are in Central Amazonia, over the bed of the Solimões-Amazon river. This behavior occurred due to the large oscillation of the values measured between the flood and ebb periods. Conductivity, transparency, turbidity, suspended material load and apparent color varied greatly between periods of high and low water in this range, especially in the extensive network of lakes connected to the left bank of the Solimões-Amazonas System. The results of the analysis, regardless of the variation in the levels observed, confirmed the classification of the System as white water. The north east zone showed a slight difference in the interpolation of the variables of Factors 1 and 2. This, as already suggested, is due to the marine influence in periods of high tides, which increase the alkalinity of the waters, and increasing the sodium and chloride load, resulting in a seasonal (periodic) variation of the ionic balance of the waters in the region; also in the northern zone, the transition pattern between black and clear waters in the Jarí River basin and its tributaries (AP) stood out.

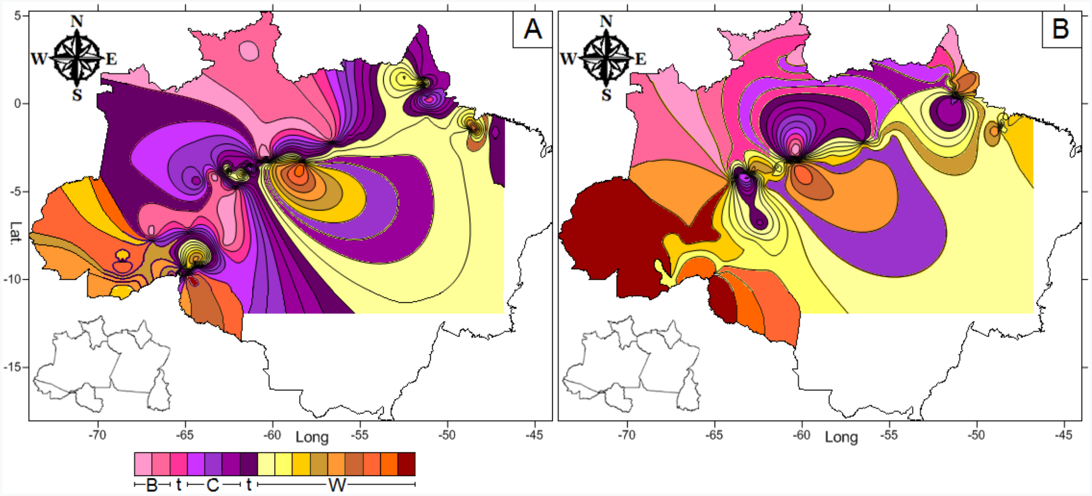

Figure 5. Linear Ordinary Kriging image interpolation of the historical series from 1995 to 2022 for the monitored environmental variables. Legend: B=Black Waters; C=Clear Waters; W= White Waters; t= transition point.

The classification of waters by typology, based on optical behavior and physical-chemical characteristics, considering the immense and complex territorial extension of the Amazon water network, proved to be the most efficient and reliable option for limnological studies. It is completely impracticable, within this large territorial extension of the Amazon, to use the classification of waters by the framework established in the CONAMA 357 legislation [28], as reinforced by the studies of Silva et al. [29]. The legislation framework adopts quality standards associated with the discharge of effluents, at levels of pollution that are harmful or dangerous for human and other life forms, not taking into account the hydrogeological and physical-chemical aspects. It is suggested, as evidenced by the data analysis in this work, to focus on the environmental conditions of each region, also taking into account seasonal variations in the water system, instead of considering water quality control based on its predominant uses.

5. CONCLUSIONS

From the seasonal study carried out between 1995 and 2022, in Sub-Basins 10 to 19 of the National Hydrometeorological Network, located in the Northern region of Brazil, the classification pattern of white, black and clear waters established by Sioli was evidenced. Seasonality was evident throughout the monitored territory, with distinct moments of high and low water. Geochemistry, in terms of typology, has a strong influence on the separation of groups and subgroups of water in the Amazon since the physical-chemical composition of the water is the mirror of its drainage area.

The framing of the waters established by the construction and overlapping (intersection) of image layers, from the interpolation technique, using data from the variables highlighted in the PCA, showed a distribution of white, black and clear waters and their respective subgroups based on geological and lithological patterns. The environmental variables pH, conductivity, turbidity, total solids and suspended solids stood out, in this framework.

Considering the immense and complex territorial extension of the Amazon water network, waters classification based on optical behavior and physical-chemical characteristics, proved to be the most efficient and reliable option for limnological studies. It is important to mention that despite the consistency of the data analyzed; the statistical methods to interpret them; and the breadth of the researched area, the scarcity of sampling must be highlighted when compared to the immense territory occupied by the river basins and sub-basins that make up the Amazon basin.

Basically, the waters in this region originate from the Central Plateau of Brazil, to the south; in the Guiana shield, to the north; in the pre-Andean and Andean region. The last two have a considerably larger area and origin than the others. Therefore, its contribution in volume of water is also greater, as well as its influence on the typological pattern of waters in the Amazon. Amazonian waters originate from rainfall directly in the river channels and their river basins; in the water table; and in the melting ice east of the Andes Mountains. It appears, in this way that the fundamental hydrochemical contribution comes from the geochemical characteristics of the drainage area, which is also noticeable through surface runoff.

CONSENT

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ETHICAL APPROVAL

This section is not applicable in this manuscript.

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