



New insights on the classification of major Amazonian river water types

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Abstract

Traditional water classifications for Amazonian rivers are based mainly on optical characteristics that do not fully capture their complexity. Today, an increasing amount of hydrochemical data indicates that the chemical composition of Amazonian rivers varies much more than this simple classification indicates. Revising river classification based on hydrochemical properties is proposed here. In this first comprehensive review of Amazonian river chemistry, we synthesized critical information from 168 scientific publications and distinguish unusual white, black, and clearwater rivers. It is shown the distribution of such rivers across the basin and the limitations of using generalized designations for river typologies. For example, some optically clearwater rivers draining carboniferous stripes have chemical properties similar to whitewater rivers, regardless of their high transparency. Furthermore, a clear or blackwater stream that becomes turbid because of soil erosion does not become a whitewater stream. Its hydrochemical parameters of acidity and nutrient poverty depend on the geology of the catchment area and remain relatively unaffected. These insights into Amazonian river classification provide a new understanding of their baseline limnological conditions. They have implications for sustainable management of freshwater systems and for monitoring potential impacts of large development projects and climate change on the Amazonian aquatic systems.

Keywords Amazon region · River and landscape ecology · Limnology · Water chemistry · River typology

Introduction

Chemical composition of waters provides important parameters for understanding some specific ecological properties (e.g., fish richness and soil fertility) and biogeochemical cycles of Amazonian river systems (Junk et al. 2011). The

water chemistry is relevant for the establishment of water typology and best management options for each river. The first scientific classification of major Amazonian rivers was elaborated in the 1950s by Sioli (Sioli 1956c) who used water color, transparency (Secchi), pH, and electrical conductivity to explain limnological characteristics of major rivers and correlate them to geological properties of river catchments. This was an innovative insight of a landscape ecology approach. It was later shown that the whitewater

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rivers and streams were distinctive of the waters draining the Andes mountains, the rivers flowing through the central lowlands were typically blackwater in composition, while clearwater types were characteristic of rivers originating in the Precambrian Shields (Konhauser et al. 1994; Sioli 1968; Stallard and Edmond 1983).

The highly turbid rivers flowing out from the Andes correspond to whitewater rivers (e.g., Amazon and Madeira), and they display transparency between 20 and 60 cm, near-neutral pH and electrical conductivity between 40 and 100 $\mu\text{S cm}^{-1}$. From the Andes, they transport nutrient-rich sediments that contain smectite and illite. The water is dominated by Ca^{2+} , Mg^{2+} , and carbonates (Furch and Junk 1997). Nutrient-rich floodplains on whitewater rivers (várzeas) are separated from blackwater and clearwater floodplains (igapós) by chemical parameters (Junk et al. 2011). Blackwater rivers (e.g., Negro) have transparency of 60–120 cm, a reddish-brown color derived from the humic acids leached from podzolic soils, pH values in the range of 4–5, and electrical conductivity $< 20 \mu\text{S cm}^{-1}$. The content of alkali-earth metals is low and contributes $< 50\%$ of the major cations, in which Na^+ predominates. The main anions are Cl^- and SO_4^{2-} . Blackwater floodplains (igapós) have low nutrient status because of the low nutrient inputs by the floods (Junk et al. 2015). Clearwater rivers (e.g., Tapajós and Xingu) have transparency > 150 cm, pH values between 6 and 7, and electrical conductivity about 10–40 $\mu\text{S cm}^{-1}$. These rivers drain weathered kaolinitic soils from the Central Brazilian Shield. Clearwaters have broad physicochemical variability overlapping in some extent the whitewaters and blackwaters features (Ríos-Villamizar et al. 2020a, 2014).

Sioli's simplified classification based on water color has, until recently, dominated the scientific discussion about the limnology and ecology of the Amazon basin. However, the main disadvantage of this traditional classification is the oversimplification of the river water which has a dynamic and complex matrix. In Sioli's time, water-chemical analyses in Amazonia were just beginning. His classification was based on very limited data, because access to the vast river basin was restricted to the large rivers, which he visited in small vessels or canoes with small outboard motors. Roads, which today provide access to interfluvial parts of the basin and allow for long hydrochemical transects, were not yet built, and geological maps provided only a large-scale and simplified view of the basin.

The substrate lithology and the erosional regime of this basin have already been described by other relevant and pioneering works, which have demonstrated and outlined a clear relationship between geology/soil geochemistry, weathering regime, and the water-chemical composition (dissolved load) of Amazonian rivers based on the main cations (Elbaz-Poulichet et al. 1999; Gaillardet et al. 1997; Konhauser et al. 1994; Stallard and Edmond 1983).

Hydrochemical data provided by scientific researches and survey programs in Amazonia have increased since 60 years. Examples include the studies of the Max-Planck-Institute cooperation (Furch 1985, 1986; Furch and Junk 1980, 1997; Junk 1973; Junk and Howard-Williams 1984; Sioli 1968), the Carbon-Amazon-River-Experiment (CAMREX) (Richey 1983; Richey et al. 1980, 1990, 2008), the Santa Barbara University cooperation (Fisher and Parsley 1979; Lesack 1993a, 1993b; Melack 1984; Melack and Fisher 1983), the Large-Scale-Biosphere-Atmosphere-Experiment (LBA) (Ballester et al. 2003; Figueiredo et al. 2010; Monteiro et al. 2014; Tomasella et al. 2009), and the Geodynamical-Hydrological-Biogeochemical project in the Amazon Basin (ORE-HYBAM) (Moreira-Turcq et al. 2003; Seyler et al. 1998; Seyler and Boaventura 2001, 2003), as well as other more recently published research (Ríos-Villamizar et al. 2020a, 2014, 2016, 2017, 2020b; Silva et al. 2019).

Thus, in light of an abundance of new research in this area, there is a need to synthesize relevant findings and reconsider traditional water classification of Amazonian rivers based on water chemistry. This paper aims to: (1) present the main parameters historically used for Amazonian water classification; (2) re-analyze, under Sioli's criteria, a data base on river chemistry; (3) provide new insights into the Amazonian water typology, and inform the sustainable management of Amazonian rivers and streams.

Materials and methods

From the literature, based on a total of 168 studies (papers, reports, and theses) published between 1949 and 2011, we collected data on hydrochemistry of 193 rivers and streams (Fig. 1 and Appendix in Supplementary Material). The literature survey was conducted via searching the websites of the Web of Knowledge, Science Direct, Google Scholar, Springer Link, and Scielo publications databases, among others. The initial search yielded 200 publications. Subsequently, we examined these publications individually and further eliminated the duplicate and irrelevant articles, such as the studies focusing on lakes or underground water. In the end, 168 relevant studies were selected for the meta-analysis. Data were extracted from the selected studies to develop a database, including river or stream name, sampling location, concentrations of the selected chemical parameters, and reference information. As the chemical parameters were presented in different units depending on each study, the unities of the selected parameters were standardized, and the concentrations of each compound were recorded in the database as $\mu\text{eq/L}$. Generally, major cations ($\mu\text{eq/L}$), eq% Ca^{2+} , eq% Mg^{2+} , eq% K^+ , eq% Na^+ , major anions ($\mu\text{eq/L}$), eq% Cl^- , eq% SO_4^{2-} , and eq% HCO_3^- were either provided by authors or calculated as needed using original data.

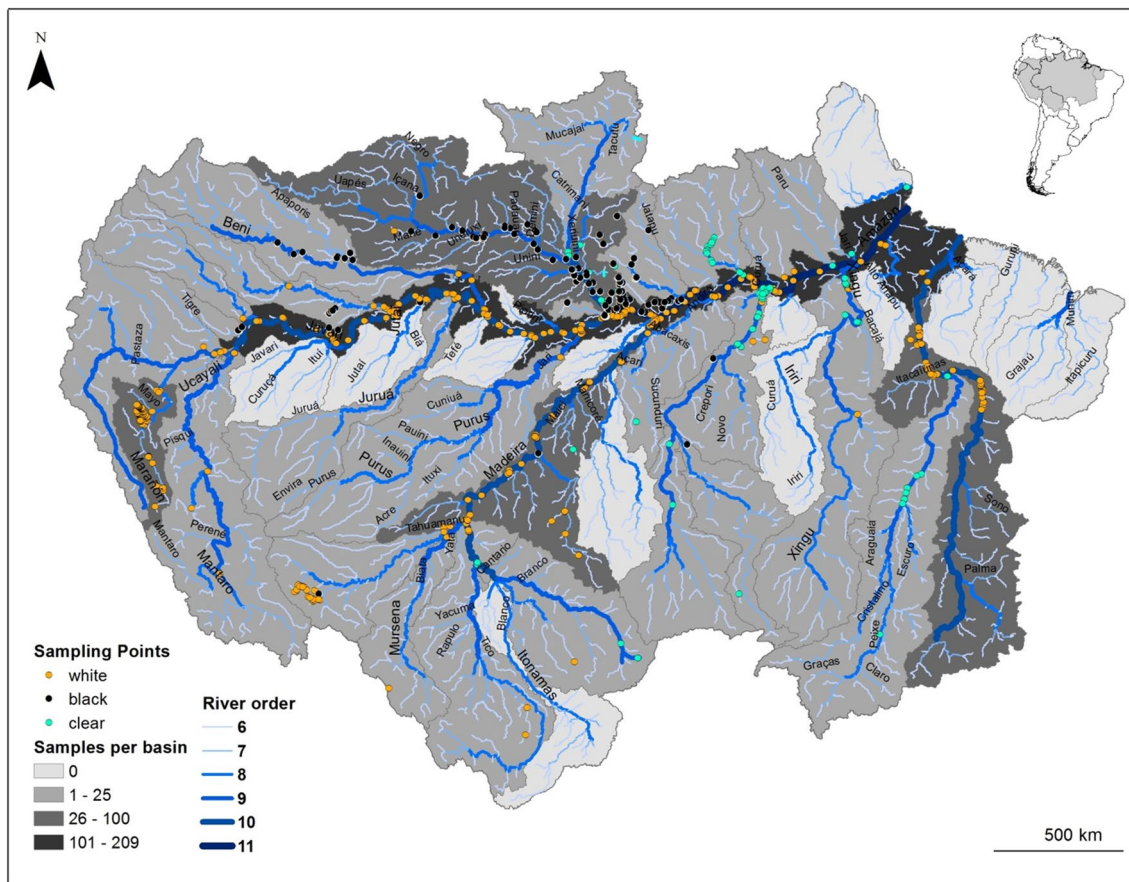


Fig. 1 Water physicochemistry sampling sites in the Amazon Basin. Dots show the locations of samples, colored by water type, identified in the 168 studies used in this paper. Also shown are the number of samples per river basin and river order. Most studies (count=209) were carried out along the main stem of the Solimões/Amazon rivers.

It was not considered limnological data on floodplain lakes, because physicochemical and biological processes involved in the ecology of standing waters differ drastically from rivers and streams ecology. In addition, the database was upgraded and completed with our own measurements. Surface water samples were collected in the Tapajós river at Itaituba and Santarem (8 and 12 December 2010, respectively) using acid-washed polyethylene bottles. The samples were kept cool in an icebox until the time of the analysis at the INPA laboratory, where these samples were filtered through Whatman GF/F fiberglass filters (0.7 μm). Laboratory analyses were carried out using standard methods (APHA et al. 2005) to obtain the concentrations of major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and major anions (HCO_3^- , SO_4^{2-} , Cl^-) which were measured using a Dionex ion chromatography (IC) system. The total suspended solids were measured by gravimetry, the water color by spectrophotometry, and the turbidity (NTU) using a turbidimeter Alifakit Plus V1.25. Electrical conductivity ($\mu\text{S cm}^{-1}$) and pH values

Other highly sampled rivers include the Negro, Madeira, Huallaga, and Tocantins. However, for most rivers, there are less than 25 samples or they remain underrepresented in the literature. River basins (shown is level 3) and river order are from Venticinque et al. (2016)

were measured in the field using portable meters WTW 315i. The water transparency (m) was also measured in the field using the Secchi disk.

Water color, conductivity, pH, and the proportions (eq%) and quantities ($\mu\text{eq/L}$) of major cations (alkali and alkaline-earth metals) and major anions were plotted in regards with the water transparency.

Results and discussion

The classification system of Amazonian waters tends to organize the large diversity of rivers and streams according to physical and hydrochemical parameters in whitewater, blackwater, and clearwater rivers. The Amazon and the Negro rivers are considered prototypes for whitewater and blackwater rivers; the Tapajós and Xingú rivers as prototypes for clearwater rivers (Sioli 1964, 1984). Geological and biogeochemical differences in the catchments of the

tributaries, however, lead to variations in the investigated parameters and result in intermediate water types. There exist a wide range of hydrochemical parameters overlapping between the three water types. Even so, the classification is useful, because it allows the discussion of scientific questions such as biodiversity and primary production in a broader context and facilitates decisions on management problems such as the use for agriculture, ranching, fishery, and forestry. An attempt was made to separate typical whitewater, blackwater, and clearwater rivers, using updated and upgraded criteria (Table 1).

The 193 rivers and streams analyzed were split in three clusters: 105 whitewater, 76 blackwater, and 12 clearwater rivers and streams (Appendix in Supplementary Material). They are separated with respect to the water color, pH, conductivity, and the proportions and contents of major cations and major anions (Figs. 2, 3, 4), which are relevant for water classification (Furch and Junk 1997; Stallard and Edmond 1983). Therefore, major cations, major anions, Ca^{2+} , electrical conductivity, HCO_3^- , pH, Mg^{2+} , Na^+ , eq% HCO_3^- , eq%

SO_4^{2-} , and eq% Ca^{2+} are considered as the key parameters of the analysis as they strongly contributed to the separation of the water types. The pH values separate electrolyte-poor rivers, which display similar values of electrical conductivity, into the blackwater or clearwater categories.

Blackwater and clearwater rivers exhibit some overlap when electrical conductivity and the proportions (eq%) of major cations and major anions are plotted in regards with transparency (Figs. 2, 3, 4). This may be because in electrolyte-poor waters, such as the typical black and clear waters, minor variations in ionic content ($\mu\text{eq/L}$) can cause significant changes in ionic composition (eq%) of the main ions (e.g., Ca^{2+} and HCO_3^-). An important point is that it is not just a parameter that defines the category. For example, clearwater rivers may even have a pH close to neutrality, but they are low in nutrients, thus falling into the category of clearwater igapós. Blackwater and clearwater streams are generally poor in nutrients and with acidic pH, but they can be differentiated by the water color and humic substance content.

Table 1 Ecological parameters of major Amazonian river types according to Junk's (Junk et al. 2011) classification based on Sioli's work (I) and updated with our study (II)

Ecological parameters	Whitewater		Blackwater		Clearwater	
	I	II	I	II	I	II
pH	7	6–8.5	<5	3.6–5.5	5–8	5.3–7.2
Electric conductivity ($\mu\text{S/cm}$)	40–100	30–760	<20	3.7–28	5–40	5.1–53.6
Transparency-Secchi depth (cm)	20–60	10–235	60–120	20–170	>150	35–355
Water color (mg/Pt/L)	Turbid	17–284	Brownish	28.5–627	Greenish	2.8–193
Humic substances (mg/L)	Low	0.18–18	High	2.3–71	Low	7.8–11
Major cations ($\mu\text{eq/L}$)	*	131.9–7916.8	**	7.4–528.7	***	45.1–432.8
Ca^{2+} ($\mu\text{eq/L}$)	–	53.9–4126.7	–	0–103.3	–	0–219.1
Mg^{2+} ($\mu\text{eq/L}$)	–	16.4–2799.4	–	0–131.7	–	9–137.8
K^+ ($\mu\text{eq/L}$)	–	5.7–207.9	–	0–168.8	–	0–46
Na^+ ($\mu\text{eq/L}$)	–	4.3–3871.3	–	4.3–382.8	–	8.7–159.2
eq% Ca^{2+}	–	30–87	–	0–60	–	0–59.8
eq% Mg^{2+}	–	3–43	–	0–68.2	–	6.6–64.4
eq% K^+	–	0.6–19	–	0–46.8	–	0–34.4
eq% Na^+	–	1–49	–	7.6–95.1	–	3.3–67
Major anions ($\mu\text{eq/L}$)	****	78.5–6820	*****	9.8–365.8	***	45.1–722.6
Cl^- ($\mu\text{eq/L}$)	–	0–3004	–	0.7–155	–	3.8–166.1
SO_4^{2-} ($\mu\text{eq/L}$)	–	0–4380	–	0–155.5	–	0.5–112.4
HCO_3^- ($\mu\text{eq/L}$)	–	46–4539.8	–	0–229.1	–	4.9–679.8
eq% Cl^-	–	0–55	–	1.8–89.9	–	2.4–72
eq% SO_4^{2-}	–	0–65.4	–	0–82.6	–	0.6–69.2
eq% HCO_3^-	–	29–99.3	–	0–97.3	–	17.8–94.1

I: Junk (Junk et al. 2011) based on the classification of Sioli (Sioli 1956c)

II: This study

* Ca^{2+} , Mg^{2+} > Na^+ , K^+

** Na^+ , K^+ > Ca^{2+} , Mg^{2+}

***variable

**** CO_3^- dominate

***** SO_4^{2-} and Cl^- dominate; -not presented

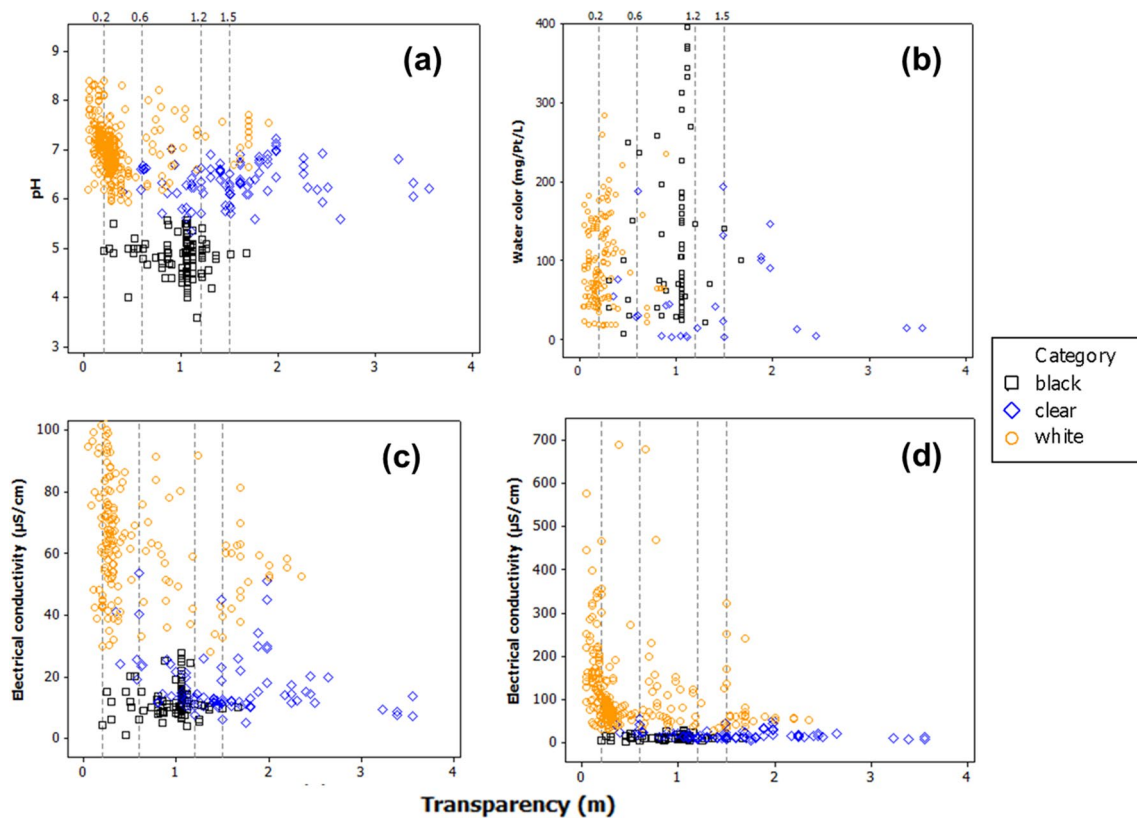


Fig. 2 Relationship between pH value (a), water color (b), electrical conductivity ranging 0–100 $\mu\text{S}/\text{cm}$ (c), electrical conductivity ranging 0–700 $\mu\text{S}/\text{cm}$ (d), and transparency of Amazonian rivers and

streams. The unusual white, clear, and black waters show transparency [<0.2 m and >0.6 m], [<1.5 m], and [<0.6 m and >1.2 m], respectively

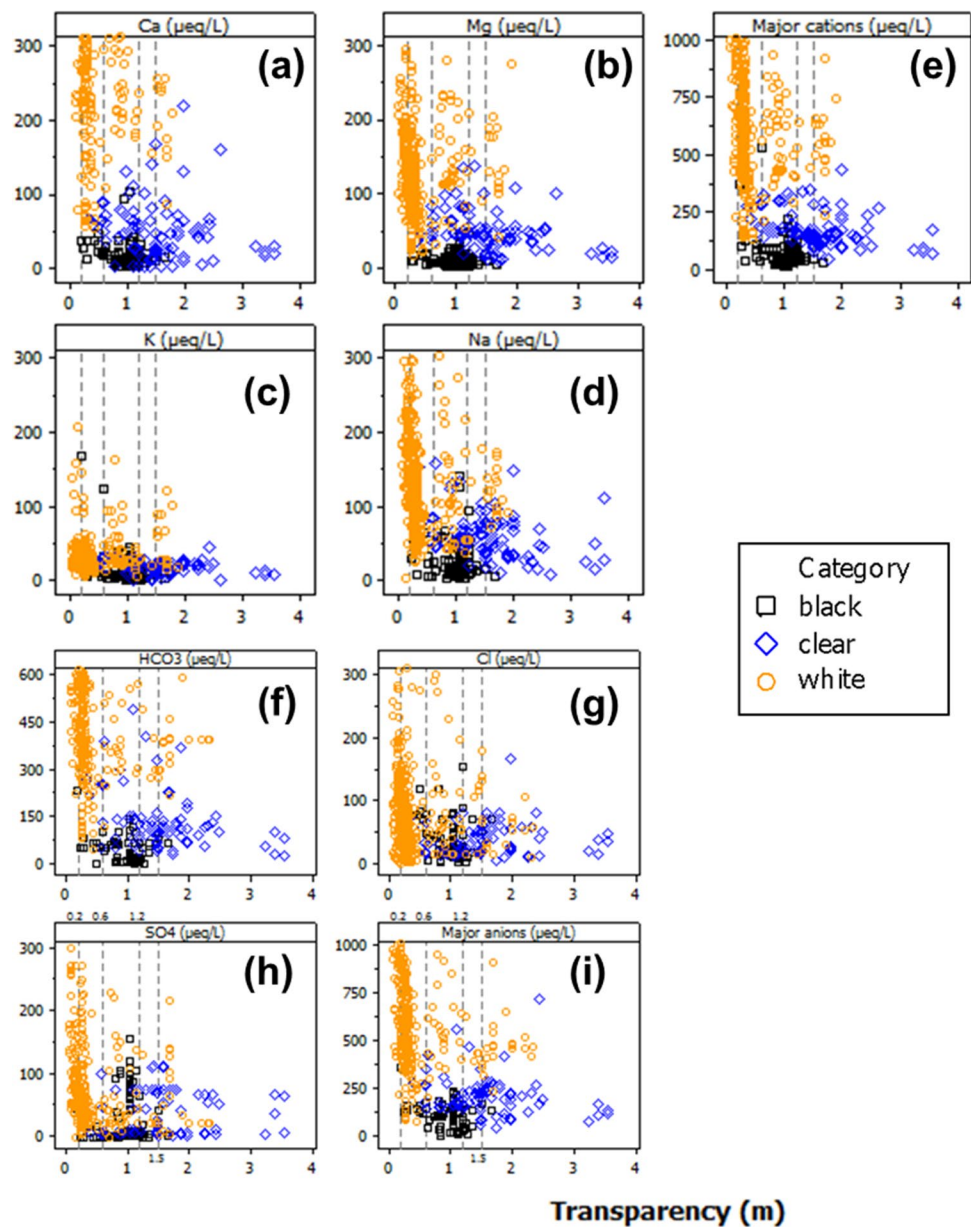
Unlike the clear differences in chemical composition between the whitewater rivers draining the Andes mountains and those blackwater rivers draining the Central Amazonian lowlands, clearwater rivers in the Shield areas are much more variable. The overall chemistry of these rivers and streams suggests an intermediate composition (Konhauser et al. 1994). The clear dominance of calcium suggests that the solute-rich waters of the whitewater rivers such as the Solimões/Amazon could be classified as "carbonate waters" (Furch 1984), and are indicative of the carbonate source (mostly limestones) in the Andes mountains (Konhauser et al. 1994; Stallard and Edmond 1983). The solute-deficient waters of the blackwater rivers such as the Rio Negro are characterized by a completely different proportion of major elements. These waters show an extremely high Si-to-cation ratio which is indicative of the podzols in the Central Amazon, and a greater proportion of K to those of the alkaline-earth metals Ca and Mg, suggesting an alkali dominance (Furch 1984; Konhauser et al. 1994; Stallard and Edmond 1983). The clearwaters of the Shield rivers and streams are represented by an intermediate composition (Konhauser et al. 1994). Our data

approach are in agreement with the findings given by different authors (Furch and Junk 1997; Sioli 1968; Stallard and Edmond 1983).

The parameters used for Amazonian river classification

We used diverse parameters to provide multiple information on the ecology of rivers, streams, connected wetlands, and their catchments. This "landscape ecology" approach was pioneered by Sioli and his water types continue to be used (Furch 1984; Junk et al. 2011; Sioli 1984). Physico-chemical parameters such as water color, suspended sediment load, pH, electric conductivity, the concentrations, and the relationships among alkali and alkali-earth metals, and major anions can easily be obtained in the field or at the lab. It is discussed here the relevant information that these parameters provide about the physicochemical conditions in rivers systems, and the pros and cons to using them for such classification.

Fig. 3 Relationship between the content of alkaline-earth metals (a, b), alkali metals (c, d), major cations (e) (sum of total concentrations of Ca^{2+} , Mg^{2+} , Na^+ , and K^+), HCO_3^- (f), Cl^- (g), SO_4^{2-} (h), major anions (i) (sum of total concentrations of HCO_3^- , SO_4^{2-} , and Cl^-), and transparency of Amazonian rivers and streams. The unusual white, clear, and black waters show transparency [<0.2 m and >0.6 m], [<1.5 m], and [<0.6 m and >1.2 m], respectively

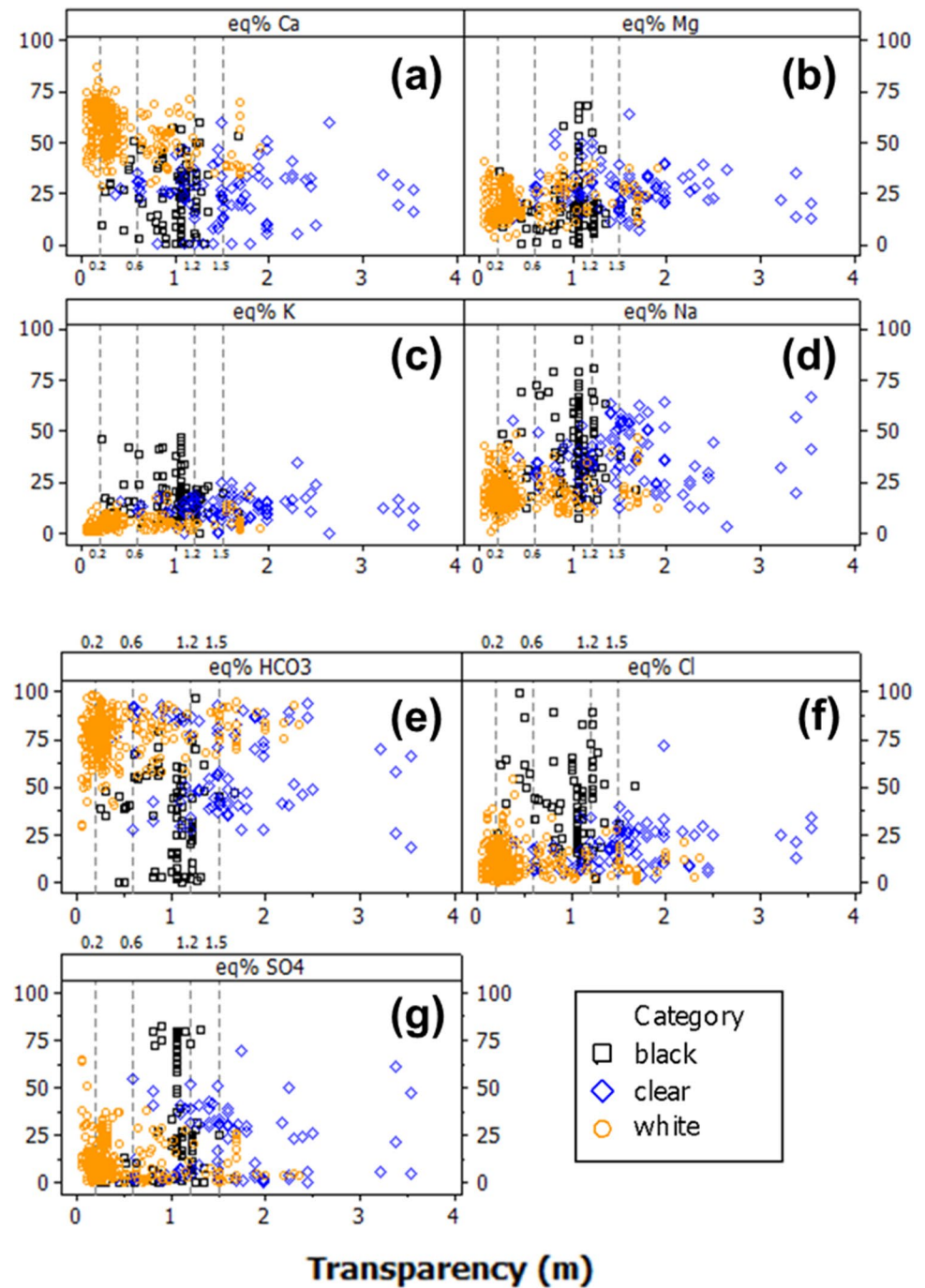


Water color

This indicates the amount of humic substances, which are produced during the decomposition of organic material. Leaves falling in the water impart a slightly brownish color. On clay soils, the humic substances are adsorbed on clay particles, and water draining from such areas is slightly colored. Dark brownish water has its origin in the extended areas of sand depositions (podzolic soils), which retain the coarse organic material and let the colored humic substances pass into the river. These soils occur over large areas in the Negro river catchment (Adeney et al. 2016). Podzolic soils account for 64% of the total

Brazilian Amazonia and 70% of the overall non-floodable area (Santos et al. 2012). Of the 6.6 million km^2 of tropical forest soils in Amazonia, it was estimated that 3.3% are podzols (Hill and Moran 1983). It was found a slightly higher estimate for the Amazonia ecoregion podzols, ~5% (335,000 km^2) (Adeney et al. 2016). Humic substances are acidic. Therefore, a dark water color is associated with low pH, low mineral content, and low fertility and primary production in water and on land. Dark water color prevents sunlight penetration and creates unfavorable light conditions for submersed primary producers, resulting in few submersed aquatic macrophytes.

Fig. 4 Relationship between the distribution (eq%) of alkaline-earth metals (a–b), alkali metals (c–d), major anions (e–g), and transparency of Amazonian rivers and streams. The unusual white, clear, and black waters show transparency [<0.2 m and >0.6 m], [<1.5 m], and [<0.6 m and >1.2 m], respectively



Suspended sediment load

This describes the amount of fine particles (mostly inorganic material) originating from basin erosion through rivers. It is easily measured indirectly with the Secchi disc that indicates light penetration in the water. In the river channel, when there is few phytoplankton production, low Secchi depth corresponds to high sediment loads, except in humic waters. Dark humic waters also have low Secchi depth because of their dissolved humic substances, as they contain very little

sediment. The amount of fine sediment load depends on the soil quality, vegetation cover (which protects soils from erosion), the roughness of the landscape (which influences erosion processes), and the slope of the river (which influences the current velocity). Suspended sediment load is very sensitive to human impact. Large-scale modification of the natural vegetation cover in the catchments (e.g., by agriculture or mining activities) increases soil erosion. Clay soils liberate large amounts of fine particles, which increase the suspended sediment load and can change transparent rivers

into muddy rivers. Sediment quality, however, depends on the geology of the catchment (Sioli 1968). In the tertiary sediments of central Amazonia, nutrient-poor kaolinites with low ion-exchange capacity dominate the fine fraction, whereas rivers from the Andes contain illite and smectite in addition to kaolinite (Irion et al. 2010). When weathered, illite liberates potassium, and smectite has a high ion-exchange capacity. Therefore, fringing floodplains of rivers draining Andean soils are fertile, while those of other rivers are of low fertility. Suspended sediments are transported downriver to the sea, but on the way downriver, they can be deposited temporarily in the fringing floodplains. After varying time spans, they become re-suspended and transported further downriver. In large, sediment-rich rivers such as the Amazon, part of the fine fraction reaches the Atlantic Ocean and builds up the delta or is transported by the northward running Brazil Current and deposited along the northern coast line (Sioli 1984). In sediment-poor rivers, the fine fraction is deposited at the bottom of Ria lakes (blocked valleys) and the water becomes transparent.

Water color and suspended sediment load are parameters that can change when the conditions in the catchment change. The water color of a stream draining the tertiary sediments of the central Amazonia basin may change from transparent to muddy when the natural vegetation cover is destroyed and when the erosion of the kaolinitic material increases. However, the water chemistry will not change, because it depends on the geology. It will indicate the water as clearwater or blackwater, regardless of an unusually high load of kaolinitic suspended matter.

pH value

Dissolved carbon dioxide (CO_2) combines with water to form carbonic acid (H_2CO_3), which can then dissociate into bicarbonate (HCO_3^-) and hydrogen (H^+) ions, the latter leading to a reduction in pH. These chemical species readily interconvert from one to another as a function of their relative concentrations, pH, temperature, and the concentrations of other buffering and complexing species. The carbonate buffering system, which consists of a gas species (CO_2) at one end of the reaction chain and several mineral species at the other (e.g., calcium carbonate, CaCO_3), is further coupled to mineral cycles, because carbonate alkalinity ($\text{Carb}_{\text{alk}} = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}]$) is controlled by the thermodynamic requirement to balance the electrostatic charge imbalance between strong base cations (e.g., calcium [Ca^{2+}], magnesium [Mg^{2+}], sodium [Na^+], and potassium [K^+]) and strong acid anions (e.g., chlorine [Cl^-] and sulfate [SO_4^{2-}]) that is created during the chemical weathering of minerals (Aufdenkampe et al. 2011). Amazonian water draining tertiary sediments and the archaic shields contain a few carbonates and bicarbonates, which are common buffers. Therefore,

pH values are slightly acidic. Distilled water saturated by the CO_2 of the air has a pH value of around 5.6. Lower pH values often indicate the presence of humic and fulvic acids, higher values indicate the presence of carbonates (Furch and Junk 1997). In Amazonia, carbonates derive mostly from marine sediments, leached by the rain from the Andes but also from carboniferous stripes in the lower part of the Amazon basin such as the Cuparí and Tocantins rivers (Fig. 5).

Electrical conductivity

This indicates the amount of electrolytes (anions and cations) in the water. Mineral-rich waters with pH values about 7 (e.g., of Andean origin, from stripes of carboniferous sediments in the lower Amazon, and from near the Atlantic coast) have relatively high electrical conductivity, while waters of other areas show low-to-very low values. In very acidic waters (pH about 3–4), the electrical conductivity is slightly increased by the high concentration of H^+ ions (Ríos-Villamizar et al. 2020a).

The total amount of, and relationship between, alkali (Na^+ , K^+) and alkali-earth (Ca^{2+} , Mg^{2+}) metals

This provides additional information about the geology. Rivers draining catchments rich in carbonates contain much more calcium and magnesium in the form of carbonates and bicarbonates than rivers draining central Amazonian tertiary sediments and the archaic shields of the Guianas and Central Brazil. In these waters, the total concentration of electrolytes is lower, and sodium and potassium (in the form of chlorides and sulfates) occur in similar or even larger quantities than the alkali-earth metals (Furch 1985, 1986; Furch and Junk 1980, 1997; Furch and Klinge 1978; Junk and Furch 1980).

Hydrochemistry and geological aspects of Amazonian rivers

At Sioli's time, the geological maps provided only a large-scale and simplified view of the Amazon basin. Nevertheless, the accuracy of geological maps has been improved significantly in the last 30 years. The explanation of differences in hydrochemistry of rivers lies on the geology, which, in some catchment areas, is extremely complex (Fig. 5). Aside from differences in concentrations, the heterogeneity of Amazonian waters is also confirmed by the relative proportions (eq%) of the major elements (e.g., Ca^{2+} , Na^+ , and HCO_3^-) (Konhauser et al. 1994). The high physicochemical variability of the rivers draining the Precambrian (archaic) shields is related to the great heterogeneity of the geology of this region (Furch and Junk 1997). The central Amazonian tertiary/cenozoic sediment basin and some of the plateaus

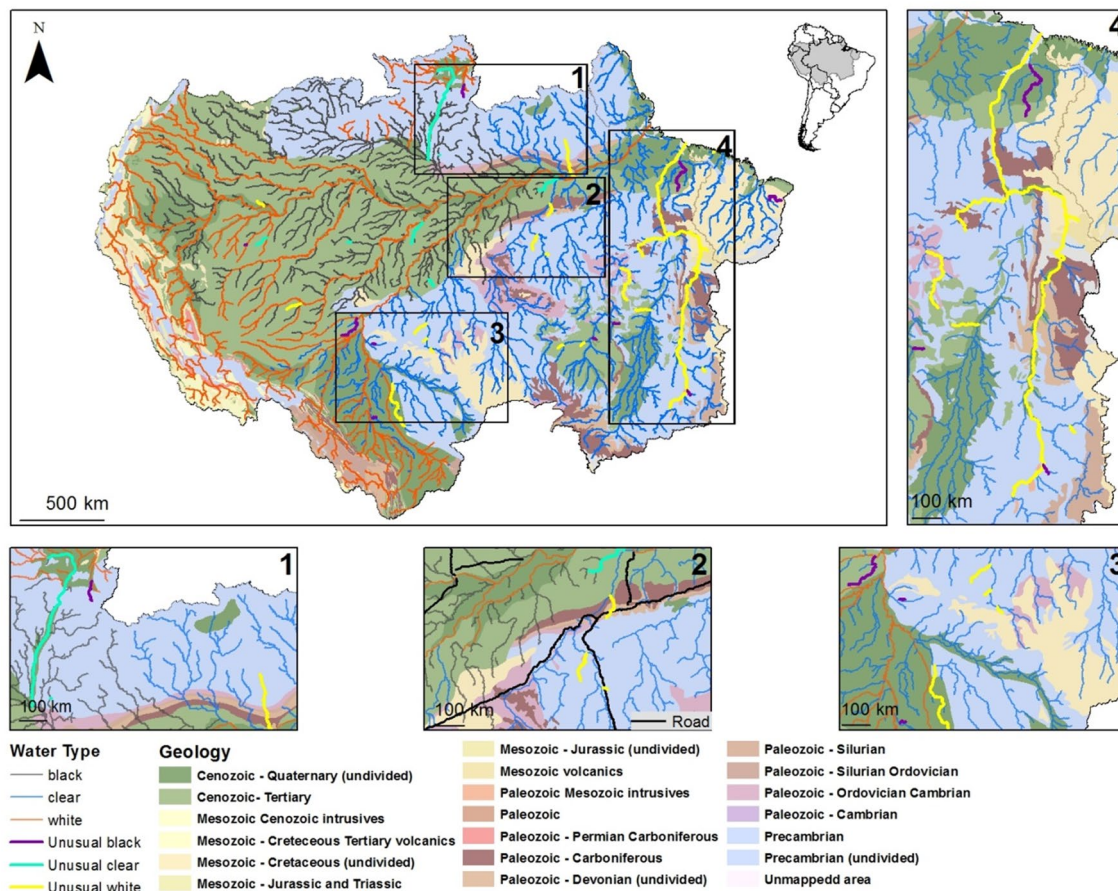


Fig. 5 Rivers colored according to their traditional classification of black, white, and clear, and overlaid on a map of the Amazon basin's underlying geologic features. “Unusual rivers” based on this analysis are highlighted in purple (black), yellow (white), and aquamarine (clear). The insets show some of the areas discussed in the text: 1. Branco (clear) and Maicuru (white); 2. Arapiuns (clear), Cupari (white) and other unusual whitewater rivers along the Transamazon highway; 3. Jaru and Blanco (white); and 4. Tocantins (white) and

unusual whitewater tributaries of Tocantins, Araguaia, and Xingu rivers. Note that many of the unusual whitewater rivers are associated with the presence of Carboniferous stripes. River shapes and traditional classifications (Venticinque et al. 2016), Geology (Schenk et al. 1999); U.S. Geological Survey South America Geologic Map (geo6ag; <https://certmapper.cr.usgs.gov/data/we/ofr97470d/spatial/shape/geo6ag.zip>; accessed April 2016)

along the highway between the cities of Cuiabá and Porto Velho, such as the Chapada dos Parecis (Furch and Junk 1980), are rather homogeneous, but other areas of the pre-cambrian shields show both large- and small-scale geological complexity, which is reflected by the high hydrochemical variability as shown along the transects south to north from Cuiabá to Manaus (Furch and Junk 1980) and Manaus to Caracarái (Furch 1984), and east to west along the Transamazon Highway from Altamira to Humaitá (Furch 1985, 1986). This becomes less evident with increasing river order, because a large river integrates all the water typologies of the catchment as the waters of different qualities mix. Low-order rivers and streams provide a better indication of the local geologic conditions than do large rivers.

Many tropical soils on stable geological surfaces have weathered to great depths and produce extremely dilute

solutions in drainage water (Markewitz et al. 2001; Stallard and Edmond 1983). The soils of the eastern Amazon region are highly weathered Oxisols, which have formed in Upper Tertiary fluvial-lacustrine sediments common along the Amazon river. Oxisols cover about 45% of the entire Amazonian basin, although they may form from a diversity of geologic substrates, including the sediments of the Amazon trough and the rocks of the Brazilian and Guyana shields. These soils (oxisols) generally contribute dilute waters to the main stem of the Amazon river (Markewitz et al. 2001; Stallard and Edmond 1983).

Some studies have indicated that the distribution of major cations and anions in the dissolved load was controlled by substrate lithology in the source regions, suggesting that we should be able to classify the chemical composition of rivers according to the geochemistry and

mineralogy of the soils through which they flow (Konhauser et al. 1994; Stallard and Edmond 1983). According to Gaillardet et al. (1997), the three main lithologies undergoing chemical weathering are silicates, limestones, and evaporites. Carbonate rocks and evaporites are weathered 12 and 60 times, respectively, more rapidly than granites or gneisses. As a consequence, evaporites have a major influence on river chemistry even if their outcrops are rather rare and concentrated in mountains (Gaillardet et al. 1997). Rivers that drain siliceous rock types are low in cations. Those that drain carbonates are relatively high in alkalinity and possess intermediate levels of cations, while those that drain evaporites are rich in sulfate and chloride and are highest in cations (Stallard and Edmond 1983).

With high rates of erosion of the varied lithologies in the source regions, enormous quantities of unweathered minerals (feldspar and mica), metal-rich clays (smectite, chlorite, and illite), and dissolved metals are transported downstream by whitewater rivers, resulting in the fertile soils of the várzea which are almost exclusively derived from the sedimentation of the suspended load (Konhauser et al. 1994). The chemistry of the dissolved size fraction in the Rio Solimões/Amazon, therefore, reflects the substrate lithology in the Andes, with the high concentration of calcium, for example, indicative of a limestone source (Konhauser et al. 1994; Stallard and Edmond 1983), while continuous leaching of the várzea soils further supplies the solute-rich river with additional metals (Konhauser et al. 1994).

The high concentration of dissolved metals in the Solimões/Amazon whitewater river is contrasted by the solute-deficient blackwaters of the Rio Negro which drains the highly weathered lateritic and podzolic terrains of the Central Amazon (Konhauser et al. 1994). Due to a lack of exposed rock, and the low rates of weathering in conjunction with the development of thick, siliceous, and aluminous soils, the suspended sediment are typically cation-depleted, consisting almost entirely of quartz and kaolinite (Konhauser et al. 1994; Stallard 1988), while the dissolved load is dominated by silicon, with extremely low levels of major cations (Konhauser et al. 1994). Clearwater rivers that drain the Precambrian Shield typically carry a limited suspended and dissolved load (Gibbs 1967), reflecting the tectonic stability which leads to low erosional rates and high leaching (Konhauser et al. 1994).

Furthermore, in these stable cratonic regions, which are favored by sedimentary rocks such as orthoquartzites, with no nutrients, or granitic and metamorphic rocks, with a limited nutrient spectrum and low erosional rate, the soils are typically depleted in nutrients (Stallard 1988). Although these conditions should give rise to extremely solute-deficient rivers, the clearwaters flowing through Precambrian

Shields have an intermediate composition (Konhauser et al. 1994).

The classification is mainly related to the geology and geomorphology. The geological and geomorphological basis of the region where rivers are originated, and drain are decisive and constitute a determining influence. The anthropic action can increase the entry of nutrients or elements (for example, mercury in gold mining exploitation and naturally occurring mercury is also common) locally and, to some extent, alter the physical and chemical composition of river stretches, such as the mercury accumulation in the tributaries of Madeira river and other whitewater rivers in the Peruvian, Bolivian, and Brazilian Amazon (Forsberg et al. 2017), but the nature of the rocks that originated the geochemical base remains the same. In a recent study, some streams flowing over Manaus municipality in the Brazilian Amazon were monitored, aiming to assess the anthropic effect on water quality. All the analyzed ions confirmed the uncontrolled entrance of untreated domestically sewage over urban area and that the capacity of maintaining natural water quality pattern is broken, reflecting the disruption of the aquatic environment (Ferreira et al. In review). Nevertheless, this was not the focus of our study.

Unusual river types

Hydrochemical parameters display large variation that can make it difficult to incorporate a specific river into a specific chemical category. For some waters, the chemical qualities do not match the optical attributes according to Sioli's water typologies, and this phenomenon shows how generalized designations for river types can be problematic (Geisler and Schneider 1976). In the following sections, we provide more details about these unusual patterns (Figs. 2, 3, 4, 5 and Appendix in Supplementary Material).

Unusual whitewater rivers

Streams on the Transamazon highway

A hydrochemical transect conducted in some of the Madeira river's right bank tributaries (Lages et al. 2013) revealed that their waters are relatively electrolyte-poor, and represent the typical environment of intense leaching and weathering that affects the rocks in the Amazonia. However, electrolyte-rich waters of the calcium-carbonate typology (whitewaters) may occur sporadically on this transect (Furch 1985, 1986) regardless of their color and transparency (Lages et al. 2013).

Cuparí river

The values of the chemical parameters in the Cuparí river, a Tapajós river right bank tributary, are similar to those observed in the Amazon river upstream from Santarem. It is relevant for classification purposes, because Tapajós and Amazon are “clearwater” and “whitewater” rivers, respectively. The amounts of many dissolved substances in the Cuparí river are higher than what is usually found in the Tapajós basin. These special hydrochemical conditions are related to the limestone layers, gypsum beds, and rhaetic diabases that frequently contact the land surface of carboniferous areas (Sioli 1968).

Tocantins river

The middle Tocantins river’s major tributaries and the Tocantins river itself also share some chemical characteristics with the classical calcium-bicarbonate-dominated rivers. It was already suggested to include this river in the whitewater typology, in spite of its high transparency and traditional classification as clearwater river (Hiraoka 1995; Montagnini and Muñoz-Miret 1999; Santos 1983). This chemical composition is likely explained by the effusive base rocks from the Parnaíba’s sedimentary basin, which is characteristic of the local geography. The Mosquito Formation, which comprises most of the southern right bank of the middle Tocantins river, is essentially made of basalt and results in a predominance of hilly terrain and dendritic drainage in many tributaries. The left bank, between the towns of Tocantinópolis and Imperatriz, is dominated by the Corda Formation, which is very calciferous (ELETRONORTE/THEMAG 1989).

Unusual clearwater rivers

Annual data sets show considerable fluctuations in physicochemical parameters for some rivers, which makes designating a specific water type difficult. Rivers draining archaic/pre-Cambrian shields (e.g., Branco river in Roraima State, Brazil) integrate tributaries of different water qualities. At their mouths, they present mixed water whose physicochemical parameters vary during the annual cycle (Ríos-Villamizar et al. 2014). The Branco river, and many of its tributaries, transport high loads of suspended matter and have the appearance of whitewaters. However, their chemical characteristics indicate low electrolyte status and a closer relationship to clearwaters.

Relevancy and accuracy of water transparency and color for river classification

Though commonly referred to, transparency and water color actually have limited usefulness for river classification because of their high variation with hydrological season, catchment disturbance, and geographical and geological factors. Hydrochemical data sets of blackwater and whitewater rivers are much closer and better-defined (even considering respective annual variability) than those of clearwater rivers. Traditional clearwater typology were based on the lower Tapajós and Arapiuns (Sioli 1956b, 1956c) Both rivers show typical high transparency, because they end in Ria lakes (‘drowned estuaries’), which were formed after the last glacial period at the mouths of blackwater and clearwater tributaries of the Amazon river by sea-level rise that submerged the lower portion of these rivers. The conditions measured by Sioli do not represent the typical physicochemical conditions of the river channels but those of the Ria lakes. The transparency of the Tapajós river increases from 85 cm at Itaituba to 245 cm at Santarem, and this corresponds with the reductions of total suspended solids and turbidity values (Table 2). The other parameters do not show major changes. It may be assumed that the sediment load of the Tapajós has increased since the 1950s because of increased erosion due to increased land use. As this will continue to occur with other transparent rivers and streams, it shows the limited accuracy of transparency for river classification, although this parameter is commonly considered as a good and direct proxy of erosion impairment.

Table 2 Hydrochemical parameters of the Tapajós river at Itaituba on the Transamazon Highway (8 December 2010) and at Santarem (12 December 2010)

Hydrochemical parameters	Itaituba (Transamazon Highway)	Santarém
pH	6.12	5.93
Electric conductivity ($\mu\text{S}/\text{cm}$)	14.2	14.3
Transparency–Secchi depth (cm)	85	245
Total suspended solids (mg/L)	33	0.67
Turbidity (NTU)	13.26	2.34
Water color (mg/Pt/L)	4.71	3.74
Ca^{2+} (mg/L)	0.81	1.16
Mg^{2+} (mg/L)	0.53	0.65
K^{+} (mg/L)	1.12	0.73
Na^{+} (mg/L)	1.07	1.12
Cl^{-} (mg/L)	0.398	0.43
SO_4^{2-} (mg/L)	0.34	0.51
HCO_3^{-} (mg/L)	8.54	9.15

In spite of Sioli's very limited database (Sioli 1949, 1951, 1954, 1956a, 1956b, 1956c, 1957, 1964, 1967, 1968; Sioli and Klinge 1961, 1962), he described other Amazonian streams that show high physicochemical variability (i.e., the pH is in the range of 4.7 to 6.4, and the electrical conductivity varies between 3.7 and 171 $\mu\text{S cm}^{-1}$) as clearwater streams. This maximum value of electrical conductivity suggests that he misidentified some carbonate-dominated whitewater streams as clearwater streams because of their high transparency, without considering the relatively high values of the dissolved chemical parameters. Our results suggest that these parameters are relevant for classifying a river on the whitewater typology, regardless of its color or transparency, if those values are maintained throughout the annual cycle typically observed in the large whitewater rivers that are subjected to predictable, high-amplitude, and long-lasting, monomodal flood pulses (i.e., > 5th order rivers along the Amazon river and its large whitewater tributaries, see Fig. 1).

Low-order rivers and streams (1–5th order), which are affected by local rains and are subjected to short, unpredictable, and polymodal flood pulses, show considerable variability in physicochemical parameters. However, according to our results, an acidic clear or blackwater stream that becomes turbid as a result of a local rain event or increased soil erosion (in areas used by agriculture and cattle ranching) does not turn into a whitewater stream. On the contrary, it remains in the clearwater or blackwater category (Junk et al. 2011), as it continues to be an acidic and electrolyte-poor stream, because the dissolved chemical parameters, which are determined by the geology of the catchment area, are relatively unaffected.

Synthesis of Amazonian river water classification

The classification of Amazonian rivers based on their physical and chemical properties has already been tried by several authors. However, extrapolation to an area as large as the Amazon poses additional difficulties. The mere management of the abundant documentation that exists in the rivers is already a challenge to be taken into account.

Although a significant increase in the number of water studies is observed, two aspects of chemical compounds in Amazonian rivers are rarely considered. One concerns the sampling of water: the collection has been unsystematic in the past and lacks basin-wide representativeness. Another is that most of the current studies only target selected analytes and chemical substances at different points in time (punctual data), which impedes the development of a database of historical series. Therefore, to systemically assess the water

typology of the Amazonian rivers and streams, it is necessary to conduct a basin-wide survey.

The most characteristic water type is the Amazon river whitewater deriving from the Andes. The water of the main stem of this river becomes diluted from about 120–200 $\mu\text{S cm}^{-1}$ near the Andes to 40–70 $\mu\text{S cm}^{-1}$ at the lower course (e.g., Santarem) by blackwater and clearwater tributaries (Duque et al. 1997; Gessner 1962; Gibbs 1967; MRAG 1993; Oltman 1968; Palma-Silva 2011; Santos and Ribeiro 1988; Stallard and Edmond 1983), but it continues to be turbid, nearly neutral, relatively electrolyte-rich water dominated by carbonates of alkali-earth metals. The whitewater-type rivers are characterized by pH values between 6 and 8.5, electrical conductivity in the range of 30–760 $\mu\text{S cm}^{-1}$, and water transparency between 10 and 235 cm. Our study reveals that some rivers draining the carboniferous stripes of the lower Amazon, many with higher than usual values of dissolved substances (Sioli 1968) but with low suspended sediment loads and high transparency, must be considered whitewater rivers (Fig. 5). Examples of this phenomenon include some tributaries of the Ji-Paraná, Tapajós, Xingu, and Tocantins/Araguaia rivers, the Tocantins river, as well as some rivers and streams near Monte Alegre region in Para State (Brazil), in the Andean/pre-Andean zone [e.g., Zongo river, upper Madeira basin (ORE-HYBAM), and in the Peruvian Amazon (DOMUS 2009)]. Of the investigated rivers, 105 (54.4%) fall within the whitewater category based on their chemical parameters.

A similarly characteristic water type is the Negro river. This blackwater river originates on the Precambrian shield of the Amazon basin's northern region and is a typical representative of the Amazonian blackwaters (Furch and Junk 1997). Its transparent red–brown color originates from a high content of dissolved humic substances (about ten times higher than found in the Solimões/Amazon river), the water is poor in electrolytes, sodium dominates among the major cations, and it shows low alkalinity. The pH and electrical conductivity values are less than 5.5 and 30 $\mu\text{S cm}^{-1}$, respectively. The extreme chemical poverty exhibited by the Rio Negro and other blackwater rivers and streams is indicative of the poor nutrient status of the Central Amazon (Konhauser et al. 1994). Seventy six (39.4%) of the investigated rivers fall within the blackwater category.

The clearwater-type rivers have their upper catchments in the central Brazilian and Guiana archaic/pre-Cambrian shields and are characterized by pH values that vary between 5.3 and 7.2, electrical conductivity in the range of 5.1–53.6 $\mu\text{S cm}^{-1}$, and water transparency up to 355 cm or even higher. However, transparency values < 50 cm are also common in these rivers. The varying amounts of suspended matter content that can be found in these rivers has already been discussed above (Table 2). We consider the total amount and relationship of alkali (Na^+ , K^+) and

alkali-earth (Ca^{2+} , Mg^{2+}) metals and carbonates as a more stable and stronger chemical parameter for the water classification than the amount of suspended solids (Furch and Junk 1980). Sioli's clearwater rivers are represented by only 12 rivers, corresponding to 6.2% of the total. The distribution of the modified classification is given in Fig. 5.

Management implications of a more accurate Amazonian river water typology

The Amazon is the largest freshwater system in the world, and its overall ecosystem function depends on complex interactions between its many and diverse rivers and freshwater ecosystems. Currently, there are over 150 dams in operation in the Amazon basin, and over 250 more are planned (Castello and Macedo 2015), many of high ecological impact (Finer and Jenkins 2012). Several examples from studies on rivers around the globe (e.g., Mekong, Congo, Red, and Yangtze) have revealed the negative and cumulative impacts of multiple hydroelectric power plants on the hydrological and hydrochemical conditions (e.g., water level, timing of flood pulse, sedimentation, and chemical quality) of rivers, with potential implications for fishing and fisheries, and other ecosystem processes (Hurd et al. 2016; Winemiller et al. 2016). The impacts of hydropower infrastructure will vary according to the water typology and sediment load of a given river. The whitewater Andean tributaries are of particular concern. Damming multiple Andean tributaries, which are the source of most sediments and nutrients that feed lowland Amazonian ecosystems and associated vegetation, could have dramatic impacts downstream (Forsberg et al. 2017). In addition to hydropower construction, other activities may also act synergistically to affect the rivers and streams in the Amazon, including roads, industrial waterways, hydrocarbon and mining exploitation, deforestation associated with roads and dams, agricultural expansion, and hydrological modifications related to climate change (Soribas et al. 2016).

The vast size of the Amazon basin, the interlocking relationships between uplands and wetlands, and the flow of water through wetlands from the Andes to the Atlantic strongly suggest that, to be effective, development planning must be based on scientific analysis and synthesis of information at scales large enough to capture and understand these ecological complexities. The classification system presented here, based on a comprehensive water chemistry dataset, is critical information for understanding the baseline (reference) conditions in Amazonian rivers, wetlands, and freshwater ecosystems. This may contribute to the development of tools for water monitoring mainly based on the “gap” between an expected typology (baseline) and the observed condition. It also may serve as a basis for

evaluating actual or potential impacts of development projects on the threatened Amazonian rivers, and for planning more effective management and conservation priorities.

About 20% of Brazil and 30% of Amazonia are covered by different types of wetlands (Junk et al. 2011). A classification system of Amazonian lowland wetlands already uses hydrochemical parameters for the differentiation between the floodplains of large nutrient-rich whitewater and nutrient-poor blackwater rivers (Junk et al. 2011). These water types represent the upper end and the lower end of the fertility gradient. Macrohabitat classifications of the nutrient-rich várzeas of the whitewater Amazon River and its large white-water tributaries and the nutrient-poor igapos of the Negro River and other large blackwater rivers are provided (Junk et al. 2012, 2015). The wetlands differ in species composition and productivity of herbaceous plants and trees, which are used together with hydrological parameters for the characterization of macrohabitats. Low fertility of blackwater river floodplains shows low resilience against disturbance and strong limitations of human use in contrast to nutrient-rich whitewater river floodplains (Ríos-Villamizar et al. 2020a).

The hydrochemical classification, presented in this paper, indicates in lower order tributaries the existence of many transitional hydrochemical stages and/or the change in water quality in these systems between rainy and dry season. These differences have not yet been considered in the general Brazilian and Amazonian wetland classification systems. They require additional research efforts for vegetation inventories to allow a specific macrohabitat classification. Only on this basis, these wetlands can become included in the general wetland classification system and respective management recommendations can be formulated for their sustainable management (Ríos-Villamizar et al. 2020a).

Conclusions

The parameters used in any water classification system cannot fully take into account the large natural variability of water bodies. While the differences between the water classes may appear to be clear, the transitions between them in nature are often fluid. Furthermore, the parameters used for the classification of river water depend upon the purpose of the exercise. For example, classifications of quality for drinking water, public health, or aquatic productivity will use other parameters than will an ecological classification. The combination of the parameters such as water color, transparency, pH, electrical conductivity, the amount and relationship between alkali and alkali-earth metals, and major anions allows distinguishing the three classical water types (white, black, and clear) as well as some unusual river water types from the Amazonian region. The major element

geochemistry of the Amazon basin rivers has been extensively documented. Our data analysis from the available literature is in good agreement with the Stallard and Sioli's observations, and confirms the general geochemical classification of the Amazon rivers (Gaillardet et al. 1997).

Although Sioli's general approach was updated, and it also required some adjustments to account for the amount and relationship between alkali and alkali-earth metals and carbonates, it continues to be valid for ecological and management purposes. However, the fact remains that Amazonian rivers show great physicochemical variability, which increases with decreasing river order. Thus, small rivers and streams indicate local geological differences better than large rivers, which represent the mean chemical conditions of large catchment areas. Our study shows that a clearwater or blackwater stream that becomes turbid as a result of a local rain event and/or increased soil erosion, in areas used by agriculture and cattle ranching, does not turn into a whitewater stream, but it continues to be an electrolyte-poor clearwater or blackwater stream, because the dissolved chemical parameters, which are determined by the geology of the catchment area, are relatively unaffected.

We are following the more recent classification of Amazonian wetlands (Junk et al. 2011), which considers first the water types, followed by some other parameters. We already know that the phanerogamic vegetation differ between blackwater igapó and várzea floodplains (Wittmann et al. 2006), with about only 30% of species in common. For animals, the scenario is complex. Some species like the Amazon-manatee (*Trichechus inunguis*) may be found in poor and rich Amazonian waters (igapó and várzea), but considering some other species like fish and birds, a more detailed survey should be done. However, this was not the focus of our study.

As the conservation and protection actions on the Amazon basin's aquatic systems must be based on scientific synthesis of information at large scales, our approach provides critical information for understanding baseline conditions in Amazonian river systems, wetlands, and freshwater ecosystems. This may contribute to the development of tools for water monitoring and for evaluating the impacts of development projects. In addition, this work may serve as a basis for planning more effective conservation and management priorities of the threatened Amazonian rivers. Hydrochemical data are still scarce for many low-to-medium order rivers and a detailed classification covering the entire Amazon basin is not yet possible. Thus, it is necessary to continue collecting water samples principally in unstudied streams and small rivers, to enhance the databases.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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