Chemistry of different Amazonian water types for river classification: a preliminary review

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Abstract

Water chemistry provides important parameters for the study of river ecology and management options of rivers and connected wetlands. Sioli, in the 1950s, established three water types (whitewater, blackwater and clearwater) for explaining limnological characteristics of the large Amazonian rivers, and related the physico-chemical parameters of these water types with the geological properties of their basins; a landscape ecology approach. Today, an increasing amount of hydrochemical data indicate that the chemical composition of Amazonian water bodies varies much more than assumed by Sioli. Nonetheless, due to its simplicity for describing the natural physico-chemical variability of Amazonian rivers, his classification is still valid. Our analysis, based in literature and field work, allowed to distinguish well among the three classical water types and to provide new preliminary insights about the limnological classification of Amazonian rivers in order to subsidize the sustainable management of water resources and wetlands.
Keywords: Amazon basin, river classification, water hydrochemistry, landscape ecology.

1 Introduction

Water chemistry provides important parameters for quantifying biogeochemical cycles and determines management options in river systems and wetlands. Pre-

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Columbian populations categorized Amazonian rivers by the color of their water, and both native and colonial inhabitants of the Amazon knew that water color was related to specific ecological properties such as fish richness or soil fertility (Junk *et al.* [1]). The first scientific classification of Amazonian water bodies was elaborated in the 1950s by Sioli [2]. He used water color, transparency, pH and electrical conductance to explain limnological characteristics of the large Amazonian rivers. The innovative aspect of his classification was the correlation of these characteristics to the geological and geomorphological properties of the river catchments, an approach used today in landscape ecology.

Whitewater rivers (such as the Amazon main course and the Juruá, Japurá, Purus, and Madeira) are turbid, with water transparency (Secchi depth) that varies between 20 and 60 cm, and have their origins in the Andes, from which they transport large amounts of nutrient-rich sediments. Their waters have near-neutral pH and relatively high concentrations of dissolved solids indicated by the electric conductivity that varies between 40–140 $\mu S\ cm^{-1}$. Blackwater rivers (such as the Negro River) drain the Precambrian Guiana shield, which is characterized by large areas of white sands (podzols). Their water transparency is about 60–120 cm, with low quantities of suspended matter but with high amounts of humic acids that give the water a brownish-reddish color. The pH values of such rivers are in the range of 4–5 and their electrical conductivity is $<20\ \mu S\ cm^{-1}$. The floodplains of blackwater rivers are of low fertility and are locally called igapós.

Clearwater rivers (such as the Tapajós and Xingu Rivers) have their upper catchments in the cerrado region of the Central Brazilian archaic shield. The transparency of their greenish waters is above 150 cm, with low amounts of sediments and dissolved solids and electrical conductivity that is in the range of 10-20 $\mu S\ cm^{-1}$, and pH that varies between 6 and 7 in large rivers. The floodplains of clearwater rivers are of intermediate fertility and also called igapós.

This simplified classification has dominated until today the scientific discussion about limnology and ecology of the Amazon basin, but Sioli's classification was based only on a very limited data base. In the meantime, the situation has changed dramatically. The National Amazon Research Institute – INPA has conducted many limnological studies and hosted high-level, national and international limnological projects, such as the cooperation with the Max-Planck-Institute for Limnology in Plön, Germany [3–5], and the CAMREX expeditions of the University of Seattle [6–8].

The aim of this paper is to analyze a preliminary data base about water chemistry of some Amazonian rivers and streams under Sioli's classification criteria, and provide some new insights in the limnological classification of Amazonian rivers and streams.

2 Material and methods

From literature we collected some preliminary data available on hydrochemistry of rivers and streams. In addition we collected water samples in the course of four field surveys during the periods of 27th October–3rd November 2009, 1st–7th March 2010, 26th September–3rd October 2010 and 3rd–12th December 2010 around the middle/lower area of the Jutaí, Tefé, Juruá and Tapajós river basins, respectively (fig. 1). The transparency (m) values were measured using the Secchi disk, and the electrical conductivity (µS cm^{-1} at 25°C), pH, and Dissolved Oxygen (mg O_2 l^{-1}) values were measured in the field using WTW instruments. In the laboratory of the INPA in Manaus (Brazil) were analyzed the water samples to obtain the values of the major cations such as Ca (mg l^{-1}), Mg (mg l^{-1}), Na (mg l^{-1}) and K (mg l^{-1}), and major anions such as Alkalinity (mg HCO_3 l^{-1}), SO_4 (mg l^{-1}) and Cl (mg l^{-1}), as well as the values of water colour (mg Pt l^{-1}), Turbidity (NTU), Total Suspended Solids (mg l^{-1}), PO_4 (mg l^{-1}), P_{tot} (mg l^{-1}), NH_4 (mg l^{-1}), NO_3 (mg l^{-1}), N_{tot} (mg l^{-1}) and Si (mg l^{-1}). All the analyses were carried out by standard methods (APHA *et al.* [9]). Using Open Stat 4.0, a free code statistical program, a principal component analysis – PCA was accomplished in order to identify which variables are more important for the analysis, and for grouping water quality types (Mardia *et al.* [10]).

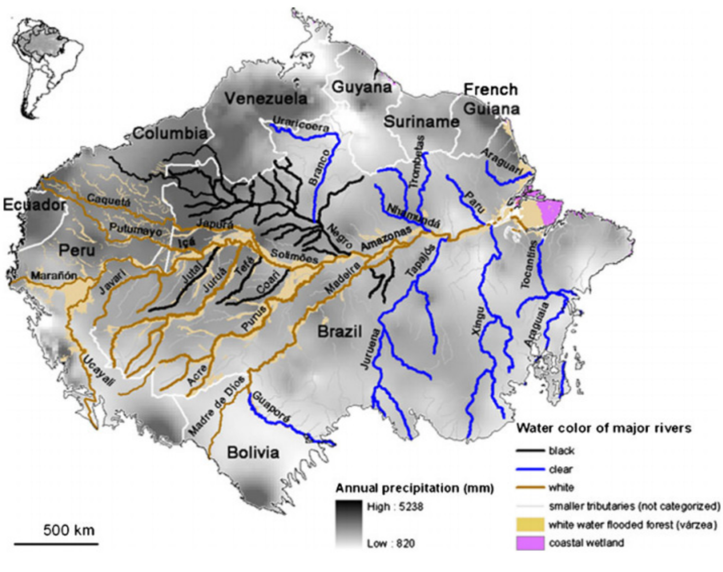

Figure 1: The distribution of major whitewater, blackwater, and clearwater rivers in the Amazon basin, from Junk *et al.* [1].

3 Results

In table 1 are presented the mean physico-chemical results of the analyzed water samples that were taken from some colorless streams (lower Tapajós basin) and Tapajós, Cuparí, Jutai, Tefé and Juruá Rivers. The physico-chemical characteristics of the Tefé and Juruá Rivers are similar to the classic/typical black and white waters, respectively (Furch and Junk [5]). The Tapajós River is characterized by having intermediate conditions between the white and black waters (Junk and Howard-Williams [11]). An intermediate and transitional pattern is also observed in the Jutai River. The colorless streams of the lower Tapajós basin show very acidic conditions and poverty in electrolytes resembling the classic black waters, with the exception of the color value which is very low in these kinds of streams.

Table 1: Mean physico-chemical characteristics of colorless streams (lower Tapajós river basin), and Tapajós, Cuparí, Jutaí, Tefé and Juruá rivers waters.

Variable	Tapajós basin			Jutaí	Tefé	Juruá
	Tapajós	Colorless streams	Cuparí			
pH	6.56	4.39	6.26	5.96	5.03	7.27
Electric conductivity (µS/cm)	14.33	15.12	59.90	8.71	7.36	191.14
Total Suspended Solids (mg/l)	10.56	0.35	6.33	46.56	7.90	51.42
Ca (mg/l)	0.52	<0.02	2.85	0.54	0.71	32.55
Mg (mg/l)	0.26	0.06	0.71	0.15	0.22	4.42
Na (mg/l)	1.50	2.27	3.88	1.21	0.40	10.19
K (mg/l)	0.93	0.43	2.39	0.74	1.41	1.98
Total P (mg/l)	0.010	0.013	0.020	0.079	0.033	0.080
HCO_3 (mg/l)	8.80	2.07	21.96	8.78	6.86	106.14
NO_3 (mg/l)	0.040	<0.010	0.230	0.111	0.014	0.031
NH_4 (mg/l)	0.19	0.12	0.38	0.21	0.13	0.062
Total N (mg/l)	0.35	0.21	0.64	0.49	0.24	0.39
SO_4 (mg/l)	0.30	0.24	7.72	0.61	4.20	2.56
Colour (mg/Pt/l)	4.02	3.44	65.08	62.78	54.90	41.61
Si (mg/l)	5.25	-	9.12	3.35	0.33	5.78
Cl (mg/l)	0.53	2.50	1.78	1.28	0.85	4.75

- = Not analyzed.

Others authors such as Silva *et al.* [12] already observed colour values in the Tapajós River water around five times higher than the value of this study, similar to the values observed in the Jufari River water, which is considered one of the Negro River's tributaries showing the highest poverty of dissolved substances (Santos *et al.* [13]). We also observed similarities between the Jufari and Tapajós River mainly in terms of the variables Cl and total Fe. On the other hand, the values of the variables pH, Ca, K and NH_4 are similar between Jufari River and the colorless streams of the lower Tapajós basin. However, the results of the Cuparí River, a Tapajós River's right bank tributary, are higher than usually is found in the Tapajós basin and the Amazon region itself, but these are in agreement with the findings of Sioli [14] especially for pH, Ca, Mg, SO_4, Fe and Si.

In contrast to the Amazonian black waters which show pH-values below 5.0 and electrical conductivity less than 25 µS cm^{-1}, the typical Amazonian white waters are characterized as carbonate waters according to Furch and Junk [5], indicating richness in carbonates and calcium, pH above 6.5 and electrical conductivity more than 40 µS cm^{-1}. On the other hand, Sioli's observations of clear waters were based at the lower Tapajós and Arapiuns (Sioli [2, 15]). Both rivers show typical high transparency because they are Ria lakes without major current, where sediments brought in by the rivers became already deposited. They do not represent the physico chemical conditions of the channels of these rivers, but those of Ria-lakes, which have been built in the large mouth bays of the black and clearwater tributaries of the Amazon River by the damming back of the river water because of the raise in sea-level after the last glacial period. Transparency of the Tapajós-water increases from 85 cm at Itaituba on Transamazon Highway to 245 cm at Santarém, 280 km far. The other parameters do not show major changes. We may assume that sediment load of the Tapajós has increased since Sioli's time because of increased erosion as a result of increased land use. But this will happen in future with other transparent rivers and streams and shows the limited value of transparency for river classification.

Furthermore, annual data sets show for some rivers considerable fluctuations in physico-chemical parameters, which makes the relation to a specific water type difficult, as shown for the Branco River (fig. 2).

Finally, the multivariate analysis indicated that the first three principal components account for over 65% of the variability in the data set. According to the first component, the more important variables are the major anions (µeq/L), HCO_3 (µeq/L), electrical conductivity (µS/cm), major cations (µeq/L), Ca (µeq/L), Mg (µeq/L), Na (µeq/L), eq% Ca, pH, Cl (µeq/L) and K (µeq/L). Accounting to the second component are the total N (µeq/L), eq% Mg, eq% Na, water colour (mg/Pt/L), eq% SO_4 and eq% K. The third component is constituted by eq% HCO_3, eq% Cl, transparency (m) and total P (µeq/L). All the loading values are above 0.2 or below -0.2 (fig. 3 and table 2).

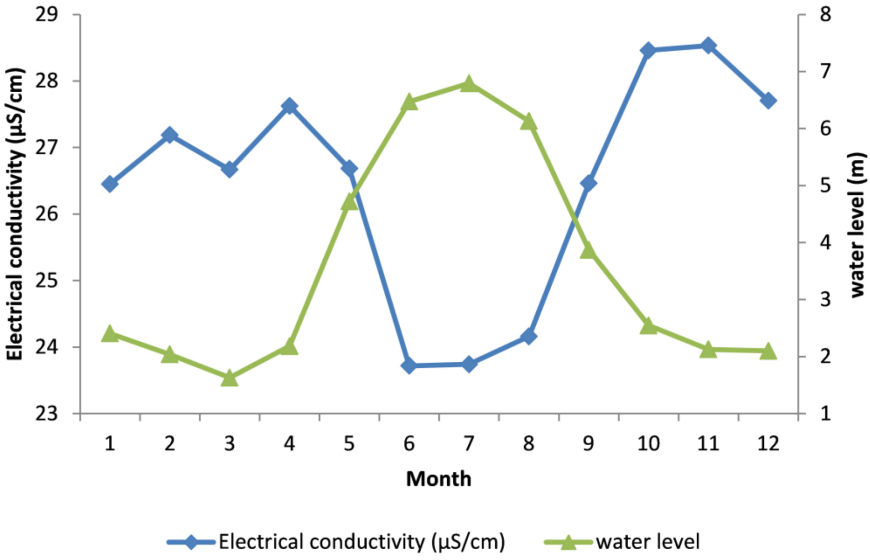

Figure 2: Water level fluctuations and seasonal variations of electrical conductivity in the Branco River at Caracarai. Monthly mean values from September 2003 to December 2009, according to data from ORE-HYBAm [16].

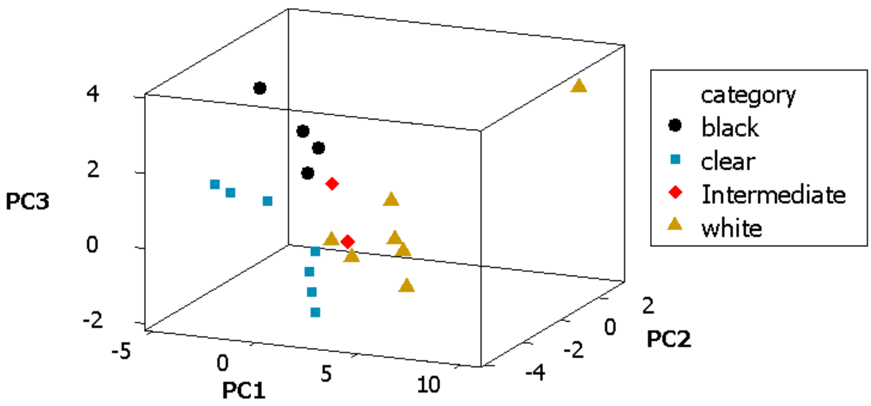

Figure 3: Scores plot of the PCA for the first (41.6% of the variance), second (14.1%) and third (9.4%) component.

Table 2: Rivers and streams used in the analysis (by water type).

Water type (category)	River or stream name	Source
Blackwater rivers	Negro, Tefé.	Leenheer and Santos [17]; Junk and Howard-Williams [11]; Furch and Junk [5].
Clearwater rivers	Tapajós, colorless streams at lower Tapajós River, Branco, Araguaia, Guaporé.	Santos [18]; Stallard and Edmond [19]; Santos *et al.* [13]; this study; INAU, unpubl. data.
Whitewater rivers	Solimões/Amazonas, Juruá, Cuparí, Tocantins.	Leenheer and Santos [17]; Santos [18]; Junk and Howard-Williams [11]; Richey *et al.* [8]; this study.
Intermediate (other rivers)	Jutaí, Bóia.	Richey *et al.* [8]; this study.

INAU: Instituto Nacional de Ciência e Tecnologia em Áreas Úmidas.

4 Discussion

Ríos-Villamizar *et al.* [20] classified several rivers and streams using the relationship between major cations (mg%). They observed that the distribution of alkali and alkaline-earth metals allows distinguishing well among the three classical/typical water types and to categorize others rivers since, generally, the latter occupy intermediate positions among that three typical water types, showing hence a transitional character, fig. 4.

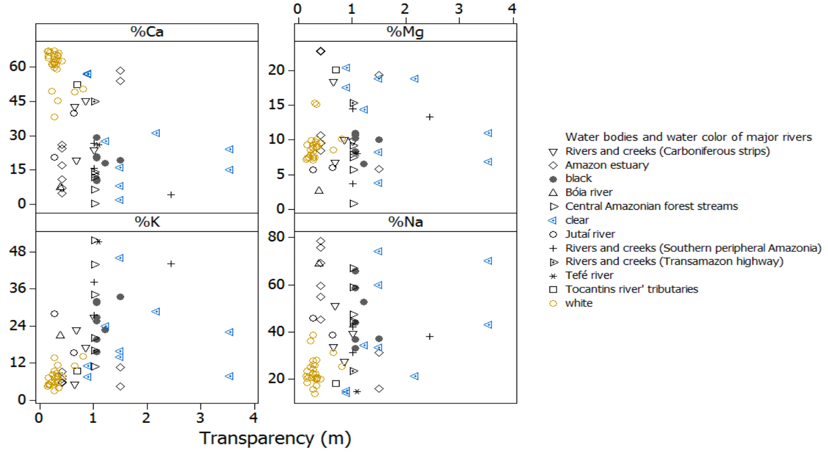

Figure 4: Relationship between the distribution of alkali and alkaline-earth metals and transparency of Amazonian rivers and streams, from Ríos-Villamizar *et al.* [20].

There are waters, along the Amazon Basin, where the chemical quality does not match with the optical attributes accordingly with the classical water type (e.g., Branco River and its tributaries, Copatana, Marauiá, Cuparí and Tocantins Rivers among others) and this indicates anew the problems arising when river types are given generalised designations (Geisler and Schneider [21]).

Today, road construction in the Amazon allows access to low-order rivers in remote areas that were previously inaccessible to Sioli and other limnologists. The Central Amazonian tertiary/Cenozoic sediment basin and some of the plateaus, such as the Chapada dos Parecis along the highway from the cities Cuiabá to Porto Velho (Furch and Junk [4]), are rather homogeneous, but other areas of the archaic/Pre-Cambrian shields show a large and sometimes small-scale geological complexity which is reflected by a large hydrochemical variability as shown by the hydrochemical transects South to North from Cuiabá to Manaus (Furch and Junk [4]), Manaus to Caracarai (Furch [22]), and the East to West transect along the Transamazon Highway from Altamira to Humaitá (Furch [3, 23]). With increasing river order, this complexity becomes hidden, because the river provides the integration of all types of waters of the entire catchment by mixing waters of different quality. Also, the geology of the pre-Andean zone is also rather heterogeneous with large old sedimentation areas (paleo-varzeas) of different ages. These sediments are strongly weathered, but still have a higher bioelement content than the tertiary sediments of the central Amazon basin and the soils on the archaic shields.

Rivers draining archaic/Pre-Cambrian shields, e.g. Branco River in Roraima State, integrate tributaries of different water quality including blackwater tributaries, and present at the mouth a mixed water whose physico-chemical parameters vary during the annual cycle.

Possibly due to the influence of the Amazon River's flood pulse, the single samples that were collected at the lower section of some Amazonian black-water rivers such as the Negro, Tefé, Uatumã and Urubu in Brazil; Nanay in Peru and some streams in Colombia can have ionic composition and/or pH-values similar to the white waters rivers and not like the typical Amazonian black waters rivers, and this fact do not allow getting a general statement about their chemical category. The low electrical conductivity values can be responsible for this phenomenon because in electrolyte-poor waters, a little oscillation of Ca or HCO_3 content can make a high variation of the respective percentage, which in the Solimões/Amazon river water would not affect the percentage in a noticeable way. The heterogeneous geology of the different tributaries may also be an explanation. For instance, the Jatapu River, an Uatumã River's lower tributary, crosses the Nova Olinda/Carboniferous Formation and probably this fact is responsible for alterations in the physico-chemical characteristics of the Uatumã River's lower part.

The most characteristic water type is the Amazon whitewater deriving from the Andes. The water of the main stem becomes diluted from about 120–200 $\mu S\ cm^{-1}$ near the Andes to 40–70 $\mu S\ cm^{-1}$ at Santarem by blackwater and clearwater tributaries [19, 24–29, this study], but it continues to be a turbid, nearly neutral, relatively electrolyte-rich water dominated by carbonates of alkali earth metals. The importance of the total amount and relationship of alkali and alkali-earth metals and carbonates can be considered as an essential chemical parameter for the classification of Amazonian water types (Furch and Junk [5]). If we do this, some rivers, draining the carboniferous stripes at the lower Amazon, where many dissolved substances can be found in higher values than usual (Sioli [14]), such as some tributaries of the Tapajós and Tocantins Rivers, the Tocantins River itself, as well as some rivers of the Andean/Pre-Andean zone such as Zongo River in the upper Madeira basin (ORE-HYBAm) have to be considered as whitewater rivers despite of a low load of suspended sediments. Even far away from the Andes, the middle Tocantins River's major tributaries and the Tocantins River itself (ELETRONORTE/THEMAG [30]), share some chemical characteristics such as electrical conductivity, pH and ionic composition with the classical Andean white-water rivers.

A similarly characteristic water type is the Negro River black water which, originated on the Precambrian shield of the northern region of the Amazon basin, is a typical representative of the Amazonian black waters (Furch and Junk [5]). Its transparent red-brown colour originates from a high content of dissolved humic substances which is about ten times higher than in the Solimões/Amazon River, the water is poor in nutrients and electrolytes with dominance of sodium among the major cations, presenting low alkalinity. The pH and electrical conductivity values are less than 5.0 and 25 $\mu S\ cm^{-1}$, respectively.

The rivers of the Sioli's clear water type have their upper catchments in the Central Brazilian and Guiana archaic/Pre-Cambrian shields and are characterized by pH-values that vary between 5.0 and 7.0, electrical conductivity is in the range of 10–53.6 $\mu S\ cm^{-1}$, the water transparency can reach up to 355 cm or still higher; but transparency values less than 100 cm are also common in these rivers. However, we consider the total amount and relationship of alkali and alkali-earth metals and carbonates as a more stable and stronger parameter for the water classification than the amount of suspended solids.

5 Conclusions

The combination of several parameters such as the amount and relationship between alkali and alkali-earth metals, and major anions especially bicarbonates and chlorides, electrical conductivity, pH, total N, water colour, suspended sediment load as transparency and total P allow to distinguish the three classical water types (white, black and clear) and other water bodies with intermediate position. The distribution of alkali and alkaline-earth metals and major anions is especially useful for the distinction of whitewater, blackwater and clearwater categories. Higher variability is shown by water bodies that not fit inside these three classic categories. Therefore, many rivers and streams have to be considered as "mixed waters" resulting from the influence of lower order tributaries with different physico-chemical properties of their waters.

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