

Chemical composition of the Acre River water, Southwestern Amazonia

Composição química das águas do rio Acre, Amazônia sul-ocidental

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ABSTRACT

The Amazon Basin is a special contributor to global biogeochemistry, particularly from the white water region related to the Andes mountains, a source of major Amazon river tributaries. White water composition and properties are rarely determined. Therefore, it is essential to know the spatial distribution and temporal variability of these waters to assess possible human influences on their chemical characterization. In this paper, a study performed in the Southwestern Amazon region, examining the chemical composition of the Acre River water is presented. This part of the Amazon Basin has not been studied sufficiently to determine the geochemistry of its white waters. pH, electric conductivity (EC), turbidity, and concentration of metals, anions and dissolved organic carbon (DOC) were measured from 2008 to 2014. Approximately 60% of the pH measurements had values between 6.5 and 7.3; 55% of the conductivity measurements had values between 30 and 60 μ S cm¹; and 50 % of the turbidity measurements had values less than 100 NTU. The major soluble elements were Ca, Si and K. These species have a natural origin (clay minerals and quartz). Toxic elements (e.g., V, Ni, Cr and Pb) and the anions NO; and SO₄²⁻ were present at concentrations below the Brazilian Standards. The Na⁺, SO₄²⁻ and Al concentrations are seasonally variable depending on water discharge. Major ions such as Mg and Ca showed a positive linear correlation with DOC.

Keywords: White water. Hydrogeochemistry. Acre River. Amazonia

RESUMO

A bacia amazônica contribui de maneira especial à biogeoquímica global, em particular a região de águas brancas relacionada com as montanhas andinas, fonte de importantes afluentes do rio Amazonas. A composição e propriedades das águas brancas não estão especificadas em grande parte. É essencial conhecer a distribuição espacial e a variabilidade temporal destas águas para, eventualmente, avaliar possíveis influências humanas sobre suas características. O presente trabalho aborda um estudo realizado na Amazônia Sul Ocidental onde foi examinada a composição química das águas do rio Acre. Esta parte da bacia amazônica não tem sido estudada suficientemente na determinação da geoquímica das suas águas brancas. Foram medidos o pH, a condutividade elétrica (EC) e a turbidez das águas, bem como a concentração de metais, ânions e carbono orgânico dissolvido (DOC) entre 2008 e 2014. Aproximadamente 60% das medições do pH tiveram valores entre 6,5 e 7,3; 55% das medições de condutividade tiveram valores entre 30 e 60 μ S cm¹; e 50 % das medições de turbidez tiveram valores inferiores a 100 NTU. Os elementos mais solúveis foram Ca, Si e K. Estas espécies químicas apresentam origem natural (minerais de argila e quartzo). Os elementos tóxicos (e.g., V, Ni, Cr e Pb), bem como os ânions NO³; e SO⁴₄ foram encontrados em concentrações abaixo dos limites estabelecidos nas Normas Brasileiras. As concentrações de Na⁺, SO²₄ e Al variam sazonalmente com a vazão. Íons com altas concentrações como Mg e Ca mostraram uma correlação linear positiva com DOC.

Palavras Chave: Águas brancas. Hidrogeoquímica. Rio Acre. Amazônia

INTRODUCTION

Several research studies have reported on chemical composition and characteristics of major rivers like Jurua, Purus, Madeira, Solimões, Negro and Amazon. Hydrogeochemistry is linked tightly to soil and rock composition, vegetation, weathering, deforestation, the use of fertilizers, and mining activities, among other factors. The Acre River is a tributary of the Purus River, in the white water Amazon region. Knowing its hydrogeochemistry is important for contributing to understand the impact of seasonality of hydrological cycle, environment and anthropogenic actions in Amazon Basin. This paper addresses these questions of interest to human health.

The Amazon white water region (JUNK, 1984; SIOLI, 1951) may be impacted by natural or anthropogenic influences leading to spatial and temporal modification of its properties caused by increasing weathering, sediment transport and urbanization. In order to improve the knowledge of hydrogeochemistry Elbaz-Poulichet et al. (1998) considered it necessary to produce large sets of data on relatively small drainage basins and proceeded to study the Mamore and Beni watersheds in Bolivia. Some conclusions show that mining activity in the Beni basin contributes to increase the concentration of Cd and Zn in the river; at the same time, the higher content of Mn in the Mamore basin reflects the predominance of carbonate rocks (MAURICE-BOURGOIN et al., 1998; SEYLER et al., 1999). The contribution of dissolved silicate phases remained small.

Rios-Villamizar et al. (2011) compiled physicochemical data on Purus River, between Seringal Caridade and Arumã in Amazonas State. They encountered pH from 5.99 to 7.12, EC from 26.36 to 91.88 μ S cm⁻¹, and turbidity from 7.72 to 42.25 NTU. Low values of pH monitored in Lábrea were explained due to local deforested areas. Similarly, for Solimões and Purus river water, Queiroz et al. (2009) reported pH values varying

between 5.9 and 7.2, and EC varying between 49 and 99 μ S cm⁻¹. Biggs et al. (2002) determined the effect of deforestation and urban population density on water chemistry in Rondônia, they encountered that watersheds > 40 % deforested have higher pH than forested watersheds and also that Na⁺, Cl⁻ and SO₄⁻² concentrations in stream were higher in urbanized catchments. Seemingly, an inverse alteration of pH occurs between watersheds in deforested areas and urban watersheds due to soil conditions and pollutant contribution.

The hydrologic cycle in Amazon region is important to the transport of elements and substances, affecting climate and ecosystems not only locally but also globally (NEILL et al., 2006). Moreover, the transport of air pollutants resulting from forest fires has intensified the seasonal concentrations of gases and aerosols, entering in the biogeochemical cycles (BARKLEY et al., 2012). The deviation of river water characteristics and quality is closely linked to soil pollution, which is affected by the indiscriminate use of soils, contamination by fertilizers, and degradation by deforestation and biomass burning (LAL, 2004). These factors contribute to the loss of environmental quality and to health hazards that affect entire populations (BRIGGS, 2003). The aerosols and volatile substances emitted in the Amazon, mainly from forest biomass burning during the dry season, affect soil, atmosphere and streams (SHRESTHA et al., 2010). Many types of organic matter, elements and ions participate in the biogeochemical cycles, influencing ecosystems through water, carbon, nitrogen, oxygen and other cycles.

Few sites in the Amazon have been continuously monitored for soil, watershed and atmospheric parameters. Studies in the Amazon region are of utmost importance to assess the anthropogenic influences on biogeochemical cycles, the extents of which affect the planet as a whole. The Southwestern Amazon region is severely affected by air pollution, flooding, drought, sanitation and health problems. Thus, river water

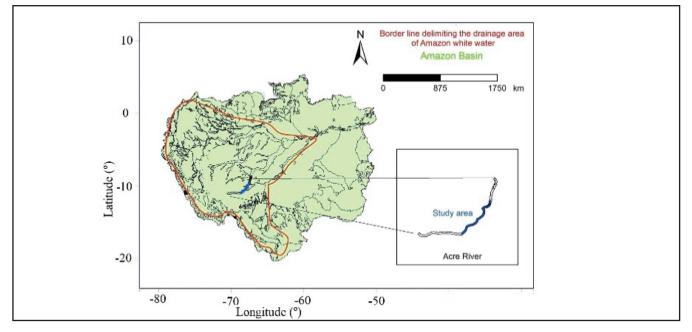


Figure 1 - The region bounded by the red line is characterized by white waters. The study area in the Acre River is depicted by a blue line between the coordinates 11°1.4'S; 68°44.0'W and 9°34.5'S; 67°31.9'W

quality monitoring require a permanent program for control and research. The objective of this study is to determine the chemical composition of the Acre River water as a component of the environmental cycles in Amazonia.

METHODS

The area bounded in red in Figure 1 corresponds to the Amazon white water region. The study area is represented with a blue color, highlighting the central part of the Acre River, between Brasileia and Porto Acre (11°1.4' S; 68°44.0' W; 9°34.5 S; 67°31.9' W), Acre State, in the Amazon Basin. The Acre River is the boundary between Peru, Bolivia and Brazil in Southwestern Amazonia. In this region, the wet season extends from October to April (seven months) and the dry season, from June to August (three months); May and September are months of transition between seasons (DUARTE, 2011). Due to common land use/land cover, geochemistry and climatology the study area acts as a single sampling point. The area (Acre River basin) is a nonindustrialized region where 400,000 inhabitants live in 35,000 km². Cattle ranching is the major contribution to the local economy. The native forest remains, even more in the western part of the basin. Watershed associated soils include cambisols, vertisols, luvisols, acrisols, ferralsols and plinthosols. X-ray diffractograms of sediments produced identical mineralogical patterns related to the presence of clay minerals and quartz (DUARTE & GIODA, 2014).

1-L plastic bottles were used to collect the water from below the surface of the river, far from the riverbanks and any visible sign of pollution or waste (WMO, 1994). The samples were collected from 2008 to 2014. The Acre River water was characterized in terms of pH, EC (Orion 3-Star, Thermo Electron Corporation, USA), turbidity (HI 93703, Hanna instruments, Italy) until 2014 and chemical composition until 2011.

The river water samples were filtered through 0.45- μ m cellulose acetate membrane (Macherey-Nagel, Germany) before analysis. To evaluate the level of membrane contaminants nanopure water was used. The carbon levels in the membranes represented less than 5% of the samples and were subtracted of them.

The dissolved organic carbon (DOC) content was determined using the TOC technique as described previously (GIODA et al., 2011). The equipment used was a TOC-V CPH/CPN (Shimadzu, Japan). Overall, samples are burnt in the combustion tube and all carbon compounds are converted to carbon dioxide (CO₂) which is measured in Non-Dispersive Infrared Gas Analyzer (NDIR). The amount of CO₂ measured is directly proportional to the amount of compounds present in the original sample. Standard solutions from 1.0 to 100.0 mg L⁻¹ were prepared from potassium hydrogen phthalate and sodium hydrogen carbonate/sodium carbonate anhydrous in MilliQ water.

The coefficient of variation of triplicate injections was less than 2%. The detection limits, based on three times the standard deviation of blanks, were 0.1 mg L^{-1} for inorganic carbon and 2.3 mg L⁻¹ for total carbon. Due to the low con-

centration of soluble trace elements in the water samples, the concentrations were determined by Inductive Coupled Plasma (ICP MS - Model Elan 6000 Perkin Elmer, USA).

Calibration solutions were prepared using standards with concentrations of 10,000 mg L⁻¹ (Perkin Elmer 29: Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Se, Cd and Pb), and monoelementary standards for Ti and Sb (100 mg L⁻¹). The calibration curve ranged from 5 to 50 mg L⁻¹ for the major species and from 0.1 to 1 mg L⁻¹ for the trace elements, and the internal standard calibration solution concentration was 400 mg L⁻¹ Rh 1% HNO₂. The ions were analyzed by ion chromatography (Metrohm, Germany) using a Metrosep A SUPPP 5-250 Metrohm column and a Metrosep A Supp 4/5 Guard column. The calibration solutions for Cl⁻, NO₃⁻ and SO₄²⁻ were prepared from standards of 1000 mg L⁻¹ (IsoSol[®], Brazil), traceable to SRM 3183, 3185 and 3181, respectively. The eluent was prepared with ultrapure water (Millipore, USA) and Na₂CO₂ and NaHCO₂ (Merck, Germany) at concentrations of 1 and 3.2 mmol L⁻¹, respectively. An external calibration was performed, and the statistical model was adapted to the linear regression by the method of least squares. The calibration curve contained concentrations ranging from 0.2 to 30 mg L⁻¹. The conductimetric detection was performed using a chemical suppression system. The regeneration of the suppressor system was performed with H₂SO₄ at 100 mmol L⁻¹ (Merck, Germany).

The ion detection limit was 10 mg L^{-1} for Cl⁻ and 50 mg L^{-1} for SO₄⁻²⁻ and NO₃⁻. A calibration check with external standards was performed to ensure an accuracy of 5%.

RESULTS AND DISCUSSION

The mean values of pH, EC and turbidity for Acre River water were 7.0, 64.9 μ S cm⁻¹ and 209 NTU, respectively (Table 1).

pH values range from 5.7 to 7.9. Approximately 60% of the pH had values between 6.5 and 7.3, and 30% above 7.3 (Figure 2). EC values range from 27.1 to 124.7 μ S cm⁻¹. Approximately 55% of the EC had values from 30.0 to 60.0 μ S cm⁻¹,

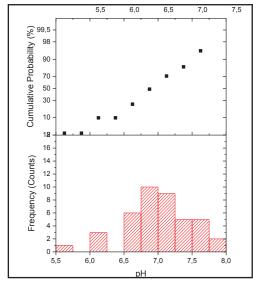


Figure 2 - Acre River pH distribution

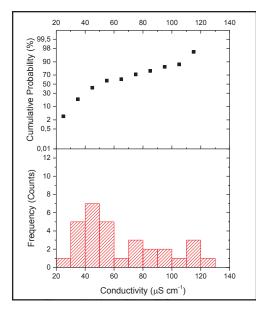


Figure 3 - Acre River EC distribution

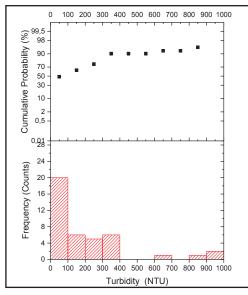


Figure 4 – Acre River turbidity distribution



Figure 5 – "Balseiros" in Acre River, Rio Branco city, February 2012

Sampling	Sea- son*	pН	EC (µS cm ⁻¹)	Turbidity (NTU)	
12/10/2008	W	6.8	110.3	17	
24/10/2008	W	7.9	95.0	21	
25/10/2008	W	7.2	100.1	10	
25/10/2008	W	7.3	113.2	9	
30/10/2008	W	6.9	116.5	38	
07/11/2008	W	7.7	96.2	16	
28/11/2008	W	6.7	57.7	389	
30/11/2008	W	6.8	55.1	91	
27/12/2008	W	6.7	52.3	195	
20/01/2009	W	6.6	39.1	133	
24/01/2009	W	7.1	53.3	869	
30/01/2009	W	6.5	37.3	389	
13/03/2009	W	6.8	42.0	80	
31/03/2009	W	6.7	38.1	300	
29/04/2009	W	5.7	46.8	250	
28/05/2009	Т	6.8	71.4	145	
06/06/2009	D	6.2	42.7	665	
25/07/2009	D	6.7	68.3	12	
15/08/2009	D	7.0	71.5	13	
15/08/2009	D	7.7	71.8	7	
12/09/2009	Т	7.1	124.7	36	
28/09/2009	Т	7.1	89.4	924	
10/10/2009	W	7.2	84.0	49	
22/12/2009	W	7.4	39.4	74	
23/12/2009	W	7.5	27.1	85	
23/02/2010	W	7.4	42.5	94	
20/04/2010	W	6.8	43.4	81	
20/05/2010	Т	7.1	52.1	49	
20/10/2010	W	6.2	38.1	290	
24/01/2011	W	7.7	42.6	322	
20/02/2011	W	7.6	49.2	329	
12/07/2014	D	6.2	-	65	
01/08/2014	D	6.9	-	130	
04/08/2014	D	7.1	-	88	
13/08/2014	D	7.4	-	327	
21/08/2014	D	7.4	-	209	
29/08/2014	D	7.9	-	140	
10/10/2014	W	6.8	-	234	
17/10/2014	W	6.8	-	194	
24/10/2014	W	6.8	-	231	
31/10/2014	W	7.2	-	981	
Mean		7.0	64.9	209	
Std. deviation		0.5	27.9	247	
*W D T - Wet Dry Transition					

Table 1 – pH, EC and turbidity for the Acre River

*W, D, T - Wet, Dry, Transition

and 42% above 60.0 μ S cm⁻¹ (Figure 3). Approximately 50 % of the turbidity had values less than 100 NTU and 90 % less than 400 NTU (Figure 4).

Overall, white water rivers in Amazon have muddy color, relatively high electric conductivity and neutral to alkaline pH (DUNCAN & FERNANDES, 2010). This characteristic is determined by the geology of the Andes Mountain and modulated by the environment (ecosystem, biodiversity and state of conservation). The influence of white water characteristic persists in the Amazon River even beyond Óbidos (EC, 2005).

The predominant water-soluble species were organic carbon compounds (41%), followed by Ca²⁺ (14%) and Si (14%). The high concentration of alkaline and alkaline earth metals (Ca²⁺, Mg²⁺, K⁺) and the lower concentration of acid ions (NO₃⁻, SO₄⁻²) explain the slightly acid to slightly basic pH of the Acre River water.

Average DOC value in Acre River was 26.5 mg L^{-1} , with minimum (maximum) value of 18.2 (40.8) mg L^{-1} . These values are in agreement with that of another study in the tropical region, where the average DOC concentration was higher than 20 mg L^{-1} (RICHEY, 1981).

The main sources of organic carbon in the Acre River are leaves, branches, trunks, roots (called "balseiros" by the Amazonian people, Figure 5) and sediments. Acre River is tributary of the Purus River where DOC represents more than 80% of the total organic carbon (MOREIRA-TURCQ et al., 2003; PATELA et al., 1999).

The Acre River water flows through several cities, contributing to the drinking water supply and receiving pollutants discharged without treatment. The observed concentration of chemical species in the Acre River water is presented in Table 2. The Brazilian Standards (mg L⁻¹) for water quality (CONAMA, 2005) are the following: Al < 0.1; Cd < 0.001; Total Cl⁻ < 250; Cr < 0.05; Cu < 0.009; Fe < 0.3; Hg < 0.0002; Mn < 0.1; Ni < 0.025; NO₃⁻ < 10.0; P < 0.020; Pb < 0.01; PO₄³⁻ < 0.025; S < 0.002; SO₄²⁻ < 250; V < 0.1; Zn < 0.18.

The concentrations of the most toxic metals (Hg < 0.001; Ni < 0.002; Pb < 0.01; V < 0.002; Cr < 0.0003; Cd < 0.001; Cu < 0.002; Zn < 0.001) in the Acre River water were below that considered in the Brazilian Standards as harmful to the environment and public health. Less toxic species, such as Al in dissolved forms, were frequently found in concentrations exciding five times the recommended values; it originates from clay mineral weathering (MARTINELLI et al., 1993; QUESA-DA et al., 2010).

Aluminum could cause damage to the central nervous system through prolonged exposure, so it must be removed from the water supply before it reaches households. Metals as Hg, Cr, Cd, Ni, V, Pb and Mn originate mainly from anthropogenic sources.

Evidences of seasonality occur for Na concentration that reaches maximum values for minimum river discharge. The seasonality is explained by the increased dilution of sediments during rainy season. Fitted curve has Reduced Chi Square = 0.85 and Adjusted R Square = 1 indicating that the sine model approximates observational data in acceptable agreement as can be seen from plot (Figure 6) and fitted curve (1):

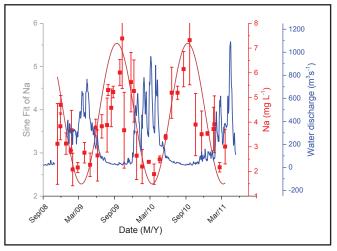


Figure 6 – Acre River seasonality of maximum Na concentration (red points) coinciding with minimum water discharge (blue line). Sine fit curve illustrates seasonality for the set of Na data points

$$Y = Y_o + A \sin \left(\Pi (X - X_c) \right) W$$
(1)

where: $Y_0 = 3.91$; $X_c = -579406.24$; A =1.63; W = 181.20; X, Y are Na concentration and time.

Such seasonality is not evident for other elements. According to Horbe et al. (2013), chemical heterogeneity is due to the contribution of soil, rocks and vegetation. Following Devol et al. (1995) there exist two types of seasonal patterns: (I) seasonal pattern with maxima of chemical concentration corresponding to minimum discharge.(e.g. Na in Figure 6) and (II) those that have cycles that are offset from the discharge hydrograph (e.g. Ca, K and others). Explanation for these facts is encountered in the relative content of discharge carrying waters originating primarily in Andean regions, and waters from tributaries and local inflow. All these waters contain high concentrations of suspended and dissolved matter.

Table 3 shows the correlation matrix resulting from non-linear fit of the chemical concentrations to water discharge. Input matrix is Table 2, excepting for species that exhibit ranges of low concentrations. 2-tailed test of significance was used with p-value 0.05. Calculations used the sine fit model and Marquardt iteration algorithm. Gray highlighted cells indicate statistically significant relationship with water discharge.

Table 3 – Correlation matrix from sine fit of concentration to water discharge. Correlation coefficients ≥ 0.3 are significant at 0.05 level

	SO ₄ ²⁻	Na	Al	S	WD*
SO ₄ ²⁻	1	0.82	-0.34	0.99	-0.42
Na	0.82	1	-0.46	0.81	-0.43
Al	-0.34	-0.46	1	-0.32	0.30
S	0.99	0.81	-0.32	1	-0.46
WD*	-0.42	-0.43	0.30	-0.46	1

*WD - Water discharge

Na, S and SO₄ are negatively correlated with discharge, so besides Na also S and SO₄ follow the (I) seasonal pattern with maxima of chemical concentration corresponding to minimum discharge. Even more, Al concentration is positively correlated with water discharge, displaying the same seasonal pattern as Na, but with the coincidence of respective maxima and minima.

The concentration of SO_4^{2-} varied between 1.3 and 11.5 mg L⁻¹, with an average value of 4.1 mg L⁻¹. These results are similar to those obtained from the Solimões and Purus rivers, whose values ranged from 3.3 to 15.8 mg L⁻¹, with an average of 5.8 mg L⁻¹ (QUEIROZ et al., 2009). In Amazon rivers, sulfur most likely came from igneous minerals and forest fires. Sulfur is an important nutrient for life and cell function. In the Acre River, nitrate concentration; soluble phosphorous was detected at low levels (P< 0.04 mg L⁻¹) explaining the lack of eutrophication in the river. High concentrations of sulfur, phosphorous and nitrogen compounds are an indicator of anthropogenic activity. However, a concentration lower than the Brazilian limit was found in this study, confirming little anthropogenic influence.

Among the dissolved metals, the predominant species were Fe and Al, representing 95% of the total metal content. The concentration of these species ranged from 0.10 to 3.10 mg L⁻¹.

The relationship between ion concentrations for some species is linear as suggested in Figure 7, where can be observed the scatter plots and fit lines for Mg and Ca versus DOC. Slope of each line denote the proportion of concentrations between Mg or Ca and DOC. The obtained ratios define values that can characterize the effect of weathering and disturbances determining the relative abundance of Mg, Ca and DOC in the river water.

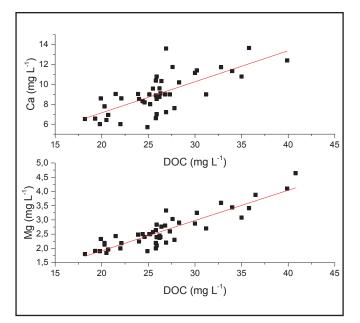


Figure 7 – Linear fit of Mg and Ca versus DOC. At the 0.05 level, the slopes are significantly different from zero. The line fit parameters are:

in parameters are.						
Intercept	Slope	Pearson's r				
-0.212	0.106	0.895				
0.914	0.312	0.728				
	-0.212	InterceptSlope-0.2120.106				

Although there are no limits for Ca_2^+ concentration in Standards, a desirable maximum for Ca_2^+ concentration should be 2 mg L⁻¹; the Acre River water have shown concentration exciding 10 mg L⁻¹. This fact leads to the classification of Acre River water as 'hard', indicating potential problems for industrial processes. The K⁺ concentration in the Acre River water was 7.6 mg L⁻¹. There are no Brazilian Standards for K⁺ concentrations. However, for example, Belgium Standard suggests a maximum limit of 12 mg L⁻¹ (BAERT et al., 1994), which is higher than the average found in this study.

Turbidity was the most affected parameter, most likely due to the large amount of sediment present in the river water. For water supply and sanitation, turbidity needs to be reduced as low as possible in treatment plants to achieve appropriate public health protection by means of the removal of particulate matter that could be associated with microbial pathogens.

CONCLUSIONS

In this work the chemical composition of the Acre River including dissolved organic carbon, and water properties like pH, electric conductivity and turbidity were established. The time variation of composition and properties revealed levels of chemical concentration, range of values and seasonality.

The Western Amazon and the Amazon as a whole link with geological history of the Andes and the immense sedimentary basin of the Amazon Rainforest. These natural sources control the presence of solutes in runoff and determine the principal characteristics of white water region. The weathering and erosion add to the marine and sand aerosols carried by wind and rain, and add to the anthropogenic disturbances from fertilizers, biomass burning and others. In this complex context the water quality of the Acre River, generally behave in accordance with Brazilian Standards.

Ionic concentrations of Na, S, SO_4 reach high values during the dry season, when the water discharge is low, meanwhile the maxima of Al concentration occur during the wet season. Aluminum is frequently found in concentrations exciding five times the recommended values

Turbidity values are very expressive, reaching hundreds of NTU, particularly during rainy season due to soil erosion. On the other hand, conventional water treatment plants are able to reduce turbidity to ensure the non-proliferation of pathogens in the water-supply system.

Little anthropogenic influence and low concentrations of Cr, Cu, Cd, Zn, Pb, Hg and Ni, were observed in the chemical composition of the Acre River. The most toxic elements present in the river water occur at low levels, below those established by Brazilian guidelines; therefore, this water is suitable for human use after appropriate treatment, except for Aluminum.

The chemical composition of the Acre River is dominated by the species Na, Mg, K, Ca, Si, S, SO₄ and organic matter from natural sources as clay minerals, tropical soils and forest vegetation. Concentration ratios of Mg and Ca to DOC have a linear, positive relationship, suggesting a common process is affecting them.

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Alejandro Fonseca Duarte: Idealizou a pesquisa teórica e experimental, realizou a inserção do tema no contexto bibliográfico atualizado, determinou a área de estudo, realizou as coletas e conservação de amostras de água, realizou as análises de pH, turbidez e condutividade elétrica, realizou as análises estatísticas, coordenou a discussão dos resultados e elaborou as seções do artigo.

Fábio Taira: Realizou as análises químicas de determinação de elementos e íons. Preparou as soluções standards para calibração e comparação de concentrações.

Adriana Gioda: Idealizou a metodologia para a realização das análises de composição química das amostras de água, realizou as análises de concentração de carbono orgânico total, concentração de elementos e concentração de íons. Realizou a preparação de soluções standards para calibração e comparação de concentrações. Participou na discussão dos resultados.