Revista Brasileira de Geografia Física

ISSN:1984-2295

Homepage: https://periodicos.ufpe.br/revistas/rbgfe

Study of Biogeochemistry and Characterization of Chemical Element Sources in River Waters of Small Watersheds: A Case Study of the Descobrimento National Park, Bahia, Brazil

Nathália Silva de Lima[1], Gean Carlos Ribeiro[2], Geovana Nascimento de Souza[3], Maikele Santos de Jesus[4], Joanna Maria da Cunha de Oliveira Santos Neves[5], Frederico Monteiro Neves[6].

[1]Postgraduate Program in Sciences and Sustainability at Universidade Federal do Sul da Bahia, Campus Paulo Freire, Centro de Formação em Desenvolvimento Territorial. E-mail: engambiental.nathalia@gmail.com, ORCID: https://orcid.org/0009-0006-3417-7041;
[2]Universidade Federal do Sul da Bahia, Campus Paulo Freire, Centro de Formação em Desenvolvimento Territorial. Fellow PIPCI - CNPq/2023 - AÇÕES AFIRMATIVAS, ORCID: https://orcid.org/0009-0001-8538-1273;
[3]Universidade Federal do Sul da Bahia, Campus Paulo Freire, Centro de Formação em Desenvolvimento Territorial. Fellow PIPCI - UFSB/2023, ORCID: https://orcid.org/0009-0006-8583-1920;
[4]Universidade Federal do Sul da Bahia, Campus Paulo Freire, Centro de Formação em Desenvolvimento Territorial. Fellow Fapesb-PROPPG/UFSB, ORCID: https://orcid.org/0009-0002-6211-5367;
[5]Doctor in Geosciences, Researcher and Professor at Universidade Federal do Sul da Bahia, Campus Paulo Freire, Centro de Formação em Desenvolvimento Territorial. E-mail: joanna.neves@ufsb.edu.br., ORCID: https://orcid.org/0000-0003-0453-5371.
[6]Doctor in Environment and Development, Researcher and Professor at Universidade Federal do Sul da Bahia, Campus Paulo Freire, Centro de Formação em Desenvolvimento Territorial. ORCID: https://orcid.org/0000-0002-8836-1307.

Artigo recebido em 12/09/2024 e aceito em 03/11/2024

A B S T R A C T

The southernmost region of Bahia is characterized by disorder in land use and occupation, responsible for environmental impacts on the region's sub-watersheds. Historical changes in land use have led to alterations in one of Brazil's main biomes, the Atlantic Forest, considered a biodiversity hotspot. In this context, the objective of this research was to evaluate the chemical composition of river waters in the region's sub-watersheds, identifying the sources of chemical elements and discussing the influences of the buffer zone. To achieve these objectives, water samples were collected at various sampling points in rivers within the Parque Nacional do Descobrimento. Sampling was conducted in the Cahy River, Japara River, Do Sul River, and Imbassuaba River. In the field, physico-chemical parameters were evaluated. In the laboratory, the following parameters were determined: alkalinity, TSS, chlorophyll-a, PO_4^{-3}, and SiO_2, F^-, Cl^-, SO_4^{-2}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{+2}, and Mg^{+2}. Data were statistically treated through factor analysis with factor extraction by principal components using the Statistica software. The results indicate that the chemical composition of river waters at different sampling points in the PND rivers is influenced by marine contribution, geological influence from the Barreiras formation, and anthropogenic influence due to the use of fertilizers from the PND's buffer zone. Monitoring the biogeochemistry of the main rivers crossing the PND provided fundamental data and information that will be used by the park management.
Keywords: watershed, monitoring, conservation unit.

Estudo da Biogeoquímica e Caracterização de Fontes de Elementos Químicos para Águas Fluviais de Pequenas Bacias Hidrográficas: Estudo de Caso do Parque Nacional do Descobrimento, Bahia, Brasil

R E S U M O

O extremo sul da Bahia é caracterizado pela desordem no uso e ocupação do solo, responsável por impactos ambientais nas sub-bacias hidrográficas da região. As mudanças históricas no uso do solo foram responsáveis pela alteração de um dos principais biomas brasileiros, a Mata Atlântica, considerado um *hotspot* de biodiversidade. Nesse sentido, o objetivo da pesquisa foi avaliar a composição química de águas fluviais de sub-bacias hidrográficas da região, identificando as fontes de elementos químicos e discutir as influências da zona de amortecimento. Considerando os objetivos propostos, foram coletadas amostras de águas em diferentes pontos de amostragem em rios do Parque Nacional do Descobrimento. As amostragens foram realizadas no Rio Cahy, Rio Japara, Rio do Sul e Rio Imbassuaba. No campo foram avaliados os parâmetros físico-químicos. No laboratório foram determinados os parâmetros alcalinidade, MPS, clorofila-a, PO_4^{-3} e SiO_2, F^-, Cl^-, SO_4^{-2}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{+2}, Mg^{+2}. Os dados foram estatisticamente tratados por meio de uma análise

fatorial com extração dos fatores por principais componentes utilizando o software Estatística. Os resultados indicam que a composição química das águas fluviais nos diferentes pontos de amostragem nos rios do PND é influenciada pela contribuição marinha, pela influência geológica da formação barreiras e antrópica devido ao uso de fertilizantes proveniente da zona de amortecimento do PND. O monitoramento da biogeoquímica fluvial nos principais rios que atravessam o PND aprovisionaram dados e informações fundamentais que serão utilizados pela gestão da unidade.
Palavras-chaves: bacia hidrográfica, monitoramento, unidade de conservação.

Introduction

Watersheds are environmental systems that can be compartmentalized into different biogeochemical domains according to the landscape characteristics in which these systems are embedded (Sioli, 1975; Oliveira et al., 2019). From this perspective, biogeochemistry studies the processes of mobilization, migration, transformation, and accumulation of chemical elements and/or molecules within landscapes. These processes are influenced by biotic, abiotic, and anthropogenic factors that coexist within a watershed area (Christophersen et al., 1994; Griffiths and Mulholland, 2021; Pei et al., 2024).

Several authors have recognized that the chemical composition of river waters is affected by processes occurring on the continental surface, such as weathering, nutrient cycling, surface runoff, and changes in land use (Berner and Berner, 2012; Pei et al., 2024). From this perspective, using environmental indicators such as the concentration of major dissolved elements, nutrients, and physicochemical parameters, it is possible to compartmentalize watersheds into distinct biogeochemical domains based on the processes controlling river water chemistry at different study points. In other words, through the chemical composition of river waters, it is possible to identify biogeochemical barriers, source areas and processes for elements, and anthropogenic interference in watersheds (Krusche et al., 2005; Costa et al., 2009; Figueiredo et al., 2014; Siefert and Santos, 2018; Pei et al., 2024).

Watersheds are environmental systems that can be compartmentalized into different biogeochemical domains according to the characteristics of the landscape in which the systems are inserted (Oliveira et al., 2019). From this perspective, biogeochemistry studies the processes of mobilization, migration, transformation and accumulation of chemical elements and/or molecules in landscapes. These processes are affected by biotic, abiotic and anthropogenic factors that coexist in a watershed (Griffiths and Mulholland, 2021).

Some authors have recognized that river chemical composition is affected by processes that occur on the continental surface, such as weathering, nutrient cycling, surface runoff and changes in land use in an area (Berner and Berner, 2012). From this perspective, using environmental indicators such as the concentration of major dissolved elements, nutrients and physicochemical parameters, it is possible to compartmentalize river basins into distinct biogeochemical domains, based on the processes controlling river water chemistry at the different points studied. In other words, through the chemical composition of river waters, it is possible to identify biogeochemical barriers, source areas and processes of elements, as well as to identify the anthropogenic interferences that occur in the watersheds (Krusche et al., 2005; Costa et al., 2009; Figueiredo et al., 2014; Siefert and Santos, 2018).

Despite the above, it is difficult to monitor river water quality in Brazil, often attributed to the scarcity of data and information available on environmental agency portals and the lack of access to data from private sources on the internet. In addition, problems such as the lack of funding to promote research aimed at assessing water quality in rivers and lakes contribute to a limited choice of study sites in various water resources in the country (Rocha, 2020).

The natural resources adjacent to the sub-watersheds within which the Descobrimento National Park is situated are exploited in various ways through extractivism, agricultural production, and fishing. Consequently, these resources are utilized in the vicinity of the park may pose threats to biodiversity and compromise the quality of water resources.

The buffer zone of the park is occupied by various rural properties where land use is diverse. Most of these properties utilize their areas for pasture, eucalyptus monoculture, and the cultivation of crops such as coffee and papaya, which are agricultural activities considered to have a high impact on the river channels that traverse the conservation unit. Additionally, other activities include fruit farming, mining, shrimp farming, and poultry farming (Pontes Junior et al., 2020).

The historical changes in land use in the region have been responsible for altering one of Brazil's primary biomes, the Atlantic Forest, and this historical context underscores the importance of conducting this research (Dean, 1996; Amorim and Oliveira, 2007). Although the data generated by this type of study alone cannot solve the environmental problems of the region, they provide essential information to develop a diagnosis of the water resources in the area, which is necessary for the implementation of natural resource management policies. The primary objective of this study is to evaluate the chemical composition of river waters in different rivers within the sub-watersheds located in the Descobrimento National Park, identifying the sources of chemical elements and the influences of the buffer zone of this conservation unit on the river waters.

This work aims to carry out a biogeochemical characterization of river waters at different sampling points within the areas of the Descobrimento National Park. Historically, land use and occupation in the region has occurred in a disorderly manner, causing a series of negative environmental impacts in the micro-watersheds of the Far South of Bahia (Almeida and Teixeira, 2010; Cerqueira Neto and Silva, 2014).

The natural resources adjacent to the sub-basins where the Descobrimento National Park is located are exploited in various ways through extractivism, agricultural production and fishing; consequently, the way in which these resources are used around the PND can represent a threat to biodiversity and compromise water resources.

The PND is under influence of the Jucuruçu river basin and adjacent watersheds. Geographically, the PND is situated in a region where several watercourses of limited length come together to form small river basins (MMA/ICMbio, 2014). The study area covers the watershed of the Jucuruçu River, which is in the Water Planning and Management Region III (RPGA III), and which is also made up of portions of the Itanhém and Peruípe River Basins - located from the border between Bahia and Minas Gerais to the Atlantic Ocean, where the mouth is located. These watersheds cover an area of 16,161 km^2 (INEMA, 2023).

As part of the Atlantic Forest biodiversity corridor, the Jucuruçu River basin is of great regional importance. Due to the occupation of the riverbanks and logging in the region, much of the riparian forest of the rivers and the Atlantic Forest has been removed, causing a huge impact on the landscape and intense silting of the river (Ferreira, 2018). From a regional perspective, the Jucuruçu, Japara Grande and Cahy rivers stand out, with the Jucuruçu being the largest among them (MMA/ICMBIO, 2014).

It can be inferred that, according to the fluvial hierarchy, the rivers in PND are first order, i.e. they are spring rivers with a low flow rate. Second-order rivers are formed from the confluence of two first-order channels. This makes the UC an area that takes on the role of protecting springs, which are responsible for water supply and drainage in the region (Lima et al., 2023). Its springs are found on the pre-littoral surfaces, which are significant elevations in the region's topography (MMA/ICMBIO, 2014).

The PND buffer zone (BZ) is occupied by several rural properties in which land use is varied. Most of these properties use their areas for grazing, eucalyptus forestry and plantations mainly of coffee and papaya, which are agricultural crops considered to have a high impact on the river channels that cross the PND. In addition to fruit farming, mining, shrimp farming and farms (Pontes Junior et al., 2020).

The historical changes in land use that have taken place in the region have been responsible for altering one of Brazil's main biomes, the Atlantic Forest, and this historical context justifies the importance of carrying out this research (Amorim and Oliveira, 2007). In isolation, the data generated in this type of work does not solve the region's environmental problems, but it does provide basic information for a diagnosis of the region's water resources, which is necessary for the implementation of natural resource management policies.

Our hypothesis is that the buffer zone has an impact on the fluvial biogeochemistry of the rivers that cross the PND. So, this study aims to perform a biogeochemical characterization of river waters at different sampling points within the domains of the Descobrimento National Park. Historically, land use and occupation in the region have been disordered, causing a series of negative environmental impacts on the micro-watersheds in the southernmost region of Bahia (Almeida and Teixeira, 2010; Cerqueira Neto and Silva, 2014; Pei et al., 2024).

Material and methods

Study Area - the Descobrimento National Park (PND) is a fully protected Conservation Unit (CU) established by a federal decree on April 20, 1999, initially encompassing an area of 21,129 hectares. Subsequently, on June 5, 2012, it was expanded by an additional 1,549 hectares, resulting in the current total area of 22,673.97 hectares. This park represents one of the last remnants of the Atlantic Forest biome in the southernmost region of Bahia and harbors immense biodiversity (MMA/ICMbio, 2014).

Among the benefits that the PND brings to the region, along with other surrounding UCs, are contributions to the microclimate, water balance, and conservation of the micro-watersheds. The predominant climate in the region is tropical humid or super-humid, with an average temperature above 18°C in the hottest month. January and February are considered the hottest months of the year, with temperatures ranging from 24 to 25°C. According to data from the National Institute of Meteorology (INMET), during the months this study was conducted (April to November) in 2023, the highest average temperatures were recorded in April, October, and November (25.61 °C; 25.75 °C; 27.2 °C), while the lowest average temperatures were recorded in May and June (22.53°C; 21.39°C) (INMET, 2023).

The CU is entirely located within the municipality of Prado in the southernmost region of the State of Bahia, between the coordinates 16°55' and 17°15' South latitude, and 39°25' and 40°10' West longitude. The park's area encompasses parts of the micro-watersheds of the Jucuruçu, Japara, Japara Grande, Ouro, Imbassuaba, Peixe, and Cahy rivers, with a notable presence of headwaters of tributaries to state rivers of regional significance, in addition to the *Só Não Vou* lagoon, located geographically at the center of the conservation unit and of great importance to the CU (MMA/ICMbio, 2014).

The topography, lithology, and soils of these areas contribute to making them essential sources of water resources in the region. The geology of the PND area is characterized by the presence of Precambrian rocks, including granitic, gneissic, schistose, and quartzitic lithotypes. However, these Precambrian lithotypes are not present within the current boundaries of the park. Tertiary Cenozoic rocks (Barreiras Group) form extensive plateaus along the Atlantic coast, interrupted near the coastline by cliffs. Lastly, Quaternary depositional formations occur in the surrounding area of the UC (MMA/ICMbio, 2014).

Water samples were collected from riverine locations within the conservation unit (CU) and at points situated in the buffer zone (BZ) of the conservation unit. Three sampling points were selected along the Japara River (identified as JP 01, JP 02, and JP 03), all located in the park's buffer zone. JP 01 is near the Nova Esperança site, JP 02 is at the bridge beside Marechal Rondon municipal school, and JP 03 is at the bridge towards Cumuruxatiba. One point on the Cahy River (RC) is in the park's buffer zone in front of the Bela Vista farm. Another point on the Do Sul River (RS) is located near the Alegria Nova Village within the Comexatibá Indigenous Land, a territory under dual protection with the Descobrimento National Park. Finally, a sampling point on the Imbassuaba River (RI) is entirely within the PND, at a location known as Só Não Vou lagoon (LSNV) (Figure 1).

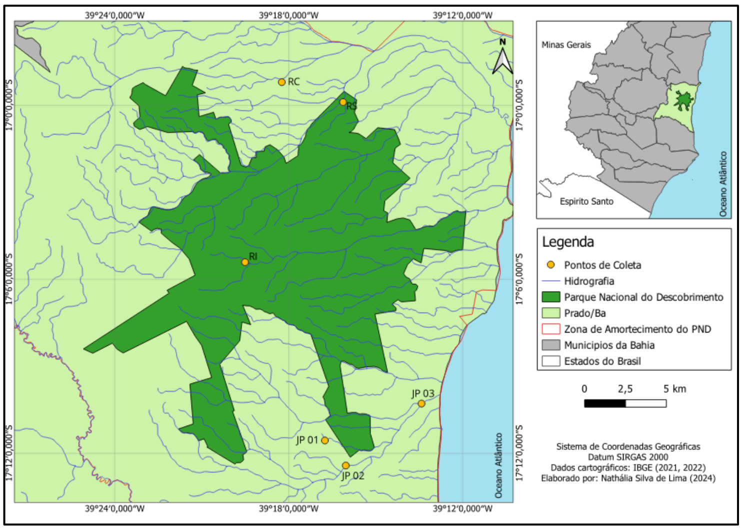

Figure 1. Map of the Descobrimento National Park, highlighting the hydrographic networks and the sampling points in this study. Japara River (JP 01, JP 02, JP 03); Cahy River (RC), Rio do Sul (RS) and Imbassuaba River (RI).

The sampling points were determined to enable the chemical characterization of river waters from the sub-watersheds within the PND (points RI and RS) and to identify the influences of the buffer zone on the chemical composition. This will be achieved through data monitored at the Japara and Cahy River points (JP 01, JP 02, JP 03, and RC). Table 1 presents the rivers where water samples were collected, along with the names and UTM coordinates of each point.

Table 1. Coordinates of the river water sampling points collected in this study.

Ponto	Rio	Coordenadas UTM	
		X	Y
JP1	Japara River	465363.16	8110422.50
JP2	Japara River	471587.34	8097433.14
JP3	Japara River	476249.32	8101403.23
RC	Cahy River	467650.36	8122011.33
RS	Do Sul River	471407.59	8120695.45
RI	Imbassuaba River	465363.21	8110391.77

Fonte: The authors, 2023.

Eight sampling campaigns were carried out during the year 2023, although seasonality is not so marked in the region, the collections took place from April/2023 to November/2023, since seasonality can affect the concentrations of physicochemical variables in rivers (Silva et al., 2008).

Following the procedures recommended by Brandão et al. (2011), at the sampling points the water was collected from the central portion of the river channel using a plastic bucket and packed in polypropylene bottles. The bottles were prepared in the laboratory by sanitizing them with a 2% (v/v) Detertec solution, a 2% (v/v) HCl solution and washing them with distilled water. A thermal box with ice was used to transport the samples to the laboratory so that they were properly preserved (Brandão et al., 2011).

The physicochemical parameters pH, electrical conductivity, temperature, redox potential and D.O. concentration was also measured in the field using a Hanna Instruments HL9829 multiparameter probe. The probe was previously calibrated with a calibration solution.

In the laboratory, suspended particulate matter (SPM) was determined using the gravimetric method adapted from the method proposed by Strickland and Parsons (1972). To determine the concentrations of SPM in the samples collected, the samples were vacuum filtered, and the glass fiber filters were prepared by drying them in an oven at a temperature of 60 °C for two hours.

Finally, the filtration process consisted of filtering approximately 250 ml of each water sample through cellulose acetate filters with a pore size of 0.45 µm. Filtering was carried out to fractionate the samples into a dissolved fraction and a particulate fraction. The filtered samples were placed in Falcon tubes and frozen, after which the concentrations of NO_3^-, NH_4, PO_4^{-3}, SiO_2, major cations and anions present in solution were determined.

The alkalinity of the water samples was also determined in the laboratory using the Gran method (1952). A volume of 50 ml of filtered water samples was added to a 100 ml beaker. This sample was stirred in a magnetic stirrer and the initial pH was measured. If the pH was higher than 5.75, a standardized solution of 0.05 M sulphuric acid (H_2SO_4) was added until the pH value reached 4.3.

The chemical analyses were performed to determine the PO_4^{-3} and SiO_2 concentrations were carried out in triplicate using the colorimetric method, using the U.V. visible spectrophotometry technique with the FEMTO CIRRUS 80 model spectrophotometer using reagents, wavelengths and specific calibration curves for each determination (Carmouze, 1994). The concentration of chlorophyll-a was determined according to Carmouze (1994), using a colorimetric method carried out in a U.V. visible spectrophotometer model FEMTO CIRRUS 80.

Another subsample was used to determine the major cations and anions in solution (F^-, Cl^-, SO_4^{-2}, NO_3^-, NO_2^-, NH_4^+, Na^+, K^+, Ca^{+2}, Mg^{+2}) using the ion chromatography (IC) technique in Metrohm equipment (Model 850 Professional IC coupled to a Model 858 Professional Sampler Processor automatic sampler), using ion exchange columns and a conductivity detector.

To analyze the factors controlling river hydrochemistry, a Piper (1994) diagram was constructed using Qualigraf software. The same software was used to calculate the hydrochemical ratios for the rivers studied in the PND. To understand the sources controlling the input of chemical elements into the river waters, a Gibbs diagram (1970) was drawn up using the Excel program with the calculated TDS concentrations and the calculated ratios between the Na^+ / (Na^+ + Ca^{+2}) concentrations. The data was statistically analyzed using a factor analysis with extraction of the factors by principal components using the software Statistic.

Finally, to enable the sub-basins to be compartmentalized, a cluster analysis or (Hierarchical Cluster Analysis) was carried out using the complete linkage method or farthest neighbor grouping technique considering the hydrochemical variables measured throughout this study at each of the sampling points, using NCSS 2024 Data Analysis software, the results were presented in the form of a dendrogram.

Results and discussion

The physicochemical parameters - pH, temperature, electrical conductivity, redox potential, dissolved oxygen concentration, alkalinity, and concentrations of suspended particulate matter and chlorophyll-a - for the sampling campaigns at the different collection points are presented in Table 2.

According to Fritzsons et al. (2009), elevated pH values (above 8.5) are typically found in areas with water bodies influenced by seawater, which consequently bring significant contributions of carbonates and bicarbonates, in regions where the water balance is negative, and in karst regions. The pH value in natural waters can vary between 6 and 8.5. Water bodies with high organic content exhibit lower pH values. The water from the Sul River point shows the presence of humic substances, evidenced by its brown-yellow coloration, characteristic of environments with high organic content. This explains why the Sul River has lower pH values compared to other sampling points over the months. Photosynthetic organisms consume and produce carbon dioxide (CO_2), which can cause pH variation, along with respiration or fermentation phenomena that produce weak acids (Nozaki et al., 2014).

June 2023 recorded the lowest temperatures among all the campaign months, with the Sul River showing the lowest temperature (20.41°C) compared to the other points. The highest temperatures were recorded in October and November 2023, with a maximum of 33.65 °C in the Cahy River in November 2023. It is worth noting the significant increase in temperature from June 2023 to October and November 2023. In watercourses, temperature variations occur; these variations are seasonal and follow the climatic changes throughout the year.

The Cahy River recorded the highest electrical conductivity values compared to the other sampling points, with maxima measured in May 2023 (144 $\mu S.cm^{-1}$) and June 2023 (133 $\mu S.cm^{-1}$). October and November 2023 stood out as the conductivity values varied significantly across all sampling points. In October 2023, elevated values were recorded at points JP 01 (226 $\mu S.cm^{-1}$), RC (179 $\mu S.cm^{-1}$), RS (131 $\mu S.cm^{-1}$), and JP 03 (126 $\mu S.cm^{-1}$), while lower values were observed at points RI and JP 02, with 70 and 63 $\mu S.cm^{-1}$, respectively. In November 2023, points JP 01 and RC exhibited a sharp decrease in electrical conductivity (48 $\mu S.cm^{-1}$ and 85 $\mu S.cm^{-1}$) compared to October 2023, whereas point RI showed a significant increase from the previous month (164 $\mu S.cm^{-1}$). Points JP 02, JP 03, and RS had similar electrical conductivity values for this month, being 137 $\mu S.cm^{-1}$, 129 $\mu S.cm^{-1}$, and 136 $\mu S.cm^{-1}$, respectively. According to Von Sperling (2007), natural waters have conductivity levels in the range of 10 to 100 $\mu S.cm^{-1}$, while river channels polluted by domestic or industrial effluents can reach up to 1000 $\mu S.cm^{-1}$.

Table 2: Physicochemical parameters - pH, temperature, electrical conductivity, redox potential, dissolved oxygen concentration, alkalinity, and concentrations of suspended particulate matter and chlorophyll-a.

	pH	Temperature (°C)	Electrical Conductivity (μS/cm)	Redox potential (mV)	Dissolved Oxygen (mg/L)	Total alkalinity (mg/L $CaCO_3$)	SPM (mg/L)	Chlorophyll a (mg/L)
RC April/23	6.17	25.76	68.00	50.8	4.86	11.33	0.0062	6.11
RC May/23	6.46	24.14	144.00	34.8	3.38	3.67	0.0040	10.31
RC June/23	6.43	22.29	133.00	40.0	7.23	12.00	0.0040	8.40
RC July/23	6.25	27.55	70.00	43.8	6.11	8.33	0.0095	6.11
RC September/23	6.16	29.88	81.00	47.1	6.24	4.67	0.0040	0.76
RC October/23	6.25	33.09	179.00	44.9	5.5	4.00	0.0058	7.60
RC November/23	6.15	33.65	85.00	45.8	6.14	4.00	0.0058	7.64
J1 April/23	5.5	29.92	49.00	90.0	6.42	6.00	0.008	9.93
J1 May/23	5.69	24.83	106.00	77.9	3.54	3.00	0.0022	9.16
J1 June/23	5.66	22.73	99.00	81.0	6.94	5.67	0.0022	9.16
J1 July/23	5.85	28.26	56.00	67.0	6.33	1.67	0.0095	10.31
J1 September/23	5.34	29.93	61.00	96.2	5.49	2.00	0.0072	2.29
J1 October/23	5.82	32.45	226.00	70.8	4.75	2.00	0.0498	4.58
J1 November/23	5.76	32.78	47.90	80.5	7.5	2.00	0.036	8.40
J2 April/23	6.14	25.20	69.00	55.6	7.32	6.00	0.0025	6.49
J2 May/23	6.03	23.59	114.00	66.9	3.66	3.00	0.0015	5.73
J2 June/23	6.21	20.84	109.00	48.3	7.18	5.67	0.0015	5.73
J2 July/23	6.10	26.51	57.00	58.1	7.00	2.67	0.0022	10.96
J2 September/23	5.94	28.32	60.00	59.3	8.31	2.00	0.0032	9.55
J2 October/23	6.07	30.80	63.00	56.7	6.14	2.00	0.0048	4.20
J2 November/23	6,00	31.84	137.00	57.9	7.40	2.00	0.0050	8.40
J3 April/23	5.65	26.48	57.00	79.8	5.42	4.67	0.0048	10.69
J3 May/23	5.68	23.39	112.00	81.0	4.64	3.00	0.0010	3.82
J3 June/23	6.07	21.35	106.00	63.3	7.00	5.00	0.0010	9.55
J3 July/23	5.74	26.9	56.00	64.9	6.08	3.33	0.0010	9.55
J3 September/23	5.76	28.96	73.00	70.5	7.16	2.00	0.0033	10.69
J3 October/23	5.90	31.03	126.00	67.2	5.65	2.00	0.0058	9.16
J3 November/23	5.94	35.57	129.00	60.0	6.70	2.00	0.0053	8.78
RS April/23	4.85	22.23	55.00	125.2	6.02	2.00	0.0015	13.77
RS May/23	4.98	22.55	105.00	121.4	3.97	0.90	0.0020	1.91
RS June/23	5.22	20.41	103.00	103.9	8.65	3.00	0.0013	5.73
RS July/23	5.29	26.52	50.00	93.9	7.05	1.00	0.0020	11.46
RS September/23	5.09	27.49	53.00	116.5	8.51	1.00	0.0008	4.20
RS October/23	5.34	30.23	131.00	102.8	6.04	1.00	0.0033	9.55
RS November/23	5.28	31.84	136.00	101.5	6.44	1.00	0.0025	6.11
RI April/23	5.30	25.24	52.00	97.8	8.74	4.00	0.0075	9.93
RI May/23	5.46	22.42	115.00	96.6	4.74	3.00	0.0025	7.26
RI June/23	5.53	21.6	109.00	90.0	6.37	4.67	0.0025	4.96
RI July/23	5.75	26.35	52.00	76.6	6.25	2.67	0.0005	13.37
RI September/23	5.45	28.83	71.00	72.3	5.73	1.33	0.0008	4.20
RI October/23	5.88	31.43	70.00	67.4	7.16	2.00	0.0022	6.49
RI November/23	6.50	33.20	164.00	22.4	6.22	1.33	0.0023	10.69

According to by Lima et al. (2023), the electrical conductivity values for all sampling points in May 2022 were lower compared to 2023. In 2022, this parameter ranged between 42.8 and 57.4 $\mu S.cm^{-1}$, while in 2023, the variation was between 105 and 144 $\mu S.cm^{-1}$. It is important to highlight that the Cahy River, in both years of the study and for the month of May, recorded the highest electrical conductivity value compared to the other sampling points.

Redox potential is related to the solubility of metals and the availability of nutrients for aquatic organisms. This parameter allows us to detect changes in the oxidation state of many ions or nutrients. Positive redox potential values indicate oxidizing conditions, while negative values indicate electron availability, or reducing conditions (Tundisi, 2008; Sousa et al., 2021). The results for redox potential at the six sampling points over the months of collection were positive, indicating oxidizing conditions in all the rivers analyzed in this study.

The significant decrease in dissolved oxygen (DO) values can be attributed to intense biological activity, primarily due to the high organic load in the receiving body of water from agricultural effluents. Another important factor to consider is that a low DO concentration at a sampling point does not necessarily indicate proximity to the pollution source; generally, the pollution occurs at an upstream location from the collection site (Nozaki, 2014; Lima et al., 2023).

The results of this study showed low alkalinity values throughout all months. Waters with low alkalinity (< 24 mg/L $CaCO_3$) have a low buffering capacity, making them more susceptible to pH changes (Chapman and Kimstach, 1992; Fritzsons et al., 2009; Brasil, 2014).

Considering what occurred at point JP 01 in October 2023, several authors attribute the accumulation of suspended particulate matter (SPM) to various factors, such as flow rate, sedimentation, siltation, floods, and tidal variations during spring and neap tides, as well as the accumulation of nutrients in the river during its hydrographic course (Mayerle et al., 2015). SPM is primarily composed of particles originating from the weathering of rocks present in the watershed, along with organic particles (Nascimento et al., 2008), which may explain the consistency in the values recorded over the sampling periods. Nascimento et al. (2008) also cites anthropogenic intervention as one of the main factors in the regulation of SPM, arising from aspects such as deforestation of riverbanks, agricultural land management practices, and dam construction within the basin.

Chlorophyll-a concentrations in the waters of the Cahy, do Sul, Japara, and Imbassuaba Rivers at all sampling points were < 1.0 µg/L, except at point RC in October 2023 (0.76 µg/L) and > 14.0 µg/L. Seixas et al. (2019) found chlorophyll-a concentrations < 1.0 µg/L and 1.2 µg/L, and the authors indicated that chlorophyll-a concentration is directly related to the amount of microalgae present in the water body. Therefore, this result suggests that the river water analyzed in their study has a low quantity of algae (Esteves, 1998; Seixas et al., 2019).

Cordeiro et al. (2021) found in their study average chlorophyll-a concentrations ranging from 4.80 µg/L to 7.70 µg/L, however, during the dry season, this concentration was higher than in other periods, averaging 8.52 µg/L. Thus, they observed that seasonality influenced this variable, and along with the dry season, the authors attributed these concentrations to factors such as reduced river depth and anthropogenic influences such as laundry activities, input of domestic and industrial effluents, and release of nutrients used in small-scale agriculture, which contributed to nutrient input, enabling phytoplankton development and consequently increasing chlorophyll-a concentrations. They also related this to decreased sediment washing from the river and exposure of water to sunlight due to removal of riparian vegetation. Similar results were found by Oliveira et al. (2014) and Aguiar et al. (2014) in their studies.

To characterize the chemical composition of river waters and determine the influence of controlling sources on the biogeochemistry of the Cahy, Japara, Imbassuaba, and do Sul rivers, Table 3 presents the concentrations of ions F^-, Cl^-, SO_4^{-2}, NO_3^-, NO_2^-, NH_4^+, Na^+, K^+, Ca^{+2}, Mg^{+2}, and TDS. Additionally, the Piper and Gibbs diagrams were used as a tool for interpreting the predominant chemical processes in river waters.

The Piper diagram was constructed based on the ionic concentrations of the Cahy, Japara, do Sul, and Imbassuaba river waters during the sampling campaigns from April/2023 to November/2023. According to the diagram in Figure 2, when observing the cations triangle, the waters were classified as mixed and sodic, whereas in the anion's triangle, the classification of the waters was entirely chloride-dominated. Analyzing the results through the overall classification, the predominant waters in this study were classified as sulfated or chlorinated calcium or magnesium waters and sulfated or chlorinated sodic waters.

From a hydrochemical perspective, sulfated waters may result from the dissolution of minerals containing sulfate in their mineralogical composition or may indicate the influence of fertilizer use (which contains sulfates). Chlorinated waters originate from the dissolution of minerals such as halite and indicate the influence of marine sediments as occurs in the region of this study. Calcic waters are influenced by the dissolution processes of rocks rich in limestone and dolomite. Magnesian waters are related to the dissolution process of minerals such as dolomite, magnesium, and serpentinite. And sodic waters derive from the dissolution of minerals such as sodic feldspars or by ion exchange from clays. They are characteristic waters of environments influenced by saline intrusion (Brasil, 1945; Nascimento et al., 2008; Sequinel et al., 2011).

The Piper diagram presented in the study by Damasceno et al. (2021), which investigated surface waters of the Gajiru and Mudo rivers located in Rio Grande do Norte, northeastern Brazil, classified the waters mainly as sodic chlorides, a behavior like that found in this study. The authors attributed this characteristic to the interaction of the waters with the different rocks existing in the study area, with part of the sample group being influenced by the Barreiras Formation.

A study conducted by Barros et al. (2011) in the Centro Sul region of the state of Ceará, Oliveira Filho et al. (2018) in the Barreiras and Pirabas aquifers in Belém/PA obtained results like those of this study. According to the overall classification of the Piper diagram, the waters were classified as sulfated or sodic chlorides.

Sequinel et al. (2011) found in their study that in the rural area near where agricultural activities were being carried out, the concentrations of calcium and magnesium in surface waters were the highest of the entire study. The authors observed that these, among other ions, may be present in the fertilizers used in agricultural activities. The results of this study corroborate with the classification of calcic and magnesian chlorinated waters found in the rivers of the PND. The authors also highlight that the ions are not completely absorbed by plants and much of them are deposited in the soil and end up being leached by rainwater, thus being detected in the surface waters of rivers adjacent to agricultural areas.

Table 3. Ionic concentrations in river water samples.

	SiO_3 (mg/L)	PO_4^{-3} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)	Cl^- (mg/L)	SO_4^{-2} (mg/L)	F^- (mg/L)
RC April/23	0.389	0.266	8.10	2.53	3.02	2.71	9.96	1.60	0.187
RC May/23	0.378	0.304	8.83	2,00	3.65	3.39	12.16	1.30	0.172
RC June/23	0.352	0.117	7.75	2.57	2.83	2.89	10.47	1.30	0.002
RC July/23	0.363	0.155	7.75	2.57	2.83	2.89	10.47	1.30	0.193
RC September/23	0.307	0.453	9.50	2.28	3.71	3.58	12.31	1.11	0.223
RC October/23	0.333	0.322	9.75	2.03	3.33	3.54	12.24	1.31	0.185
RC November/23	0.183	0.322	8.63	1.65	3.64	3.48	12.23	1.31	0.191
J1 April/23	0.255	0.509	5.60	0.58	3.87	1.55	8.13	1.31	0.152
J1 May/23	0.318	0.527	5.46	0.45	2.95	1.54	8.40	1.06	0.002
J1 June/23	0.202	0.36	6.38	0.55	3.7	1.88	9.87	1.25	0.002
J1 July/23	0.330	0.378	6.74	0.73	2.96	1.84	10.81	1.45	0.16
J1 September/23	0.315	0.527	6.75	0.7	3.38	2.14	11.04	1.43	0.174
J1 October/23	0.251	0.751	4.81	0.54	2.79	1.76	7.76	0.92	0.145
J1 November/23	0.322	0.322	6.58	0.64	3.04	2.09	13.64	1.29	0.158
J2 April/23	0.288	0.602	5.43	0.22	0.9	1.07	8.57	1.25	0.145
J2 May/23	0.326	0.322	7.05	0.24	1.41	1.13	10.98	1.58	0.002
J2 June/23	0.303	0.266	7.39	0.34	1.15	1.43	11.70	1.66	0.184
J2 July/23	0.217	0.676	6.65	0.39	0.91	1.34	10.53	1.74	0.146
J2 September/23	0.315	0.471	7.01	0.27	1,00	1.41	10.85	1.55	0.161
J2 October/23	0.270	0.341	7.73	0.81	1.02	1.27	11.35	2.56	0.236
J2 November/23	0.255	0.378	6.88	0.58	1.22	1.46	11.47	1.43	0.21
J3 April/23	0.300	0.397	6.93	0.77	2.27	1.61	9.90	1.74	0.164
J3 May/23	0.352	0.173	7.20	0.54	2.24	1.84	10.93	1.88	0.002
J3 June/23	0.315	0.173	6.64	0.42	1.97	1.8	10.75	1.84	0.002
J3 July/23	0.288	0.248	6.13	0.73	1.77	1.76	9.61	2.02	0.002
J3 September/23	0.300	0.341	7.28	0.4	1.66	1.78	11.04	1.87	0.002
J3 October/23	0.270	0.043	7.32	0.55	2.13	1.87	11.10	1.70	0.171
J3 November/23	0.232	0.229	7.40	0.51	1.91	1.78	11.10	1.53	0.002
RS April/23	0.300	0.190	7.85	0.76	2.56	1.99	11.08	1.45	0.156
RS May/23	0.236	0.078	8.15	0.71	2.54	2.15	11.92	1.58	0.002
RS June/23	0.187	0.173	7.81	0.72	2.56	2.26	12.05	1.65	0.002
RS July/23	0.251	0.155	7.98	0.77	2.12	1.93	11.56	1.81	0.002
RS September/23	0.165	0.115	8.20	0.27	2.55	2.43	11.83	1.52	0.172
RS October/23	0.236	0.397	8.30	0.68	2.43	2.5	12.30	1.56	0.164
RS November/23	0.307	0.136	7.97	0.66	2.42	2.4	15.60	1.86	0.184
RI April/23	0.228	0.08	7.14	0.87	3.42	2.22	10.44	1.57	0.169
RI May/23	0.262	0.099	7.19	0.54	1.51	1.66	10.07	1.76	0.002
RI June/23	0.146	0.004	8.15	0.59	1.86	1.94	11.77	2.02	0.002
RI July/23	0.206	0.058	7.96	0.85	2.03	1.99	11.42	2.20	0.151
RI September/23	0.300	0.039	8.79	0.82	2.2	1.8	12.72	1.84	0.002
RI October/23	0.326	0.043	12.67	0.88	2.45	2.99	19.67	2.58	0.179
RI November/23	0.345	0.043	9.14	0.87	2.5	2.55	15.71	1.74	0.204

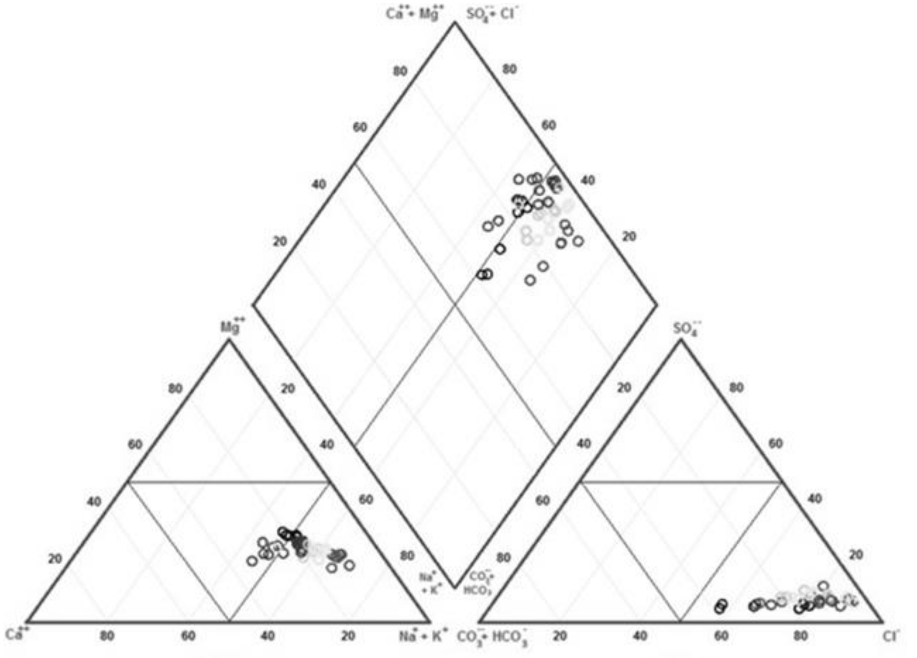

Figure 2. Piper diagram with the classification of the waters of the Japara, Imbassuaba, Cahy and Sul rivers, according to ionic concentration.

The Gibbs diagram takes into consideration that the chemical composition of water is mainly controlled by processes such as atmospheric precipitation, interaction with rocks through weathering, and evaporation/crystallization. Given these factors for its construction, the Gibbs diagram is an important tool in biogeochemistry to understand the chemical evolution of natural waters and the processes that control chemical composition (Marandi and Shand, 2018). Based on the values of total dissolved solids and the ratio $Na^{+}/(Na^{+}+Ca^{+2})$, Figure 3 shows how the points RC, JP 01, JP 02, JP 03, RS, and RI are distributed. All samples were found to be fully inserted in the lithological dominance region, indicating that the rivers of the PND present a dominance of lithological influence regarding the ionic composition present in the samples of river waters.

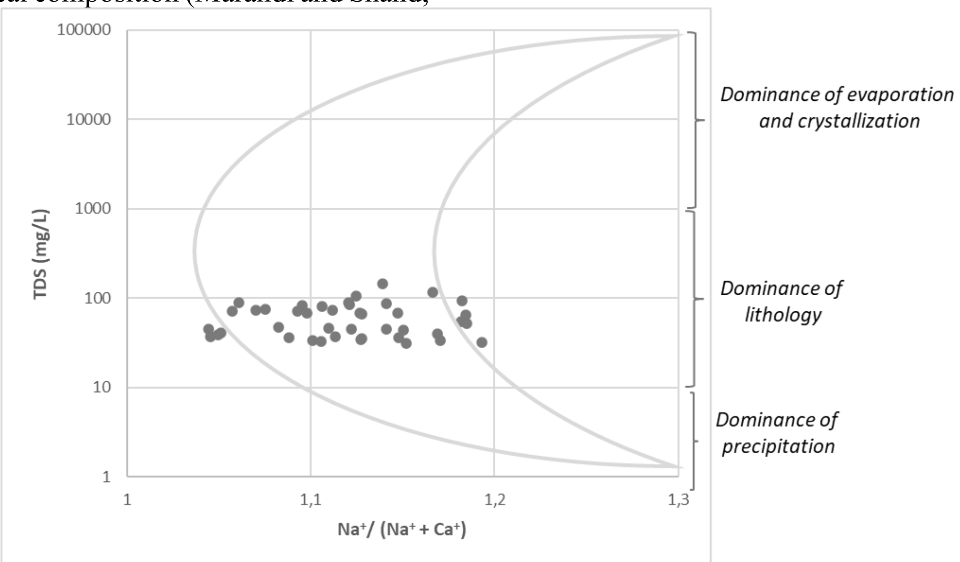

Figure 3. Distribution of samples from points RC, JP 01, JP 02, JP 03, RS and RI in the Gibbs diagram. Source:

A study conducted by Silva et al. (2021) found results like those of this study for the Poxim-Açu River, located in the Sergipe River basin. The water samples from this river were situated in the dominance of precipitation and lithology; however, the authors observed a clear evolution towards lithological dominance. Marandi and Shand (2018) explain this evolution towards weathering dominance; according to these authors, the interaction with rocks becomes the most important process and usually occurs relatively quickly, with the ionic dominance of the water shifting to Ca^{2+} and HCO_3^-.

Queiroz et al. (2012), in a study of the fluvial waters of the Paquequer River basin, showed that weathering is the main natural source of elements for the rivers in the studied basin. This fact corroborates with what was found in this study. The explanation provided by the author is that silica is the most abundant element in the chemical composition of this river; however, sodium also presents high concentrations in these waters. Part of the Na^+ found in this study originates from natural sources (soil/rock and precipitation), mainly from the weathering of sodium feldspars. The other portion originates from anthropogenic sources and possibly from pasture areas.

The data were statistically analyzed through a factorial analysis with factor extraction by principal components using Statistical Software. This statistical analysis allows for a better correlation structure among the variables analyzed in the present study. Figure 4 shows the graphical representation of the 5 factors over the months of the study at the six sampling points.

From the factorial analysis, 5 factors were extracted explaining together 82.67% of the observed variation in the data (Table 4, Table 5, Figure 4).

Table 4. Correlation values established for the 5 factors extracted from the factor analysis.

	F1	F2	F3	F4	F5
pH (LOG)	-0.060807	**-0.89737**	0.044445	-0.224234	-0.118138
Ca^{+2} (LOG)	-0.035475	-0.166545	**0.916256**	0.116881	0.027408
Mg^{+2} (LOG)	0.441334	0.079843	**0.852954**	0.070299	0.06996
Na^+ (LOG)	**0.879558**	0.090429	0.326529	-0.143513	-0.004901
K^+ (LOG)	0.240681	0.396225	**0.795323**	-0.056563	0.030721
Cl^- (LOG)	**0.940588**	-0.062645	0.071563	0.003652	0.112744
SO_4^{-2} (LOG)	0.340727	-0.177707	**-0.477662**	**0.5399**	-0.317212
Alkalinity (LOG)	**-0.418884**	**0.710983**	0.289367	-0.187027	-0.242038
NO_3^- (LOG)	0.009901	-0.08398	-0.038414	**0.95715**	0.002183
PO_4^{-3} (LOG)	**-0.602382**	0.133869	-0.062949	0.014425	**0.656898**
F^- (LOG)	0.166313	0.106067	0.109731	0.048321	**0.787527**
Si^+ (LOG)	0.045083	**0.609807**	0.040123	0.053231	0.370692

Table 5. General summary of the factor analysis with the scores, eigenvalues and percentage of each of the 5 factors extracted that explain the variation in the data in this study.

		Eigenvalue	% Total variance
F1	Na-Cl -Mg(+)/PO_4-HCO_3 (-)	3.39	28.23
F2	HCO_3-Si (+)/pH (-)	2.72	22.69
F3	Ca-Mg-K (+)/SO_4 (-)	1.48	12.30
F4	NO3-SO4 (+)	1.33	11.10
F5	F-PO4 (+)	1.00	8.35
		9.92	**82.67**

Factor 1 is positively related to the concentrations of Na^+, Cl^-, Mg^{+2}, and negatively related to the concentrations of PO_4^{-3} and HCO_3^-, accounting for 28.23% of the observed variation in the data. The positive correlation between the concentrations of Na^+, Cl^-, Mg^{+2} suggests the marine influence (marine spray) from the marine sedimentary deposits of the Barreiras Geological Formation in the region. The negative correlations between the concentrations of PO_4^{-3} and HCO_3^- suggest the influence of agricultural additives in the buffer zone of the PND and may be influencing the chemical composition of these waters, as well as the liming process of the soil in this buffer zone.

Factor 2 is positively related to the concentrations of Si and HCO_3^- and negatively related to pH values, explaining 22.69% of the observed variation. This relationship can be justified by the weathering process that occurs in the watershed area.

Factor 3 is positively related to the concentration of Ca^{+2}, Mg^{+2}, and K^+ and negatively related to the concentration of SO_4^{-2}, explaining 12.30% of the observed variation in the samples. This positive correlation can be explained by the weathering action and the influence of the mineralogy that occurs in the Barreiras Formation. The influence of sulfate can be explained by the marine influence of the sedimentary deposits of the Barreiras Formation and by the marine influence (marine spray) in the study area, considering that we are studying a small coastal watershed. The SO_4^{-3} present in the river waters also suggests that there may be an influence of agricultural additives in the buffer zone of the PND.

Factor 4 explains about 11% of the observed variance in the samples and is positively related to the concentrations of NO_3^- and SO_4^-, reinforcing the hypothesis of the influence of agricultural additives in river waters. This factor also shows a negative correlation with pH, Na^+, K^+, and HCO_3^-, which can be explained by the dilution process caused by rainfall.

Factor 5 explains about 10% of the observed variance in the data and is positively related to the concentrations of PO_4^{-3} and F^-. This positive correlation can be explained by the influence of weathering activity and the mineralogical composition of the Barreiras Formation, which occurs in the study area.

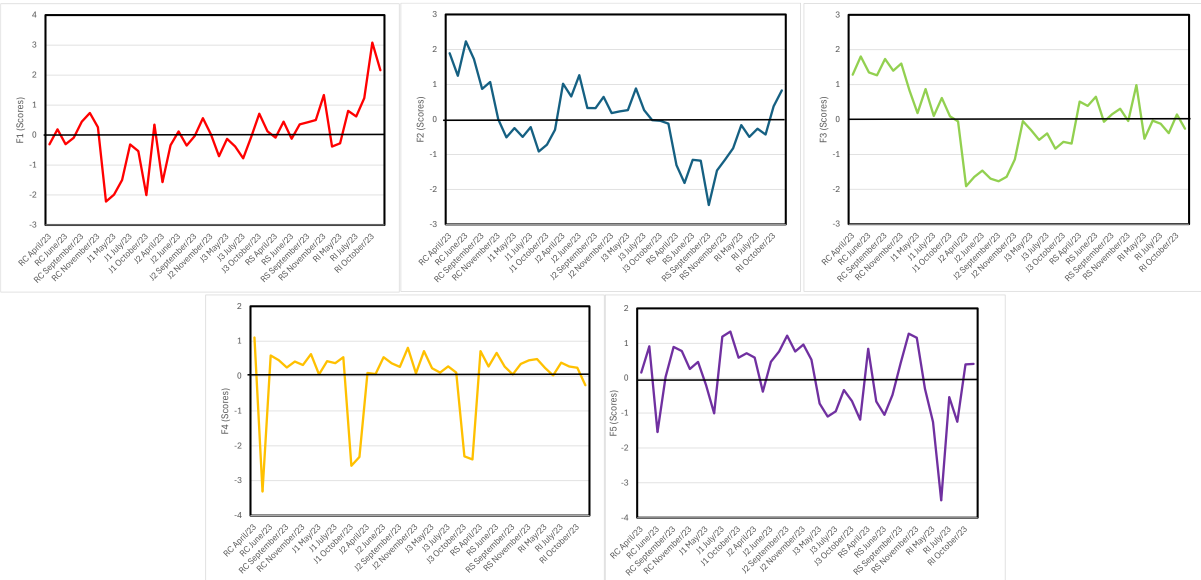

Figure 4. Graphical summary of the factor analysis with the scores and the 5 factors that explain the variation between the sampling points.

Considering the results from the statistical analysis, it can be inferred that three main factors influence the river waters analyzed in the PND, namely: marine influence, geological influence, and influence of the Barreiras Group, in addition to negative influences from the use of agricultural additives in the buffer zone of the UC. Due to the various activities carried out in the buffer zone of the PND, this unit presents a complex context, being surrounded by vast areas of pastures for cattle breeding and forestry, activities that are very common in the southernmost region of Bahia and have fostered intense deforestation and rural exodus. There are also plantations of coffee, cocoa, pepper, papaya, and passion fruit, as well as mining activities, shrimp farming, and poultry farms.

Regarding the marine influence, Silva (2021), studying salinization in northeastern Brazil, shows Na^+/Cl^- ratios like those of seawater. This fact is explained by the author due to the influence of marine aerosols (marine spray) incorporated into atmospheric water vapor during the evaporation of seawater. This occurs when clouds enter the continent and precipitation causes these components to encounter the surface, reaching surface waters. The region studied by the author is about 40 km from the coast, marine spray particles can travel long distances from the source region, reaching about 250 km from the coast, and even lighter droplets, which move more easily, can move more than 500 km away from the coast. Therefore, as justified by the authors and evidenced in this study, the increase in the levels of some elements responsible for the increase in salinity and their respective correlation with seawater may also be partly related to the influence of marine aerosols.

Regarding dilution by rainwater, as shown in Figure 3, the year 2023 experienced a period of rainfall scarcity, with the maximum precipitation of the year occurring in April (144.44 mm), in the other months there was no recorded precipitation, or it was below 60 mm. According to our data, the composition of river waters could be strongly influenced by atmospheric precipitation. Rain, in addition to washing the basin lands, also provides the dilution of ions present in the river channel. Chemical composition is of utmost importance in determining environmental factors and can be classified based on the dissolved elements found.

Hierarchical cluster analysis is a multivariate analysis method used to divide samples into classes or groups, which is why it was used to help compartmentalize the sub-basins in this study. Samples are grouped because they are similar in terms of the variables studied (Longhi, 1997; Ferreira et al., 2020). The dendrogram is the most widely used representation in cluster analysis, as in addition to the sequence of groupings, it shows the similarity with which the groups are formed. The dendogram is made up of arcs that represent the grouping between the clusters, the distance of each arc represents the similarity that resulted in the grouping to which the ends are connected. Figure 5 shows the dendogram for the hydrochemical variables analyzed throughout the study.

The graph shows that the sampling points were divided into two groups, one formed by the Rios Japara 02 and 03 (Rows 3 and 4) and the other formed by the Rios do Sul and Imbassuaba (Rows 5 and 6). These last two were also found to have the lowest similarities in relation to the other sampling points. This lower similarity is due to the points being located within the conservation unit, suffering less interference from the CU's buffer zone. The highest similarities were found in Rio Cahy (Rows 1) and Rio Japara 01 (Rows 2).

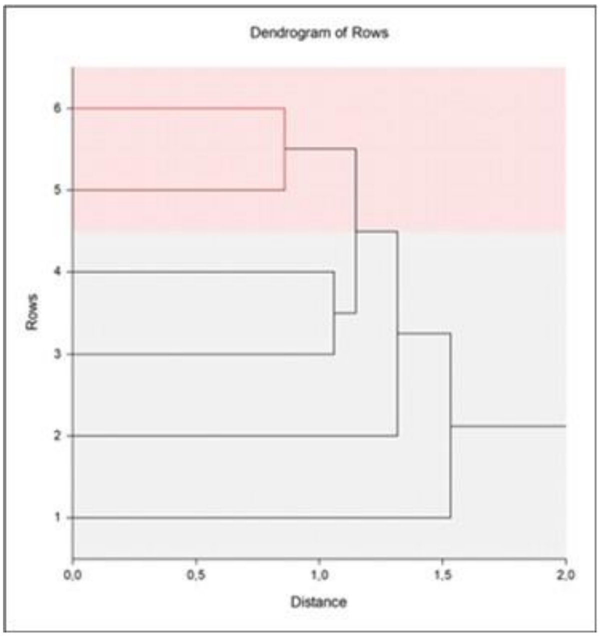

Figure 5. Dendogram obtained from the hydrochemical variables evaluated at the six monitoring points, namely (1) Rio Cahy, (2) Rio Japara 01, (3) Rio Japara 02, (4) Rio Japara 03, (5) Rio do Sul and (6) Rio Imbassuaba.

According to the data, it can be inferred that the rivers in the PND differ from one another, with points RI and RS, located in the conservation unit, being less chemically influenced by the surrounding activities than points JP 01, 02, 03 and RC, which are in the buffer zone. The cluster analysis reinforced what was pointed out throughout the study, that the AZ influences the chemical composition of the CU's river waters. Works such as those by Malfatti et al. (2018) also used cluster analysis to compartmentalize river basins and sub-basins and identify similarities between sampling points.

We can therefore compartmentalize the sub-basins of the Descobrimento National Park into: Area 1 - Imbassuaba river (RI) and Do Sul river (RS), influenced by rock weathering processes, marine influence, dilution by rainwater; Area 2 - Rio Japara 01 and 02 (RJ 01 and RJ 02); Area 3 - Rio Japara 01 (JP 01); Area 4 – Cahy River (RC), the last three areas being influenced by soil liming and the use of pesticides in the buffer zone, in addition to the factors mentioned.

Conclusions

Based on the data analyzed in this research, it was possible to verify that the pH values are not high, ranging from 4.85 to 6.46, typical of water with a high organic content. Point RS presents the lowest values throughout the year due to specific characteristics of its water, namely, humic substances and a brownish-yellow coloration. Despite being high, electrical conductivity is within the standards for natural waters and did not reach the range of values for river channels polluted by domestic or industrial effluents. On the other hand, the redox potential values found over the six-month collection period indicate that the water has oxidizing conditions.

The alkalinity parameter showed low values throughout the months, which consequently have a low buffering capacity, making pH susceptible to change. In October, there was a significant accumulation of suspended particulate matter, but for the other months, a constancy in the values was recorded. Based on the data analyzed, it can be said that the sections in the Japara River, Imbassuaba River, Cahy River, and Do Sul River are within the parameters established by current legislation within the ranges established by some authors.

The graphical result of the Piper diagram for the study area indicates that the waters of the PND rivers are sulfated or chlorinated with calcium or magnesium and sulfated or chlorinated with sodium. From a hydrochemical perspective, these results indicate marine influence, geological influence from the Barreiras Formation, and signs of fertilizer use in the studied waters. From the results obtained in the Gibbs diagram, it was possible to infer that the rivers of the PND present a dominance of lithological influence regarding the ionic composition present in the samples of river waters, confirming the results presented in the Piper diagram.

Finally, from the statistical analysis, 5 factors were extracted that together explained 82.67% of the observed variation in the data. It can be concluded that the variations can be justified by factors such as the influence of the Barreiras Geological Formation, which occurs in the region, and the influence of agricultural additives in the buffer zone (BZ) of the PND, as well as the soil liming process in this BZ. Throughout the environmental monitoring period carried out during the year 2023 to analyze fluvial biogeochemistry in the main rivers crossing the PND, it was possible to provide unprecedented and fundamental data and information that will be used to assist in the management of the conservation unit.

Finally, the dendrogram shows that the sub-basins analyzed have similarities, however, points RI and RS located within the UC are the ones that show the least similarity in chemical composition when compared to the other points, being less impacted by the BZ of the unit. It can be concluded that the sub-basins studied were divided into four areas, with area 1 containing points RI and RS with similar chemical composition and influenced by rock weathering processes, marine influence and dilution by rainwater. Areas 2, 3 and 4 include points RJ 01, 02, 03 and RC, which are also influenced by the factors in area 1 and by liming the soil and the use of agricultural additives in the BZ.

Throughout the period of environmental monitoring carried out to analyze fluvial biogeochemistry in the main rivers that cross the PND, it was possible to provide unprecedented and fundamental data and information that will be used to help manage the conservation unit.

Acknowledgement

The authors would like to thank the Universidade Federal do Sul da Bahia (UFSB) for its institutional support, which helped with the logistics of the fieldwork. We would also like to thank ICMbio and the management of the Descobrimento National Park for their support throughout the research. The authors would like to thank Prof. Dr. Emmanoel Vieira da Silva Filho, from the Universidade Federal Fluminense (UFF), Department of Geochemistry, for carrying out the ion chromatography analyses. The authors would like to thank the CNPq and Fapesb funding agencies for the scientific initiation grants awarded by PROPPG Notice No. 01/2023 - (PIPCI/PIBITI-UFSB) and for the financial support through PROPPG/UFSB 07/2023 (Process No. 23746.006629/2023-40).

References

Aguiar, C.P.O., Peleja, J.R.P., Sousa, K.N.S., 2014. Qualidade da água em microbacias hidrográficas com agricultura nos municípios de Santarém e Belterra, Pará. Revista Árvore 38, 983 –992. https://doi.org/10.1590/S0100-67622014000600003

Almeida, T.M., Teixeira, A.C.O., 2010. Inter-relações entre fatores físicos e socioeconômicos na dinâmica de uso da terra no Extremo Sul da Bahia. Revista Geográfica Acadêmica 4, 64 -72.

Amorim, R.R., Oliveira, R.C., 2007. Degradação ambiental e novas territorialidades no Extremo Sul da Bahia. Revista Caminhos de Geografia 8, 18 –37. https://doi.org/10.14393/RCG82215514

Barros, A.A.F., Gomes, G.E., Lima, A.E.O., Palácio, H.A.Q., Lima, C.A., 2011. Avaliação da qualidade da água para irrigação na região Centro Sul no estado do Ceará. Revista Brasileira de Engenharia Agrícola e Ambiental 15, 588 –593. https://doi.org/10.1590/S1415-43662011000600008

Berner, E.K., Berner, R.A., 2012. Global Environment: Water, Air and Geochemical Cycles – Second Edition. Princetown University Press. ISBN 140084276X, 9781400842766.

Bonelli, N., Deegan, L., Neill, C., Thomas, S., Aufdenkampe, A.K., Richey, J.E., 2005. Efeitos das Mudanças do Uso Da Terra na Biogeoquímicas dos Corpos D'água da Bacia do Rio Ji-Paraná, Rondônia. Acta Amazonica 35, 197- 205. htt ps://doi.org/10.1590/S0044-59672005000200009.

Branco, S.M. Hidrologia aplicada à engenharia sanitária. 3.ed. São Paulo: CETESB/ ASCETESB, 1986. 616 p.

Brandão, C.J., Botelho, M.J.C., Sato, M.I.Z., Lamparelli, M.C., 2011. Guia nacional de coleta e preservação de amostras: água, sedimento, comunidades aquáticas e efluentes líquidas. São Paulo: CETESB; Brasília: ANA.

Brasil, Lei nº 7.841, de 08 de agosto de 1945. Institui o código de águas minerais. Rio de Janeiro, 08 de agosto de 1945.

Brasil, Ministério da Saúde. 2014 Fundação Nacional de Saúde. Manual de controle da qualidade da água para técnicos que trabalham em ETAS, Brasília: Funasa, 112 p.

Carmouze, J.P. O metabolismo de Ecossistemas Aquáticos: Fundamentos teóricos, métodos de estudo e análises químicas. São Paulo. Edgard Blücher, 253p. 1994.

Cerqueira Neto, S.P.G., Silva, L.T., 2014. O que é o Extremo Sul da Bahia no século XXI em tempos de globalização? Geografares, 23-37. https://doi.org/10.7147/GEO18.8407

Chapman, D., Kimstack, V., 1992. The selection of water quality variables In: CHAPMAN, D (Ed.). Water quality assessment. London: Chapman & Hall Ltd., 51-117.

Christophersen, N., Clair, T.A., Driscoll, C.T., Jeffries, D.S., Neal, C., Semking, R.G., 1994. Hydrochemical Studies In: Moldan, B. and Cerny, J., Biogeochemistry of Small Catchments: A Tool of or Environmental Research. SCOPE 51. John Wiley & Sons Ltd (Eds), 448pp.

Cordeiro, C.A.M., Sampaio, D.S., Holanda, F.C.A.F., 2021. Engenharia de pesca: aspectos teóricos e práticos. In: Moura, H.T.G.S, Sousa, J.A., Veras, G,C., Nunes, Z.M.P. (Ed.) Influência sazonal e antrópica na qualidade da água em ecossistemas aquáticos da Amazônia oriental: qualidade de água em ecossistemas amazônicos. V. 2. 1.ed. Guarujá, SP: Editora Científica Digital.

Costa, F.F., Lima, W.N., Dias, J.C., 2009. Avaliação Hidrogeoquimica em Áreas Selecionadas na Bacia Hidrográfica do Rio Maracanã (Nordeste do Pará). Holos Environment 9, 167- 182. https://doi.org/10.14295/holos.v9i2.1581

Damasceno, M.B., Souza, R.F., Diniz Filho, J.B., Castro, V.L.L., 2021. Caracterização hidroquímica de águas superficiais dos rios Guajiru e do Mudo, Bacia Hidrográfica do rio Doce, RN, Nordeste do Brasil. Pesquisas em Geociências 48, 1-22. https://doi.org/10.22456/1807-9806.102566

Dean, W., 1996. A ferro e fogo: A história e a devastação da Mata Atlântica brasileira. São Paulo: Companhia das letras, 484 p.

Esteves, F.A., 1998. Fundamentos de limnologia. 2ª Ed. – Rio de Janeiro: Interciência, 226 p.

Ferreira, R.R.M., Paim, F.A.P., Rodrigues, V. G.S., Castro, G.S.A.2020. Análise de cluster não supervisionado em R: agrupamento hierárquico. Campinas, São Paulo: EMBRAPA, 2020.

Figueiredo, J.A., Noriega, C.D., Oliveira, E.M.C., Neto, R.R., Barroso, G.F., Filho, M.A., 2014. Avaliação biogeoquímica de águas fluviais com ênfase no comportamento dos compostos de nitrogênio e fósforo total para diagnoses provenientes do sistema aquático Bacia do Rio Doce, no Espírito Santo. Geochimica Brasiliensis 28, 215-226. DOI:10.5327/Z0102-9800201400020009

Fritzsons, E., Mantovani, L.E., Neto, A.C., Hindi, E.C., 2009. A influência das atividades mineradoras na alteração do pH e da alcalinidade em águas fluviais: o exemplo do Rio Capivari, região do carste paranaense. Engenharia Sanitária Ambiental 14, 381-390. https://doi.org/10.1590/S1413-41522009000300012

Gibbs, R.J., 1970. Mechanisms controlling world water chemistry. Science 170, 1088–1090.

Gran, G., 1952. Determination of equivalent point in potentiometric titration. Analyst 77, 661-671.

Griffiths, N., Mulholland, P.J., 2021. Long-term hydrological, biogeochemical, and clim atological data from Walker Branch Watershe d, East Tennessee, USA. Hydrological Proces ses. DOI: https://doi.org/10.1002/hyp.14110.

INMET. Instituto Nacional de Meteorologia, 2023 . Mapa de estações meteorologicas-Estação automática de Itamaraju/Ba. Disponível em: https://mapas.inmet.gov.br/. Acesso em: 01/05/2024.

Krusche, A.V., Ballester, M.V.R., Victoria, R.L., Bernardes, M.C., Leite, N.K., Hanada, L., Victoria, D.C., Toledo, A.M., Ometto, J.P., Moreira, M.Z., Gomes, B.M., Bolson, M.A., Neto, S.G., Bonelli, N., Deegan, L., Neill, C., Thomas, S., Aufdenkampe, A.K., Richey, J.E., 2005. Efeitos das Mudanças do Uso Da Terra na Biogeoquímicas dos Corpos D'água da Bacia do Rio Ji-Paraná, Rondônia. Acta Amazonica 35, 197- 205. DOI: https://doi.org/10.1590/S0044- 59672005000200009

Lima, N.S., Fukuda, J.C., Neves, F.M., Neves, J.M.C.O.S., 2023. Estudo da Biogeoquímica Fluvial nos Domínio do Parque Nacional do Descobrimento, Extremo Sul da Bahia. Revista Brasileira de Geografia Física 16, 1552 – 1564. https://doi.org/10.26848/rbgf.v16.3.p1552-1564

Longhi, S. J. 1997. Agrupamento e análise fitossociológica de comunidades florestais na sub-bacia hidrográfica do Rio Passo Fundo-RS. Tese (Doutorado em Ciências Florestais), 215p. Universidade Federal do Paraná. Curitiba.

Malfatti, M.G.L., Cardoso, A.O., Hamburger, D.S. 2018. Identificação de regiões pluviométricas homogêneas na bacia hidrográfica do Rio Paraná. Revista de Geociências, São Paulo, v. 37, n. 2, p. 409-421.https://doi.org/10.5016/geociencias.v37i2.11564

Marandi, A., Shand, P., 2018. Groundwater chemistry and the Gibbs Diagram. Applied Geochemistry 7, 209 – 212. http://dx.doi.org/10.1016/j.apgeochem.2018.07.009

Mayerle, R., Narayanan, R., Etri, T., Wahab, A.K.A., 2015. A case study of sediment transport in the Paranaguá Estuarine Complex. Ocean Engineering 106, 161-174. https://doi.org/10.1016/j.oceaneng.2015.06.025

M/ICMBIO. Plano de Manejo Parque Nacional do Descobrimento. Brasília: Moderna, 2014. v. 2. Disponível em: https://www.icmbio.gov.br/portal/images/stories/docs planos de manejo/parna_descobrimento_pm_v1.pdf. Acesso em: 10 fev.

Nascimento, S.A.M., Barbosa, J.S.F., Cruz, M.J.M., Lima, C.M., 2008. Hidrogeoquímica e índice de saturação dos minerais no sistema aquífero do Alto Cristalino de Salvador, Bahia. Revista Brasileira de Geociências 39, 230 – 237. http://dx.doi.org/10.25249/0375-7536.2009392230237

Nozaki, C.T., Marcondes, M.A., Lopes, F.A., Santos, K.F., Larizzatti, P.S.C., 2014. Comportamento temporal de oxigênio dissolvido e pH nos rios e córregos urbanos. Atas de Saúde Ambiental – ASA 2, 29-44.

Oliveira, E.A., Pires, R.S., Oliveira, R.S., Furtado, V., Herrmann, H.J., Andrade, J.S., 2019. A universal approach for drainage basins. Scientific Reports 9, 1-10. https://doi.org/10.1038/s41598-019-46165-0.

Oliveira Filho, O.B.Q., Toro, M.A.G., Silva, W.C.M., 2018. Caracterização hidrogeoquímica dos sistemas aquíferos barreiras e pirabas da região metropolitana de Belém (RMB) e investigação de possíveis misturas entre as águas. Cadernos De Geociências 14, 8–23.

Oliveira, P.C.R., Nogueira, M.G., Sartori, L.P., 2014. Differential environmental impacts on small and medium size rivers from center of São Paulo state, Brazil, and regional management perspectives. Acta Limnologia Brasiliensia 26, 404 – 419. https://doi.org/10.1590/S2179-975X2014000400008

Pei, W., Xu, O., Lei, Q.; Du, X., Luo, J., Qiu, W., An, M., Zhang, T., Liu, H., 2024. Interactive impact of landscape composition and configuration on river water quality under different spatial and seasonal scales. Science of The Total Environment, 950, 175027, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2024.175027.

Piper, A.M., 1994. A graphic procedure in the geochemical interpretation of water-analyses. Eos Trans. Am. Geophys. Union 25, 914–928. https://doi.org/10.1029/TR025i006p00914

Pontes Júnior, E., Fernandes, G.W., Almeida Neto, P.P., 2020. Fatores a serem observados na criação de Áreas Protegidas: o caso do Parque Nacional do Descobrimento (Prado/BA). Sociedade & Natureza 32, 1-16. DOI: 10.14393/SN-v32-2020-39010

Queiroz, L. A. V.; Silveira, C. S.; De Mello, W., Alvim, R. B., Vieira, M.D., 2012. Hidrogeoquímica e poluição das águas fluviais da bacia do Rio Paquequer, Teresópolis (RJ). Geociências (UNESP. Impresso), v. 31, p. 606-621.

Seixas, M.A.C, Gonçalves, J.L., Gonçalves, G.A., 2019. Programa de monitoramento da qualidade das águas superficiais, comunidades aquáticas e hidrosedimentológico. Biolaqua ambiental [online]. Disponível em: https://www.elera.com/arquivo/novo/Meio%20Ambiente/PCH%20Verde%204A%20-%20Relat%C3%B3rio%20dos%20Programas%20Ambientais%202019_I.pdf. Acesso em: maio de 2024.

Sequinel, R., Arrúa, M.E.P., Costa, W., 2011. Um levantamento das concentrações dos íons NO_3^-, PO_4^{3-}, K^+, Ca^{2+} E Mg^{2+} presentes nas águas do Rio Verde e sua correlação com as atividades humanas existentes na área. Revista Publicatio – Ciências Exatas e da Terra, Ciências Agrárias e Engenharias 17, 29 – 37. DOI: 10.5212/Publ.Exatas.v.17i1.0003

Siefert, C.A.C, Santos, I., 2018. Dinâmica do Carbono Orgânico e Processos Hidrológicos na Escala da Bacia Hidrográfica: Uma Revisão. Revista Brasileira de Geomorfologia 19, 3-16. DOI: https://doi.org/10.20502/rbg.v19i1.1248.

Sioli, H., 1975. Tropical River as expressions of their terrestrial environments. In:Tropical Ecologycal Systems Trends in Terrestrial and aquatic research. Golley, F.B.& Medina, E., (Eds). NY, Springer-Verlag. Ecological studies, 275-288.

Silva, A.E.P., Angelis, C.F., Machado, L.A.T., Waichaman, A.V., 2008. Influência da precipitação na qualidade da água do Rio Purus. Acta Amazônica 38, 733 – 742. https://doi.org/10.1590/S0044-59672008000400017

Silva, R.R.M., Monteiro, A.S.C., Alves, J.P.H., 2021. Origem da água do reservatório do POXIM: uma visão hidrogeoquímica. In: Oliveira, R.L.(Ed.) Recursos Hídricos: Gestão, planejamento e técnicas em pesquisa. 1.ed. Editora científica digital 1, 1-280.

Sousa, M.J.A., Gonçalves, M.F., Oliveira, J.D., Lopes, C.K.S., 2021. Índice de qualidade da água da sub-bacia do Riacho Cacau, Portal da Amazônia Imperatriz – MA. Research, Society and Development 10, 1-18. DOI: http://dx.doi.org/10.33448/rsd-v10i2.12631

Strickland, J.D.H.; Parsons, T.R., 1972. A Practical Handbook of Seawater Analysis. 2nd edition. Ottawa, Canada, Fisheries Research Board of Canada, 1-310.

Tundisi, J.G., 2008. Limnologia, São Paulo: Oficina de Textos, 1-632.

Von Sperling, M., 2007. Estudos de modelagem da qualidade da água de rios. UFMG, 1-452.