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Intervening Factors in the Groundwater Salinization Process, Cachoeira River Basin, Northeastern Brazil

Fatores Intervenientes no Processo de Salinização das Águas Subterrâneas, Bacia Hidrográfica do Rio Cachoeira, Nordeste do Brasil

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Abstract

Hydrogeochemical diagrams and multivariate statistics were applied herein to identify the factors that potentially influence the salinity of water in the crystalline aquifer of the Cachoeira River Basin region, located in the southern portion of the State of Bahia. Data from the hydrogeological database of the Companhia de Engenharia Hídrica e de Saneamento da Bahia (CERB) were applied. The groundwater was predominantly classified as calcium-bicarbonate, with salinity levels ranging from fresh to brackish. The cation that prevails in the region is Ca^{2+}, while carbonate and bicarbonate are the dominant anions. Factor analysis enabled the determination of two factors that explain approximately 93% of the total variance of the data. Hierarchical cluster analysis resulted in five distinct groups based on dissolved ion concentrations. This study indicates that the natural mechanisms that control the chemical composition of groundwater are mainly related to the weathering of rocks and evaporative processes, with the most significant parameters related to the variability of water salinity being Ca^{2+}, Mg^{2+}, K^+, Fe (total), and Cl^-.

Keywords: Crystalline aquifer; Hydrogeochemistry; Multivariate statistics

Resumo

Diagramas hidrogeoquímicos e estatística multivariada foram aplicados com o objetivo de identificar os fatores que potencialmente influenciam na salinidade das águas no aquífero cristalino da região que engloba a bacia hidrográfica do rio Cachoeira, situado na porção sul do Estado da Bahia. Os dados utilizados são provenientes do banco de dados hidrogeológicos da Companhia de Engenharia Hídrica e de Saneamento da Bahia (CERB). As águas subterrâneas foram classificadas predominantemente como cálcica-bicarbonatada com salinidade variando entre doce e salobra. O cátion que prevalece na região é o Ca^{2+}, enquanto o carbonato e bicarbonato correspondem aos ânions dominantes. Com a análise fatorial foi possível reconhecer dois fatores que explicam, aproximadamente 93% da variância total dos dados. A análise de agrupamentos hierárquicos resultou em 5 grupos distintos baseados nas concentrações dos íons dissolvidos. Este estudo indica que os mecanismos naturais que controlam a composição química das águas subterrâneas estão relacionados, principalmente, com o intemperismo das rochas associadas a contribuições da evaporação, e os parâmetros mais significativos na variabilidade da salinidade das águas são o Ca^{2+}, Mg^{2+}, K^+, Fe (total), Cl^-.

Palavras-chave: Aquífero cristalino; Hidrogeoquímica; Estatística multivariada

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1 Introduction

The chemical composition of groundwater is influenced by several factors such as the rock type, water residence time in the aquifer, mineral dissolution rate, and geochemical processes that occur along the flow (Appelo & Postma 2005). Many studies relate the water–rock interactions to the chemical composition of the groundwater, as the components define its quality. In this context, Gomes and Franca (2019) state that the studying the groundwater chemistry can provide information on anthropogenic interference and dissolution/precipitation processes. Water salinization, a frequent problem in northeastern Brazil, can affect freshwater reservoirs, and poses a risk for human health and to many natural systems (Alves et al. 2021). The literature (Fontes et al. 2015; Guo et al. 2018; Jia et al. 2020) highlights that salinization occurs as a function of climatic conditions, reservoir age, rock solubility, marine aerosol deposition, etc.

Studies carried out in the Cachoeira River Basin (CRB) indicate that, owing to the level of salinity, the waters only have a limited usability. Paula, Rego and Santos (2008), through hydrogeochemical studies, observed that the geology and water deficits are the main factors that determine salinity levels in the Salgado River Basin, a tributary of the Cachoeira River. Figueiredo (2005) stated that there is a medium to high potential for the risk of salinization of soils in the Cachoeira River Basin when the water is used for irrigation, mainly in the sub-basin region of the Colônia River. In this region, urban water supply occurs through superficial catchment points along dam reservoirs (Cardoso et al. 2020; Sousa, Soares & Santana 2018), while according to information provided in the well description sheets, rural areas and industrial centers use tubular wells. The Agência Nacional de Águas e Saneamento Básico (ANA) published a report that recommended the adoption of new water sources in the region and adaptation of the existing system (Agência Nacional de Águas e Saneamento Básico 2010), considering that in terms of water availability, the CRB presents significant spatial and temporal variations in flows owing to rainfall levels.

The CRB's groundwater use has been limited because of the occurrence of saline water in some of its sections, and according to Engelbrecht et al. (2019), owing to the lack of studies on the CRB, there are no technical guidelines for the planning and management of surface and underground water resources, with uncertainties persisting as to the volume of water that can be exploited in a sustainable manner. However, it is believed that these waters constitute a relevant resource, mainly in dry periods, because despite having a medium hydrogeological potential, they are very important, considering that they cover a large area (Secretaria de Estado de Planejamento e Avaliação 1999).

Hence, the objective of the present study is to identify the groundwater salinization factors in the Cachoeira River Basin, Bahia (Brazil) through the integration of multivariate statistical and hydrogeochemical studies. This can help define the variables that result in salinization, benefiting the qualitative management of waters and enabling the maximization of the integrated use of the region's water resources.

2 Study Area

The CRB, located in the northeastern Brazil, has an area of approximately 4,500 km^2, and covers 10 municipalities (Firmino Alves, Santa Cruz da Vitória, Floresta Azul, Ibicaraí, Jussari, Itapé, Itororó, Itaju do Colônia, Itabuna, and Ilhéus) with approximately 600,000 inhabitants. The main watercourses that compose the CRB are the Colônia, Salgado, and Cachoeira rivers. The study area represents an important socio-ecological system for southern Bahia, as it contains medium and small locations with rural characteristics that are undergoing progressive urban and industrial growth. Agricultural activity consists of the shaded cultivation of cocoa in the Atlantic Forest areas and extensive cattle ranching in the Itabuna–Itapetinga Depression (Paula, Silva & Souza 2012).

Located in the eastern portion of the São Francisco Craton, the area is part of the geological domain of the Itabuna–Salvador–Curaçá Belt that formed during the Paleoproterozoic as a result of the collision between the Gavião, Jequié, and Serrinha blocks. Currently, this region is completely eroded in the central portion, with an exposed crystalline basement of high-grade metamorphic rocks (Vlach & Lama 2002). The Itabuna Belt consists of granulitic rocks with predominant tonalitic, trondhjemitic and gabric compositions. Kinzigitic gneisses, quartzites, iron formations, manganese formations, and a barite outcrop in tectonic intercalations of a tectonic nature also exist (Barbosa & Dominguez 1996). The mineralogical composition of the main lithologies of the Itabuna Belt was provided by Barbosa et al. (2003).

Due to regional geological conditions, the hydrogeological domain of crystalline rocks constitutes a fissure aquifer in the basin area. Hydrogeologically, these rocks function as reservoirs that have secondary permeability, with water circulation occurring through fractures and open and interconnected joints. The aquifer's recharge mostly occurs from the infiltration of meteoric waters (Secretaria de Estado de Planejamento e Avaliação 1999). Previous studies have revealed a considerable hydrogeochemical versatility in the composition of groundwater in the BHRC area (Secretaria de Estado de Planejamento e Avaliação 1999; IBGE 2013; Teramoto et al. 2018). These studies identified the presence of bicarbonate (sodium, mixed, calcium), sodium (mixed), chlorinated (mixed), and sulfated (mixed) facies in the granulitic rocks. Notably, the granulitic rocks of the Itabuna Belt are predominant in the area and have important hydrogeological potential. In other lithologies, only bicarbonate (sodium and calcium) facies have been classified.

In the study area, three distinct climatic domains can be identified according to the Koppen classification: humid tropical climate (Af), monsoon climate (Am), and tropical climate with dry winter season (Aw), with an average annual precipitation of 800 mm. The water deficit presents considerable variations from the upper course of the basin (highest levels) towards the coast.

The predominant soil classes in the area include haploid chernossol, eutrophic red–yellow argisol, dystrophic red–yellow argisol, dystrophic red–yellow latosol, dystrophic yellow latosol, and hydromorphic spodosol. The main chemical attributes of soils are available from Nacif (2000), whose studies have indicated the presence of vermiculite and smectite clays in chernosol, and kaolinite in argisols and yellow latosols, while in the red–yellow latosol, there is the presence of gibbsite. X-ray diffractometry performed on the chernosol silt fraction (B horizons) has revealed the presence of plagioclases, nepheline, biotite and quartz.

3 Materials and Methods

The present study was developed from the compilation of 19 groundwater samples from a crystalline aquifer provided by the Companhia de Engenharia Hídrica e de Saneamento da Bahia (CERB) distributed at the CRB. The Resolution of the Conselho Nacional do Meio Ambiente (CONAMA) No. 357 of March 17, 2005 (Conselho Nacional do Meio Ambiente 2005), which provides guidelines for the classification of water bodies adopts definitions for the classification of fresh, brackish, and saline waters. This classification was used herein, using Qualigraf software version 1.17 (Mobus 2014), to calculate salinity using total dissolved solids (TDS) levels. The ionic classification of waters was performed using the Piper's triangular diagram (Piper 1944).

The origin of the chemical composition of groundwater was identified using the method proposed by Gibbs (1970), where the relationship between the cations Ca^{2+} and Na^{+} and the anions Cl^{-} and HCO_3^{-} versus TDS is plotted in a diagram to identify the natural mechanisms responsible for the composition of water: atmospheric precipitation, weathering, and evaporation. This method was chosen owing to its frequent application in the literature (Aghazadeh, Chitsazan & Golestan 2017; Hui et al. 2021; Kumar et al. 2015). The chloro-alkaline indices (CAI) were applied to investigate the occurrence of ionic exchange reactions that generally occur between clay minerals, and the permanence or movement of groundwater in the aquifer (Tarawneh, Janardhana & Ahmed 2019). Positive index values indicate the involvement of direct ion exchange reactions (base exchange) and negative index values suggest reverse ion exchange (chloro-alkaline imbalance) (Zhang et al. 2020).

The speciation modeling and saturation index (SI) calculations were developed using PHREEQC Interactive software version 3.6.2 (Parkhurst & Appelo 2013). Changes in the saturation state were used to identify important reactions in the control for the composition of water (Trabelsi & Zouari 2019). When the SI values are positive, there are appropriate physical and chemical conditions for the precipitation of mineral phases, that is, the groundwater is supersaturated in relation to a specific mineral. Otherwise, when the SI is negative, the dissociated products do not precipitate owing to the undersaturated condition (Chidambaram et al. 2011).

To identify the groups of variables that interrelate and result in the salinization of the waters, multivariate statistics were applied through the factor analysis technique. Cloutier et al. (2008) and Gomes and Franca (2019) applied this technique in different regions as a qualitative water management tool. Multivariate statistical analysis was performed using SPSS Statistics version 27 and Minitab version 19 software. Hierarchical cluster analysis was applied to classify the groups based on their similarities. To that end, standardized variables, the Ward connection method (minimum variance method) and the Euclidean Distance for the formation of the similarity matrix were used (Palácio et al. 2009).

4 Results and Discussion

4.1 Hydrogeochemistry

A descriptive summary of the analyzed parameters is presented in Table 1. The variables exhibited a high level of dispersion evidenced by the high values of standard deviation, as well as strong asymmetry. The pH varied between 4.88 and 8.78, indicating the presence of acidic to slightly alkaline groundwater. The electrical conductivity (EC) varied between 75.80 and 9440.00 $mS.cm^{-1}$, with an average value of 1838.43 mS.cm^{-1}; 21.05% of the studied samples had an EC up to 250.00 mS.cm^{-1}, 36.84% had values between 250.00 to 750.00 mS.cm^{-1}, and 42.11% had values above 750.00 mS.cm^{-1}, indicating the wide variation in the concentration of salts dissolved in the groundwater. Salinity, represented by the total dissolved solids (TDS), presented the following classification: 57.90% of the waters were fresh and 42.10% were brackish.

Table 1 Descriptive summary of the analyzed parameters.

Parameter	N	Average	Median	Minimum	Maximum	Variance	Standard deviation
EC	19	1838.43	647.90	75.80	9440.00	7344306.50	2710.40
pH	19	7.30	7.33	4.88	8.78	1.01	1.01
TH	19	641.18	106.00	16.40	4960.00	1659052.31	1288.04
Turbidity	19	18.93	3.35	0.00	135.00	1417.38	37.65
Acidity	19	2.96	1.10	0.00	16.30	25.47	5.05
TDS	19	1195.01	421.10	49.30	6136.00	3102978.97	1761.53
Na^+	19	142.68	73.60	8.00	456.00	22282.63	149.27
K^+	19	8.91	2.46	1.00	55.50	256.65	16.02
Ca^{2+}	19	327.34	62.20	3.60	2230.00	380641.53	616.96
Mg^{2+}	19	76.15	12.30	2.00	662.00	27181.16	164.87
CO_3^{2-}	19	6.60	0.00	0.00	64.50	283.33	16.83
HCO_3^-	19	205.74	162.00	12.30	506.00	22235.65	149.12
Cl^-	19	391.27	18.20	5.47	2280.00	493699.50	702.64
SO_4^{2-}	19	139.75	7.16	0.68	1860.00	177510.39	421.32
F^-	19	1.01	0.27	0.00	7.18	3.52	1.88
NO_2^-	19	0.01	0.00	0.00	0.04	0.00	0.01
NO_3^-	19	0.14	0.05	0.00	1.18	0.08	0.28
SiO_2	19	47.82	53.90	0.80	92.20	668.28	25.85
Fe_{total}	19	1.63	0.39	0.06	9.81	7.41	2.72

It was identified that the hydrochemistry in the crystalline aquifer presented a considerably varied classification (Figure 1). The waters were classified as calcium-bicarbonate (42.1%), calcium-chloride (15.8%), mixed-chloride (10.5%), sodium-chloride (10.5%), sodium-bicarbonate (10.5%), sodium-mixed (5.2%) and mixed-mixed (5.2%). This wide variation suggests that various chemical processes occur in the subsurface.

Calcium-bicarbonate waters (P3, P5, P7, P13, P14, P15, P18, and P19), classified as fresh, were identified in the eastern portion of the basin, a region with a high rainfall rate influenced by the Af climate. Calcium-chloride waters (P10, P11, and P12) were noted in the western portion of the area with an Aw climate, presenting the highest levels of TDS among the analyzed wells and characterized brackish waters. The mixed-mixed water (P17) was found in the central portion of the basin, with Am climate, showing the lowest TDS content.

From the analysis of ionic relationships, calcium is the cation that prevails in the region, while carbonate and bicarbonate are the dominant anions. Calcium was mostly found in the form of Ca^{+2} and secondarily as $CaCO_3$. Carbon, present in the bicarbonate anion, predominantly occurred in the HCO_3^- form and to a lesser extent as CO_2, CO_3^{2-}, and $CaCO_3$.

Trabelsi & Zouari (2019) linked the sources of bicarbonate concentrations in groundwater to the dissolution of carbonate minerals, and CO_2 from soils or bacterial degradation of organic contaminants. Teramoto & Chang (2020), when considering the absence of carbonate rocks in the CRB area, argued that the presence of HCO_3^-, the main anion in the groundwater, indicated water–rock interactions. As the substrate of the area predominantly corresponds to granulites of tonalitic, trondhjemitic, or gabric composition with mineralogical assemblages of hornblende and plagioclase, the reactions presented in

Equations 1, 2 (plagioclase hydrolysis), and 3 (amphibole hydrolysis) represent the water–rock interactions wherein HCO_3^- is produced by the hydrolysis of silicates:

$$CaAlSi_3O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^- + 4Si(OH)_4 \quad \textbf{(1)}$$

$$2NaAl\ Si_3O_8 + 2CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4Si(OH)_4 \quad \textbf{(2)}$$

$$Ca_2Mg_2Si_8(OH)_2 + 14CO_2 + 22H_2O \rightarrow 2Ca^{2+} + 5Mg^{2+} + 14HCO_3^- + 8Si(OH)_4 \quad \textbf{(3)}$$

The presence of chlorinated waters, according to Gomes & Cavalcante (2017), is related to marine aerosol deposition and evaporation, which increase the chloride concentration in the groundwater, favored by the proximity to the Atlantic Ocean. In studies carried out by Engelbrecht et al. (2019) it was identified that evapotranspiration rates in the CRB area are up to 85%, indicating that this is an important factor. Thus, the concentrations of Cl^-, as well as Na^+, SO_4^{2-}, and Mg^{2+}, can be related to the interaction of precipitated meteoric waters with marine aerosols and subsequent evaporation (Teramoto et al. 2019).

Santos, Santos & Santos (2009) indicated that Na^+, K^+, Ca^{2+} and Mg^{2+} are important indicative parameters of the process of concentration by the evaporation of chemical species dissolved in the waters of superficial reservoirs in the Brazilian semiarid region. Araújo et al. (2015) and Teramoto & Chang (2020) verified that the number of marine aerosols deposited in different sampling points of the Cachoeira River is significant, accounting for significant fluxes of Na^+, Mg^{2+}, and Cl^- ions. However, as per the reactions presented in Equations 1 to 3, the presence of Ca^{2+}, Na^+, and Mg^{2+} ions can also result from the hydrolysis of silicates.

The Gibbs diagram (Figure 2) indicates that the natural mechanisms that control the major ionic composition of groundwater in the study area are related to rock weathering and evaporation. The freshwater samples classified as calcium-bicarbonate are associated with granulites and latosols. Bicarbonate, the dominant anion in the area, has its source associated with the water–rock interactions through the hydrolysis reaction of silicates, or as described in the Gibbs diagram, with the weathering of rocks. Evaporation is the dominant process that controls the composition of the brackish water samples classified as calcium-chloride in this study.

The groundwater in the study area was characterized with positive and negative values of CAI-I and CAI-II (Table 2). At 4 sites, CAI-I and II were found to be positive, indicating direct ion exchange, and at 15 sites, CAI-I and II were negative, indicating a reverse exchange reaction.

During the direct ion exchange reaction, Na^+ ($\pm K^+$) ions from the surface of clay minerals are displaced by Ca^{2+} ($\pm Mg^{2+}$) ions present in the water, resulting in the enrichment of water in Na^+ ($\pm K^+$) (Alves et al. 2021). Direct ion exchange with clay materials is generally observed when water is being salinized (Slama & Bouhlila 2017). This situation was observed in samples P9, P10, P11 and P12. Theoretically, the Na^+ rich smectites from the aquifer matrix can provide the ions for the solution. In the reverse ion exchange reaction, the opposite occurs: part of the Ca^{2+} ($\pm Mg^{2+}$) ions present in clay minerals are exchanged for Na^+ ($\pm K^+$) and there is an increase in the concentration of Ca^{2+} ($\pm Mg^{2+}$) in the solution (Dinka 2019; Huang et al. 2018), as confirmed by the analysis of the ionic relationships of groundwater that identified Ca^{2+} as the predominant cation. According to Silva, Barbosa and Santos (2021) the reverse ion exchange process is a significant result of the weathering of silicates, which are common minerals in the study area.

Salts dissolved in their ionic form are responsible for the salinity of water, so the analysis of the chemical speciation parameters allows the identification of the elements that cause the salinization of groundwater in the CRB area. Carbon was available in 73.68% of the samples in the form of HCO_3^- and in 21.05% as CO_3^{2-}. Calcium, chloride, fluoride, potassium, magnesium and sodium were found only in the following forms: Ca^{2+}, Cl^-, F^-, K^+, Mg^{2+}, and Na^+, respectively. Ferrous iron was prevalent as Fe^{2+} (78.95%), as well as $Fe(OH)^{3-}$, $Fe(OH)^+$, and $Fe(OH)_2$. When in the ferric state (Fe^{3+}), it was found as $Fe(OH)_3$ (57.89%), $Fe(OH)^{2+}$, and $Fe(OH)^{4-}$, which according to Gomes et al. (2017), are insoluble forms that precipitate in case of a high turbidity.

The negative SI of the groundwater for halite, gypsum, fluorite, chrysotile, and siderite demonstrated the undersaturation of these minerals. The strong correlations between gypsum IS versus TDS (correlation coefficient $R^2 = 0.82$) and halite IS versus TDS (correlation coefficient $R^2 = 0.87$) indicate that these minerals remain dissolved during the flow of groundwater in the samples used in modeling. Gypsum ($CaSO_4$) dissolves in the water to produce Ca^{2+} and SO_4^{2-}, according to the reaction in Equation 4:

$$CaSO_4.2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \quad \textbf{(4)}$$

The dissolution of halite and gypsum can lead to significant increases in Na^+, Cl^-, Ca^{2+}, and SO_4^{2-}.

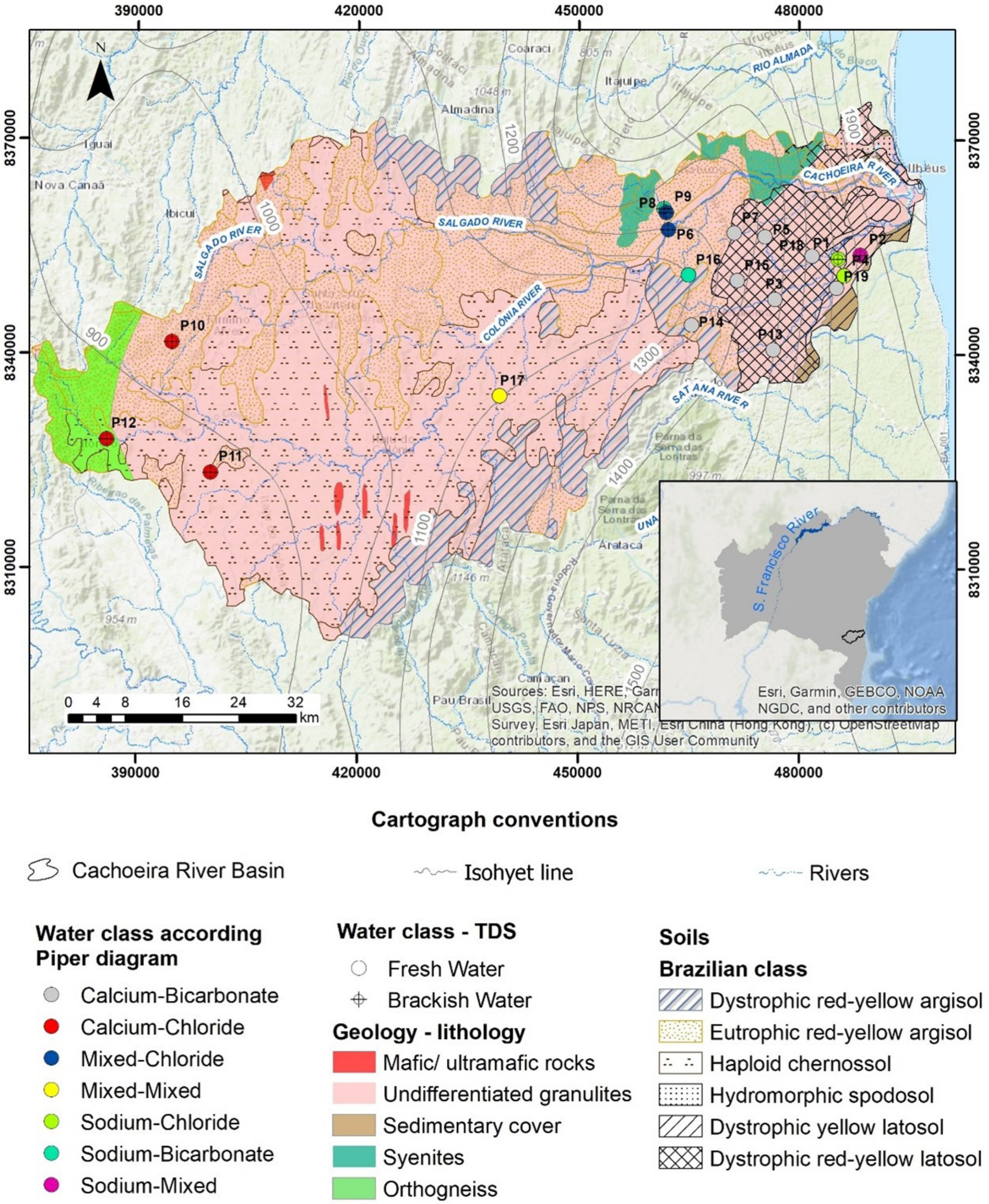

Figure 1 Simplified geological map of the study area showing analyzed wells, soil classes, and water classification based on total dissolved solids and Piper diagram, and the isohyet line.

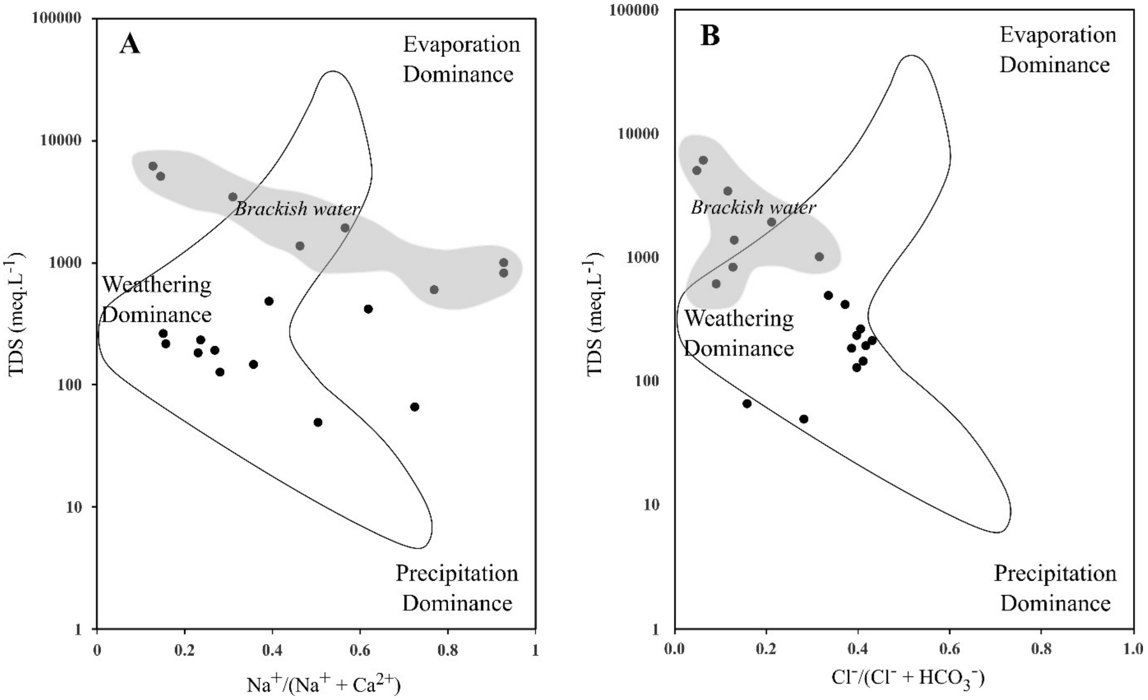

Figure 2 Gibbs diagram indicating the mechanisms that determine the main ionic composition of the waters: A. TDS versus Gibbs's ratio I; B. TDS versus Gibbs's ratio II.

Table 2 Calculated parameters for the assessment of hydrochemical processes.

Wells	$CAI-I=\dfrac{Cl^- -\left(Na^+ + K^+\right)}{Cl^-}$	$CAI-II=\dfrac{Cl^- -\left(Na^+ + K^+\right)}{\left(SO_4^{2-}+HCO_3^- + NO_3^-\right)}$
P1	-2.95	-0.94
P2	-1.67	-1.32
P3	-0.80	-0.13
P4	-25.33	-0.95
P5	-0.72	-0.15
P6	-0.08	-0.12
P7	-0.89	-0.36
P8	-0.24	-0.84
P9	0.48	2.77
P10	0.80	8.55
P11	0.34	0.90
P12	0.75	0.98
P13	-3.45	-0.40
P14	-2.68	-0.35
P15	-2.86	-0.51
P16	-0.55	-0.58
P17	-0.77	-0.35
P18	-1.55	-0.22
P19	-2.46	-0.17

4.2 Multivariate Statistical Analysis

Table 3 shows the correlation matrix for the twelve attributes that were used in the factor analysis. From a total of 66 correlation coefficients, 100% had significant values. Of these, approximately 74% were in the range $0.6 \leq |r| < 0.9$, indicating a strong correlation according to Palácio et al. (2011). The remaining 26% were in the range $0.3 \leq |r| < 0.6$, indicating moderate correlation.

It appears that there was a strong correlation between electrical conductivity and chloride (r = 0.98), calcium (r = 0.98), magnesium (r = 0.94), potassium (r = 0.91), sulfate (r = 0.74) and sodium (r = 0.72), indicating the possible influence of these ions on the increase in water salinity in the area. Chloride demonstrated a strong correlation with TDS (r = 0.98), electrical conductivity (r = 0.98), calcium (r = 0.96), potassium (r = 0.92), magnesium (r = 0.91), total iron (r = 0.90), sulfate (r = 0.65), and sodium (r = 0.65), indicating, once again, the relationship of these ions with the increase in water salinity. Chloride is also a good indicator of the effect of evaporation/evapotranspiration.

Total iron was strongly correlated with calcium (r=0.96), electrical conductivity (r=0.91), TDS (r=0.91), and chloride (r=0.90). It is a frequent component of groundwater coming from ferromagnesian minerals. At the CRB, the high levels of iron are likely related to the significant presence of rocks and mafic dikes, which supply substantial amounts of iron oxides to some soils (Nacif 2000). The content in the studied wells varied between 0.08 and 9.81 $mg.L^{-1}$. Bicarbonate only showed a strong correlation with sodium (r = 0.81). Bicarbonate can form the highly water-soluble sodium bicarbonate salt ($NaHCO_3$). The Na^+ ion can originate from the dissolution of silicates, the evaporation of water containing marine aerosols (Teramoto & Chang 2020), or ionic exchanges between water and clay minerals. The moderate correlation between bicarbonate with TDS and EC (r = 0.59) indicates a low influence on the salinization of the area. The correlation with calcium (r = 0.49) and magnesium (r = 0.44) may reflect that the predominant origin of these ions is the weathering of silicates and not carbonate dissolution (Morán-Ramírez et al. 2016). The absence of carbonate rocks in the study area should also be considered, thus strengthening the indication that the hydrolysis of silicates is the main reaction for the water–rock interactions.

Three factorial analysis simulations were carried out to obtain better results in the applied convenience tests. In the first one, all 18 physical–chemical parameters were used. The KMO index showed a result of 0.507 and the Bartlett's sphericity test did not present significance (p <0.01), indicating that the variables analyzed were not correlated. In the second simulation, the three parameters (pH, SiO_2, and NO_2^-) that exhibited low communalities, less than 0.600 (Franca et al. 2018), were excluded as this indicates a low level of explanation of the parameter by these factors. The KMO index and Bartlett's sphericity test still indicated insignificance. In the third simulation, the parameters NO_3^-, F^-, and CO_3^{2-} were eliminated, as once again, they presented low commonalities. The model developed with twelve parameters proved to be favorable with a KMO index of 0.776 and Bartlett's sphericity test was significant at p <0.01.

The factor analysis showed two factors with eigen values greater than 1.0. The first factor explained the total variance of the attributes by approximately 70% and the second by 23%. These results indicate that the two factors represent approximately 93% of the total variance of the data (Table 4).

Table 3 Correlation matrix between the physical-chemical parameters of groundwater.

	TDS	EC	TUR	TH	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
EC	1.00										
TUR	0.94	0.94									
TH	0.96	0.96	0.97								
Na^+	0.72	0.72	0.48	0.54							
K^+	0.91	0.91	0.96	0.95	0.39						
Ca^{2+}	0.98	0.98	0.98	0.99	0.58	0.95					
Mg^{2+}	0.94	0.94	0.96	0.99	0.50	0.94	0.97				
Cl^-	0.98	0.98	0.93	0.94	0.65	0.92	0.96	0.91			
SO_4^{2-}	0.74	0.74	0.78	0.84	0.41	0.72	0.79	0.88	0.65		
HCO_3^-	0.59	0.59	0.39	0.46	0.81	0.31	0.49	0.44	0.48	0.41	
Fe_{total}	0.91	0.91	0.99	0.95	0.44	0.95	0.96	0.94	0.90	0.76	0.38

Table 4 Factor loads, commonalities and variance explained by the factor analysis of the 12 attributes analyzed after rotation by the varimax method.

Variables	**Factorial Loads**		**Communalities**
	Factor 1	**Factor 2**	
TDS	**0.861**	-0.497	0.989
EC	**0.861**	-0.497	0.989
Turbidity	**0.961**	-0.228	0.976
TH	**0.951**	-0.300	0.994
Na^+	0.285	**-0.919**	0.926
K^+	**0.968**	-0.130	0.953
Ca^{2+}	**0.935**	-0.339	0.989
Mg^{2+}	**0.952**	-0.260	0.975
Cl^-	**0.871**	-0.405	0.922
SO_4^{2-}	**0.791**	-0.221	0.675
HCO_3^-	0.188	**-0.922**	0.885
Fe_{total}	**0.953**	-0.193	0.945
Variance explained by factors (%)	8.4369	2.7802	11.2171
Accumulated variance (%)	0.703	0.232	0.935

With approximately 70% of the explanation of the total variance of the attributes, Factor 1 demonstrated a high positive correlation between the attributes TDS, EC, turbidity, TH, potassium, calcium, magnesium, chloride, sulfate, and iron, with factorial loads greater than 0.791, indicating that they most significantly controlled characterization of the water salinity. The variables with the highest factorial loads, were K^+ (0.968), turbidity (0.961), Fe_{total} (0.953), Mg^{2+} (0.952), TH (0.951), and Ca^{2+} (0.935). According to Brodnjak-Vončina et al. (2002), the variables in question may be linked to the natural weathering process of the geological components of rocks and soils. Potassium has a clay-origin, while iron and magnesium sources are related to ferromagnesian rocks and minerals, with calcium being related to the calcium plagioclases of mafic/ultramafic rocks and to chernosols.

Factor 2, with approximately 21% of the explanation of the total variance of the attributes, showed a high correlation between bicarbonate and sodium, reinforcing the hypothesis of the presence of sodium bicarbonate, which contributes minimally to the salinity of groundwater. The identified factorial loads were: -0.932 and -0.910, respectively. Thus, the indicators that represent these factors were defined as factor 1: groundwater mineralization component related to chemical weathering and evapotranspiration; and factor 2: groundwater mineralization component associated with the presence of soluble salts.

The multivariate cluster analysis technique, applied to the attributes explained by factors 1 and 2 from the factor analysis, grouped samples with chemically similar characteristics. The groups obtained were defined by the first major difference between the rescheduled cluster coefficients. The parameters for factor 1 generated two similar groups (Figure 3), with a cut-off point of nine. Group 1, from factor 1 comprised 84% (16 wells) of the groundwater samples. It was characterized by waters with substantial chemical variability. The wells were in the central–eastern portion of the basin, an area with high rainfall where latosols predominate. Group 2, from factor 1 comprised three wells (16% of the groundwater samples) that were distinguished from the others because they were in a different climatic band in the extreme western part of the basin with lower average rainfall. These had water with the highest level of salinity in the area, with EC between 1090 and 2280 mS.cm^{-1}. These wells were associated with chernosols and argisols. Factor 2 parameters generated three similar groups, with a cut-off point of four. Group 1, from factor 2 comprised four wells. The samples had a sodium content between 316 and 456 mg.L^{-1}, with an average of 368.25 mg.L^{-1}. The average concentration of bicarbonate ions was 453 mg.L^{-1}. This group characterized wells with high salinity levels (P1, P6, P11, and P12). Group 2, from factor 2 comprised six wells, wherein the average sodium content was 181.15 mg.L^{-1}. The bicarbonate varied between 59.9 and 250 mg.L^{-1}. This group represented the wells with an intermediate level of salinity (P2, P4, P7, P8, P9, and P10). Group 3, from factor 2 comprised nine wells. Groundwater samples in this group had a sodium content between 8 and 28 mg.L^{-1}. The maximum bicarbonate concentration was 181 mg.L^{-1}. This group included wells with low salinity levels.

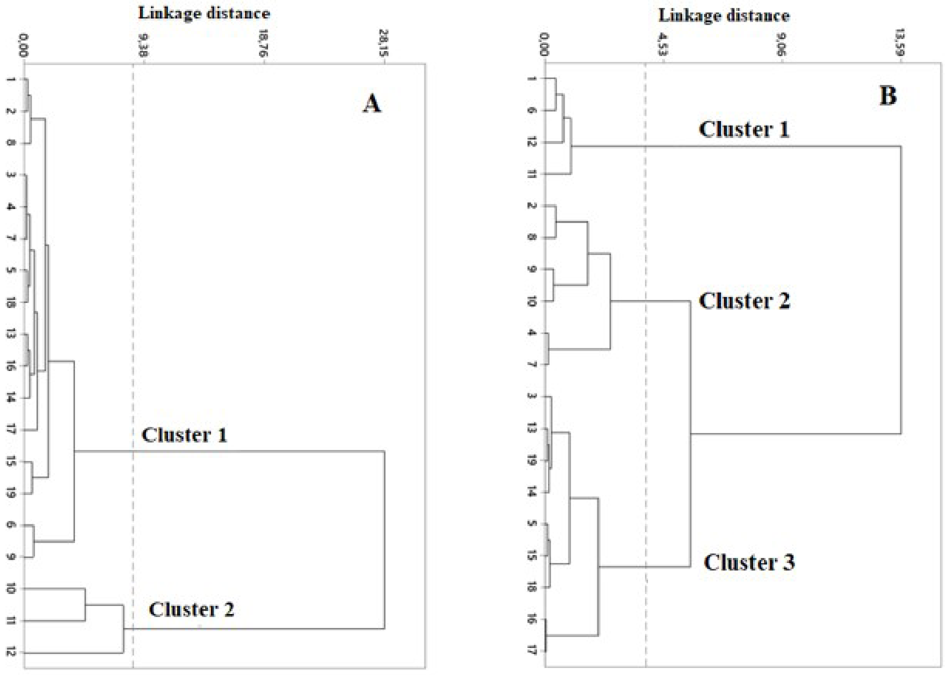

Figure 3 Dendrogram resulting from the hierarchical grouping analysis of the variables explained by: A. Factor 1; B. Factor 2.

5 Conclusions

In the present study, the combined use of hydrogeochemical diagrams and multivariate statistical analysis to understand the factors that lead to water salinization proved to be efficient. The geochemical composition of the groundwater comprises two main types: calcium-bicarbonate and calcium-chloride. The salinity distribution indicates that fresh and brackish water can be found and that climatic characteristics influence their chemical quality. The western portion, with a climate characterized by low humidity and scarce rainfall, presents groundwater that is more mineralized than that in the eastern portion of the area. The increase in salinity, related to the increasing concentrations of Na^+, Cl^-, Ca^{2+}, and SO_4^{2-}, is associated with the effect of direct ion exchange during the contact between rock and water, evidenced by the saturation index and the chloro-alkaline index. Meanwhile, Fe_{total}, Mg^{2+} and HCO_3^- sources are related to chemical weathering during the silicate hydrolysis reaction. Although HCO_3^- is the most abundant ion in the groundwater in the study area, it is not a dominant element in salinization. Water quality is also related to the evapotranspiration process. The proximity of the study area to the Atlantic Ocean causes marine aerosols to be transported and deposited, often concentrating K^+, Na^+, Mg^{2+}, and Cl^- ions. The multivariate statistical analysis allowed the identification of the parameters responsible for the variations in water quality and confirmed the role of the geochemical process of water–rock interactions, with weathering and evapotranspiration explaining the water salinization in the region. The present study contributed to enhancing the understanding of the processes that result in salinization and affect water quality, supporting the development of planning and sustainability strategies for water resources.

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Author contributions

Jamille Evangelista Alves: conceptualization; formal analysis; methodology; writing-original draft; writing – review and editing; funding acquisition; visualization. **Sérgio Augusto de Morais Nascimento:** methodology; funding acquisition; supervision. **Maria da Conceição Rabelo Gomes:** formal analysis; methodology; validation; supervision.

Conflict of interest

The authors declare no potential conflict of interest.

Data availability statement

All data included in this study are available on request in Companhia de Engenharia Hídrica e de Saneamento da Bahia (CERB).

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