Revista Brasileira de Recursos Hídricos
Brazilian Journal of Water Resources
Versão On-line ISSN 2318-0331
RBRH, Porto Alegre, v. 27, e21, 2022
Scientific/Technical Article

https://doi.org/10.1590/2318-0331.272220220018

Geochemical modeling of the evaporation process in salinized reservoirs in the semi-arid region of Northeastern Brazil

Modelagem geoquímica do processo de evaporação em reservatórios salinizados no semiárido do Nordeste do Brasil

Adnívia Santos Costa Monteiro[1], Eveline Leal da Silva[2], Nívia Raquel Oliveira Alencar[1], Crislaine Melo Cardoso[1], Igor Santos Silva[1], Roseane dos Santos Nascimento[1] & José do Patrocínio Hora Alves[1]

[1]Universidade Federal de Sergipe, São Cristóvão, SE, Brasil
[2]Instituto Federal de Educação Ciência e Tecnologia do Piauí, Campus Floriano, Floriano, PI, Brasil

E-mails: adniviacosta@gmail.com (ASCM), evelineleal@ifpi.edu.br (ELS), niviaquel@hotmail.com (NROA), crislaine.a@hotmail.com (CMC), ssantos.igor@hotmail.com (ISS), roseane-santos31@hotmail.com (RSN), jphalves@uol.com.br (JPHA)

Received: March 07, 2022 - Revised: June 22, 2022 - Accepted: July 18, 2022

ABSTRACT

The geochemical characterization of saline water in reservoirs located in semi-arid regions is an important issue to be addressed, as it allows us to understand the deterioration of water quality caused by evaporation. In this study, the Gibbs diagram, ionic ratios and geochemical modeling were employed to decipher the geochemical processes that affect the chemical water evolution of three saline reservoirs located in the semi-arid region of Sergipe state, Northeastern Brazil. The reservoirs geochemical processes mainly include sea salt dissolution, silicate weathering, ion exchange, with a limited contribution from the dissolution of carbonates. Geochemical modeling confirmed that evaporation-crystallization is the main mechanism that controls the chemical composition of water, leading to increased concentrations of Na^+, Mg^{2+}, Ca^{2+} and Cl^-, and reduction of HCO_3^- by precipitation of calcite and dolomite. Furthermore, the simulated models reproduced the trend observed in the real hydrochemical data and indicated excellent agreement between the simulated ion concentrations and the real ion concentrations for most of the larger ions. The highest deviation was observed for HCO_3 whose actual concentrations were much higher than those predicted by the modeling, attributed to kinetic restrictions concerning calcite precipitation.

Keywords: Geochemical modeling; Evapoconcentration; PHREEQC; Ionic ratios.

RESUMO

A caracterização geoquímica de águas salinas em reservatórios localizados em regiões semiáridas é uma questão importante a ser abordada, pois permite compreender a deterioração da qualidade da água causada pela evaporação. Neste estudo, o diagrama de Gibbs, razões iônicas e modelagem geoquímica foram empregados para decifrar os processos geoquímicos que afetam a evolução química da água de três reservatórios salinos localizados no semiárido do estado de Sergipe, Nordeste do Brasil. Os principais processos geoquímicos envolvidos na composição química da água dos reservatórios foram a dissolução do sal marinho, intemperismo dos silicatos, troca iônica, com uma contribuição limitada da dissolução de carbonatos. A modelagem geoquímica confirmou que a evaporação-cristalização é o principal mecanismo que controla a composição química da água, levando ao aumento das concentrações de Na^+, Mg^{2+}, Ca^{2+} e Cl^-, e redução do HCO_3^- pela precipitação de calcita e dolomita. Além disso, os modelos simulados reproduziram a tendência observada nos dados hidroquímicos reais e indicaram excelente concordância entre as concentrações iônicas simuladas e as concentrações iônicas reais, para a maioria dos íons maiores. O maior desvio foi observado para o HCO_3^-, cujas concentrações reais foram muito mais elevadas que as previstas pela modelagem e isso tem sido atribuído a restrições cinéticas na precipitação da calcita.

Palavras-chave: Modelagem geoquímica; Evapoconcentração; PHREEQC; Razões iônicas.

INTRODUCTION

Salinization is one of the biggest threats to freshwater systems, especially in arid and semiarid regions. Salinization has increased in recent decades as a result of climate change and anthropogenic impacts such as agricultural production, industrial inputs and human-accelerated weathering (Müller & Gachter, 2011; Connor et al., 2012; Swinton et al., 2015; Kaushal et al., 2017; Singh, 2018).

Salinization can make water unsuitable for human consumption and irrigation, in addition to resulting in aquatic ecosystem health impacts (Peck & Hatton, 2003; Nielsen et al., 2003; Merchán et al., 2015). It is therefore important to understand salinization processes in order to identify the main factors that drive lake and reservoir salinization and, thus, attempt to implement actions that improve the water quality of these environments.

The literature has highlighted that high evaporation and the return of irrigation flows are the main processes involved in water salinization (Koh et al., 2007; Johansson et al., 2009; Lerman, 2009; Abdel Wahed et al., 2014, 2015; Guo et al., 2018; Jia et al., 2020). In some regions salinity increases in the dry period, when evaporation and water discharges from agricultural areas are higher, decreasing during the rainy season, due to reduced evaporation and increased freshwater inflow rates (Guo et al., 2015; Liu et al., 2020a)

Droughts also have a significant impact on surface water salinization. In southwestern Australia a severe drought between 1997 and 2009 led to increased salinity, from pre-dry to dry conditions, for a number of saline lakes. However, the magnitude of salinity variation was not the same for all lakes. Salinity control processes varied for different lakes, and only a few of these lakes had their controls altered as a result of the drought. The larger lakes displayed increases in salinity controlled predominantly by evaporation, while the salinity controls shifted from predominant evaporation during the pre-dry period to evaporation and mineral evaporite reactions such as cyclic halite dissolution/precipitation during the dry period in the smaller lakes dry (Elsdon et al., 2009; Tweed et al., 2011).

In the Brazilian Northeast, due to adverse weather conditions, with little rainfall, cyclical drought and high evaporation periods, water storage in reservoirs has been a strategy used to meet the region's freshwater demands (Palácio et al., 2011). However, salinization of accumulated water is a recurrent problem in the region and it has been highlighted that this is not only due to excessive evaporation, but also irregular demands, which can lead to the permanence of accumulated water for long periods of time with no renewal, which can also contribute to salinization evolution (Santos et al., 2000; Souza Filho & Campos, 2002; Meireles et al., 2007; Palácio et al., 2011; Fontes et al., 2015).

The impacts of salinization, irregular demands and large periods without water renewal have been highlighted by Santos et al. (2000) and Alves et al. (2021) in studies concerning reservoirs located in Northeastern Brazil. For Santos et al. (2000), the salinization of reservoirs located in southwestern Bahia has increased with reservoir age and/or the hydraulic retention time, while Alves et al. (2021) observed that the salinization process in reservoirs located in the state of Sergipe intensified in reservoirs with longer hydraulic retention time and with low demand for accumulated water.

Detailed knowledge concerning the processes that control salinization is essential to be able to define actions to be taken to mitigate its effects on aquatic resources (Merchán et al., 2015). The geochemical approach through the analysis of ionic ratios and geochemical modeling is extremely useful to explain the chemical evolution of waters submitted to salinization processes (Banks et al., 2004; Abdel Wahed et al., 2014; Bouzourra et al., 2015; Farid et al., 2015; Jia et al., 2020; Vallejos et al., 2020, Alves et al., 2021). However, most geochemical modeling studies employing PHREEQC refer to the simulation of water-rock interaction processes (reverse modeling), with few studies dealing with the simulation of the evolution of waters subjected to successive evaporations (direct modeling).

The net effect of evaporation is to remove pure water from the solution, increasing the concentrations of dissolved species. Evaporation occurs in all climates, but only in relatively arid regions does evaporation affect dissolved constituents, making this the greatest water composition control process (Drever, 1982). Examples of studies concerning saline lakes located in arid regions and whose chemical water compositions are controlled by evaporation include assessments in Lake Khakassian/Siberia (Banks et al., 2004) and Lake Qarum/Egypt (Abdel Wahed et al., 2015). In these studies, the chemical evolution of water due to progressive evapoconcentration was simulated using direct PHREEQC modeling.

This study is noteworthy for comprising the first to deal with the water hydrogeochemistry from salinized reservoirs located in the semiarid region of northeastern Brazil. In this context, it aims to identify the main geochemical processes related to the salinization of reservoir waters, through ionic ratios and geochemical modeling. Specifically, the main objective is to elucidate whether the salinization of the waters is a result of the region's high evaporation rates, which can reach 2,000 mm year^{-1}. An overview of the hydrochemical water status of each reservoir is presented and geochemical PHREEQC modeling is employed to assess geochemical water evolution resulting from successive evaporation processes. In this way, the study contributes to understanding the deterioration of water quality caused by the evaporation process and can contribute to the implementation of actions that minimize the effects of evaporation.

MATERIAL AND METHODS

Study area

The study area comprises the Algodoeiro and Três Barras reservoirs located in the São Francisco River hydrographic basin and the Glória reservoir included in the Sergipe River hydrographic basin (Figure 1). The reservoirs are located in the state of Sergipe, northeastern Brazil, distributed throughout the Sergipe territory in the Alto Sertão (Algodoeiro, Glória) and Médio Sertão (Três Barras) regions. They were designed to mainly serve agriculture and human supply, but currently, given their salinization, are only used for fishing, leisure and animal watering. The Algodoeiro and

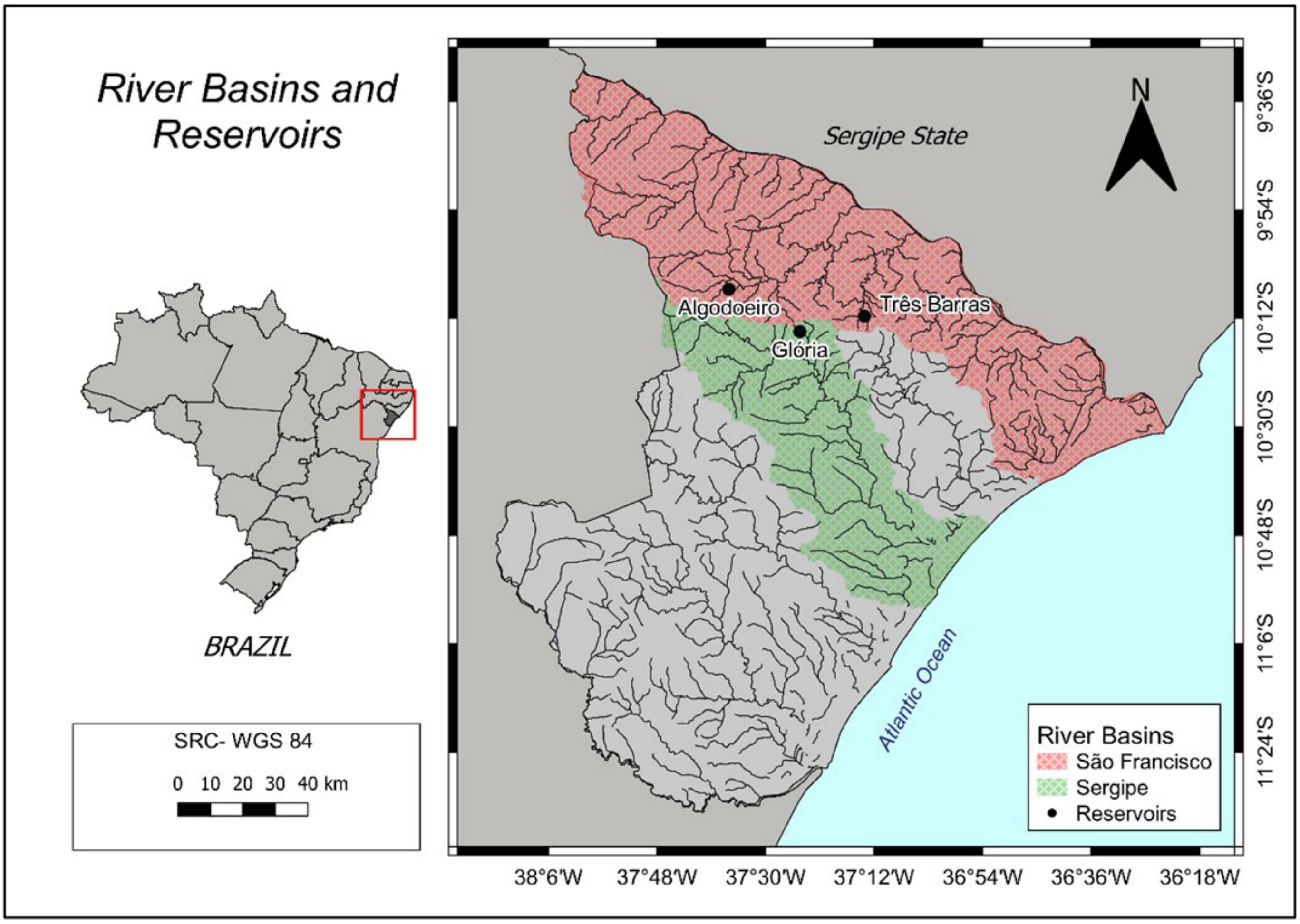

Figure 1. Map of the study area indicating the location of the investigated reservoirs.

Glória reservoirs were classified as eutrophic and hypertrophic, respectively, concerning Trophic State Level (Melo et al., 2018).

The Algodoeiro reservoir, located in the city of Nossa Senhora da Glória, was built from 1964 to 1996. It is formed by the Alagadiço stream dam and presents an accumulation capacity of 1,868,830 m^3, occupying 32.68 km^2, with main dam length of 348 m and maximum height of 15 m (Melo et al., 2018).

The Três Barras reservoir is located in the city of Graccho Cardoso and was built from 1953 to 1957. As its name suggests, it is formed by the damming of the Lajeiro, Tiros and Algodão streams, with an accumulation capacity of 7,989,600 m^3, occupying 74 km^2, with main dam length of 243 m and maximum height of 21.2 m (Alencar, 2020).

The Glória reservoir is located in the municipality of Nossa Senhora da Glória and its construction began in 1957 and concluded in 1958, by damming the Pau de Cedro stream. This reservoir comprises an earth-type dam, with a hydrographic extension of 4.3 km^2 and capacity to accumulate 586.700 m^3 (Melo et al., 2018).

All three reservoirs were built by the Brazilian National Department of Works Against Droughts (in Portuguese, *Departamento Nacional de Obras Contra as Secas* - DNOCS).

The Alto Sertão region present a dry sub-humid climate, with little or no excess water during the year. Under the influence of low latitudes, the average temperature ranges between 24°C and 26°C and the average annual rainfall rates vary between 500 mm and 800 mm, poorly distributed throughout the year and irregular from one year to another. The wettest period comprises from May to August and the driest months are from October to February. The Middle Sertão, on the other hand, presents a tropical rainy climate with a dry summer, intermediate between the dry to the semiarid climate. Average annual rainfall rates range from 800 mm to 1600 mm, with an average annual temperature of 23.9 °C, and November comprising the hottest month (25 °C) and August, the coldest (21 °C) (Monteiro et al., 2021).

Geology and hydrogeology

The geology in the reservoir area is predominantly represented by the Neo- and Mesoproterozoic domains of the Sergipana Fold Belt. Over 80% of the territory is occupied by Macururé Group lithotypes, represented mostly by granatiferous micaschists, fine metarhythmites, metavulcanites, metagrauvacs, fine metarenites and massive metasiltites. The presence of leucocratic granites and granodiorites and a small fraction of fine and coarse sands with clayey and conglomeratic levels are also noted (Bomfim et al., 2002a, 2002b).

Granitic intrusions constituted by biotite quartz diorites and biotite quartz monzodiorites of gray color, medium grained and porphyritic texture, (plagioclase phenocrystals), with a matrix composed of plagioclase, quartz, potassium feldspar, biotite and amphibole occur in the Macururé Domain (Sousa et al., 2017).

The predominant soils are neosols and planosols in the vicinity of the Algodoeiro and Glória reservoirs, and luvisols in the Três Barras reservoir region (Bomfim; et al., 2002a). Flatsoils are generally shallow with a sandy surface horizon followed by a dense clayey and poorly permeable horizon. Luvisols are also shallow and are characterized by a high contrast in texture between the A and Bt horizons, which may present stony surfaces. These two soil classes contain large amounts of easily weatherable primary minerals (>80% are silicates). Neosols are poorly evolved soils, consisting of mineral material or organic material less than 20 cm thick, without any type of diagnostic B horizon.

The Crystalline and Metasediments/Metavulcanites hydrogeological domains are predominant in the reservoir region. They present a “fractured aquifer” behavior, as no primary porosity is noted in these types of rocks and the occurrence of groundwater is conditioned to a secondary porosity represented by fractures and joints. In general, the flows produced by the wells are small and, due to the lack of circulation, the effects of the semi-arid climate and the type of rock, the produced water is mostly brackish (Bomfim et al., 2002a, 2002b).

Cenozoic surface formations are also observed in the Três Barras reservoir region, constituted by packages of sedimentary rocks that cover the oldest rocks of the Sedimentary Basins, Sergipana Fold Range and Gneissic Basement. In hydrogeological terms, it presents a “granular aquifer” behavior, characterized by primary porosity and high permeability in sandy soils, which, in general, confers excellent conditions for water storage and supply brackish (Bomfim et al., 2002a, 2002b).

Sampling and analysis

Data obtained from the Water Quality Monitoring Program of the Sergipe State Watersheds (Alves et al., 2018) were used for the following variables: temperature, pH, electrical conductivity, total dissolved solids, sodium, potassium, calcium, magnesium, chloride, sulfate and bicarbonates. Surface water samples were collected at a sampling station in the Algodoeiro (653,348 E, 8,881,000 N), Três Barras (694,250 E, 8,872,612 N) and Glória (674,696 E, 8,868.002 N) reservoirs.

Ten sampling campaigns were carried out in the dry and rainy seasons in the years 2013, 2014, 2017, 2018 and 2019. The samples were collected in polyethylene bottles and stored on ice until reaching the laboratory. The pH and temperature were measured in the field. The other parameters were determined in the Water Laboratory at the Technological and Research Institute of the State of Sergipe (ITPS), using the methodology described in American Public Health Association (2012). Electrical conductivity was measured with a conductivimeter and total dissolved solids were calculated by measuring electrical conductivity. To determine the ionic composition, the samples were vacuum filtered through 0.45 μm membranes. Ionic concentrations were determined by ion chromatography using an ion chromatograph model Dionex – ICS 3000 with conductivity detection.

The precision of the analyses was determined through the ion balance, employing Equation 1:

$$A = \left(\frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \right) x100 \tag{1}$$

where: ∑cations = sum of the concentrations of Ca^{+2}, Mg^{+2}, Na^{+} and K^{+}, in meq L^{-1}; ∑anions = sum of the concentrations of HCO_3^{-}, SO_4^{-2+} and Cl^{-} in meq L^{-}1, and A comprisse the error percentage of the ion balance.

The value of A for the samples ranged from – 8.5% to 3.7% with an absolute mean value of 3.5% for the Algodoeiro reservoir, from – 4.7% to 2.5% with an absolute mean value from 2.1% for Três Barras and from –5.5% to -5.2% with an absolute mean value of 3.7% for Glória. These values are in agreement with the absolute mean values reported by Merchán et al. (2015), which ranged from 2.5% to 4.4% when assessing salinization in an irrigation basin in Spain, and with the absolute mean values indicated by Alves et al. (2021), which ranged from 2.5% to 3.0% when evaluating reservoirs undergoing salinization in Northeastern Brazil. According to El Yaouti et al. (2009), a ± 10% error in the ion balance is acceptable for this type of study.

Multivariate statistical analysis

The Principal Component Analysis (PCA) is a multivariate statistical technique used to reduce the dimensionality of a dataset while maintaining the reliability of the original data. The PCA in this study transforms the set of data that define the chemical characteristics of reservoir waters into new variables, called principal components, which are orthogonal (not correlated) and organized in descending order of importance, concentrating the most relevant information in the first principal components (Singh et al., 2004; Shrestha & Kazama, 2007; Zhu et al., 2017; Zhang et al., 2018). This allows for the identification of differences between samples from the same reservoir, between reservoirs and between seasonal periods (dry and rainy), as well as potential influencing factors.

The PCA was applied to the data set for the three reservoirs, considering each sample collected as an object and the measured parameters as variables. The data matrix consisted of 29 objects (water samples collected in the reservoirs) and 10 variables (temperature, pH, total dissolved solids, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^{-}, HCO_3^{-}). The PCA indicates the principal components (PC), the eigenvalues and the percentage of variance associated with each of the components, as well as the weights corresponding to the participation of each parameter measured in the composition of each PC.

Data were normalized using the z-score technique, where the normalized data have a average equal to 0 and a variance equal to 1. Normalization is always recommended in the case of water quality data, which comprise parameters with very different variances, thus reducing the influence of highly variable parameters (Khalil & Ouarda, 2009).

A ANOVA one-way analysis of variance was used to assess potential significant differences between samples from the same reservoir collected in the dry (August to December) and rainy (May to July) periods.

All tests were performed using the PAST – Paleontological Statistics program, version 3.04 (Hammer et al., 2001). A value of 0.05 was adopted as the critical level for all statistical tests, at a confidence level of 95%.

Geochemical modeling

The PHREEQC software (Parkhurst & Appelo, 2013) has been widely employed for geochemical modeling (Abdel Wahed et al., 2014; Merchán et al., 2015; Liu et al., 2017, 2020a; Barzegar et al., 2018).

In direct geochemical modeling, the PHREEQC simulates the evaporation process considering that reservoir water geochemically evolves through successive evaporations of an initial sample, with progressive removal of mineral phases when saturation limits are reached, producing a more concentrated final sample.

The modeling was applied separately in each of the reservoirs. As a starting point for the simulation, a less saline water sample (initial sample) was used, with moles of water being removed as a function of the evaporation factor, until obtaining a more saline sample (final sample). Table 1 presents the chemical characteristics of the initial and final samples, alongside the evaporation factor used in the geochemical reservoir modeling. These factors (% of removed water) led to the best modeling reproduction of the real reservoir data (final sample).

The models were designed to simulate the evaporative concentration of 1 L of less saline water, by removing moles of water in 40 steps, with the sample in each step being balanced with the partial pressure of CO_2 in the atmosphere ($1.0x10^{-3.5}$ atm). During the modeling, the mineral phases calcite, dolomite, gypsum and halite were allowed to precipitate if they reached oversaturation (Abdel Wahed et al., 2014).

The saturation index (SI) of the mineral phases was also calculated using thermodynamic data from the phreeqc.dat or wateq4f.dat databases, according to the following equation:

$$SI = log\left(PAI / K_{ps}\right) \quad (2)$$

where PAI is the product of the ionic activity of the dissociated ions in the solution and K_{ps} is the product of the solubility of the chemical constituents involved, at sample temperature.

RESULTS AND DISCUSSION

Reservoir hydrochemistry

Descriptive statistics of the measured parameters are shown in Table 2. The pH values ranged from 7.5 to 9.0 with mean values of 8.2 ± 0.3 for Três Barras, 8.3 ± 0.3 for Algodoeiro and 8.6 ± 0.2 for Glória, indicating that the water samples were slightly alkaline. Electrical conductivity (EC) ranged from 4107 to 15821 µS cm^{-1}, with an average of 11816 ± 2698 for Três Barras, 5818 ± 1765 for Algodoeiro and 11051 ± 1636 for Glória, while TDS varied from 2658 to 8860 mg L^{-1}, with an average of 7407 ± 1554 for Três Barras, 3572 ± 1016 for Algodoeiro and 6993 ± 1318 for Glória. The higher EC and TDS values for the Três Barras and Glória reservoirs may be due to their older age in relation to the Algodoeiro reservoir and a significant evaporation influence. Greater age leads to increased residence time for water-rock interactions, which contribute to greater minerals dissolution and, therefore, increased TDS (Santos et al., 2000; Singh et al., 2008). Evaporation decreases reservoir volume, which also contributes to increased TDS. During the period of this study, average decreases in reservoir volumes in relation to total capacity of 58% for Três Barras; 35% for Glória and 25% for Algodoeiro were observed (Agência Nacional de Águas, 2021).

According to the Richards diagram (Delgado et al., 2010), which classifies waters for agricultural purposes based on EC values, the waters of the three reservoirs present a very high risk of salinization for use in irrigation (mean EC > 2250 µS cm^{-1}).

The reservoir waters presented, on average, a total of cations and anions, respectively, of 2245 and 4243 mg L^{-1} at Três Barras, 1034 and 2039 mg L^{-1} at Algodoeiro and 2244 and 4228 mg L^{-1} at Glória. Thus, the cationic abundance in relation to the total of cations was on average, Na^+ (70%), followed by Mg^{2+} (17%), Ca^{2+} (11%) and K^+ (2%) at Três Barras, Na^+ (71%), Mg^{2+} (17%), Ca^{2+} (10%) and K^+ (2%) at Algodoeiro and Na^+ (63%), Mg^{2+} (19%), Ca^{2+} (11%) and K^+ (7%) at Glória. The anions presented, on average, an abundance in relation to the total anionic content, of Cl^- (91%), SO_4^{2-} (5%) and HCO_3^- (4%) at Três Barras, Cl^- (82%), SO_4^{2-} (9%) and HCO_3^- (9%) at Algodoeiro and Cl^- (80%), SO_4^{2-} (12%) and HCO_3^- (8%) at Glória. Regarding TDS, the cations and anions on average constitute, respectively, 30 and 57% at the Três Barras reservoir, 29 and 57% at Algodoeiro and 32 and

Table 1. Chemical water sample characteristics used in the geochemical modeling of the investigated reservoirs.

Reservoir/	Três Barras 65% water removal		Algodoeiro 10% water removal		Glória 18% water removal	
Parameter	Initial sample	Final sample	Initial sample	Final sample	Initial sample	Final sample
pH	8.2	8.5	8.5	8.6	8.2	8.5
TDS (mg L^{-1})	3952	8860	3758	5039	4340	8110
Na^+ (mg L^{-1})	794.0	2238	903.6	1143	1026	1235
K^+ (mg L^{-1})	15.40	54.30	31.13	36.13	47.40	153.5
Ca^{2+} (mg L^{-1})	77.58	179.6	159.8	110.4	217.2	198.2
Mg^{2+} (mg L^{-1})	147.6	251.0	195.8	182.8	343.8	374.9
SO_4^{2-} (mg L^{-1})	34.20	46.79	59.19	65.92	124.0	128.2
Cl^- (mg L^{-1})	1645	4656	2198	2375	2493	3270
HCO_3^- (mg L^{-1})	139.2	204.7	204.2	203.6	247.9	621.9

Table 2. Descriptive statistics of the measured water parameters for the Três Barras, Algodoeiro and Glória reservoirs. Minimum value (Min), maximum (Max), mean ± standard deviation (Mean ± SD) and number of samples (N).

Reservoir/	**Três Barras N = 10**		**Algodoeiro N = 9**		**Glória N = 10**	
Parameter	**Min-Max**	**Means ± SD**	**Min-Max**	**Means ± SD**	**Min-Max**	**Means ± SD**
pH	7.5-8.6	8.2 ± 0.3	7.7-8.6	8.3 ± 0.3	8.2-9.0	8.6 ± 0.2
T (°C)	24.7-29.0	26.9 ± 1.3	24.1-30.4	26.9 ± 1.9	23.4-28.9	26.4 ± 1.7
EC (µS cm $^{-1}$)	6056-15821	11816 ± 2698	4107-9124	5818 ± 1765	7750-12835	11051 ± 1636
TDS (mg L^{-1})	3952-8860	7407 ± 1554	2658-5109	3572 ± 1016	4340-8110	6993 ± 1318
Na^+ (mg L^{-1})	794.2-2238	1569 ± 372	449.1-1143	729.1 ± 247.4	1026-2014	1426 ± 267.5
K^+ (mg L^{-1})	15.42-54.30	34.61 ± 11.64	15.09-36.13	23.37 ± 7.38	47.40-251.8	126.0 ± 69.0
Ca^{2+} (mg L^{-1})	77.58-394.3	252.0 ± 106.6	77.34–159.8	101.7 ± 26	64.61-793.1	248.2 ± 225.4
Mg^{2+} (mg L^{-1})	147.6-751.0	389.4 ± 172.2	141.1-250.4	179.8 ± 34.56	262.3-756.0	406.0 ± 154.7
SO_4^{2-} (mg L^{-1})	34.20-984.6	221.9 ± 338.9	23.00-504.3	177.8 ± 168.6	62.88-2113	483.7 ± 625.0
Cl^- (mg L^{-1})	1645-4797	3843 ± 875	1037-2375	1682 ± 545.9	2493-4073	3398 ± 493.6
HCO_3^- (mg L^{-1})	139.2-216.9	178.1 ± 23.1	121.5-204.2	179.2 ± 29.18	97.50-621.9	346.5 ± 173.6

EC = electrical conductivity; TDS = total dissolved solids.

61% at Glória. Ionic compositions were not statistically different (ANOVA) between the dry and rainy periods at the three reservoirs.

Hydrochemical parameters, including pH, TDS and main ions, were applied to the PCA to identify differences between reservoirs and possible factors influencing these differences. The PCA results, including percentage of variance, cumulative percentage of variance and the contribution weights of each variable, are displayed in Table 3.

The first two components together represent 74.1% (PC1 55.0%; PC2 19.1%) of the information contained in the initial variables. Based on the contribution loading of each variable (Table 2), PC1 is strongly associated (loading > 0.700) with TDS and most of the larger ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-), while PC2 displays a moderate positive association with TDS (loading = 0.565), Na^+ (loading = 0.591) and Cl^- (loading = 0.624).

Figure 2 shows the location of the samples in the plane formed by the PC1 and PC2 eigenvalues. The projection of the original variables (in green) was also included to visualize the degree of participation of each original variable in the principal components. The projection of the original variables indicates that samples located in the negative PC1 and PC2 quadrant presented lower TDS values and lower ionic concentrations, while samples distributed in the positive PC1 and PC2 quadrant display higher TDS, Na^+ and Cl^- values.

The plane formed by PC1 and PC2 separated the samples from the three reservoirs into three distinct groups. The group formed by samples from the Algodoeiro reservoir is located in the negative PC1 and PC2 region, separated from the samples from the other reservoirs, due to lower ionic concentrations and TDS values.

Table 3. Experimental parameter loadings for the first two principal components (in bold, strong weights > 0.700 and moderate weights < 0.700 and > 0.500).

Parameter	**PC1**	**PC2**
pH	0.512	0.146
TDS (mg L^{-1})	**0.784**	**0.565**
Na^+ (mg L^{-1})	**0.727**	**0.591**
K^+ (mg L^{-1})	**0.788**	-0.424
Ca^{2+} (mg L^{-1})	**0.749**	0.008
Mg^{2+} (mg L^{-1})	**0.886**	0.002
SO_4^{2-} (mg L^{-1})	0.671	-0.474
Cl^- (mg L^{-1})	**0.775**	**0.624**
HCO_3^- (mg L^{-1})	0.642	-0.492
Total variance (%)	55.0	19.1
Cumulative variance (%)	55.0	74.1

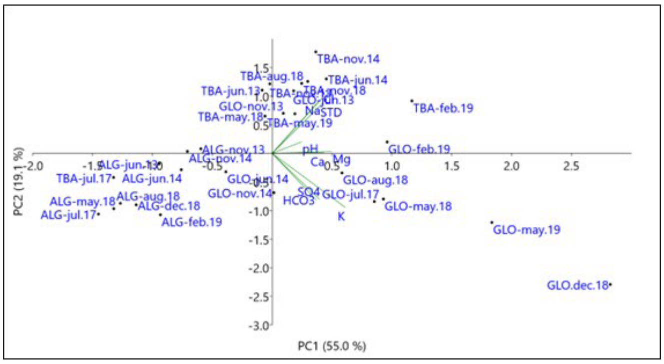

Figure 2. Location of reservoir samples in the plane formed by the first two principal components PC1 × PC2. The projection of the original variables appears in green. Sample code = name of reservoir-month.year of sampling. ALG = Algodoeiro; TBA = Três Barras; GLO = Glória.

In general, the group formed by samples from the Três Barras reservoir occupied the positive region of PC1 and PC2, while the group of samples from the Glória reservoir was distributed in the positive PC1 region and negative PC2 region. The loadings indicate that the samples located on the positive side of PC2 display higher TDS, Na^+ and Cl^- values, while samples located on the negative side of PC2 present higher K^+, HCO_3^- and SO_4^{2-} concentrations. Therefore, the differences between the Três Barras and Glória reservoirs are a consequence of chemical water variations due to evaporation, leading to increased salinization at Três Barras in relation to Glória. According to the Hardie-Euguster model, modified by Drever (1982), successive evaporation processes can lead to calcite precipitation, followed by gypsum, progressively removing HCO_3^- and SO_4^{2-} and increasing Na^+ and Cl^- (Drever, 1982; Abdel Wahed et al., 2015).

Reservoir hydrogeochemistry

Ions dissolved in water can originate from a variety of natural processes, such as atmospheric precipitation, weathering and evaporation. The Gibbs diagram (Gibbs, 1970) is widely used to distinguish the effects of these different processes. The diagram is built by plotting the $Na^+/(Na^+ + Ca^{2+})$ ratios as a function of TDS and is shaped like a "boomerang". Waters with $Na^+/(Na^+ + Ca^{2+}) < 0.5$ are located to the left of the middle part of the "boomerang", as they present higher Ca^{2+} and HCO_3^- concentrations compared to Na^+ and Cl^-, indicating that the final dominant mechanism is weathering. Waters with high $Na^+/(Na^+ + Ca^{2+})$ are distributed at the extremes of the "boomerang". Waters resulting from salinization by evaporation are located on the upper right side, while less saline waters due to the influence of recent precipitation and which have not had enough time of contact with minerals for geochemical changes to occur are located at the lower right (Marandia & Shand, 2018).

Reservoir water samples are characterized by high $Na^+/(Na^+ + Ca^{2+})$ values and TDS concentrations and, thus were positioned at the upper right of the diagram (Figure 3), indicating evaporation as the main mechanism responsible for current chemical water characteristics. The semi-arid conditions of the region favor the continuous water evaporation over a very long period of time, causing a dramatic effect on reservoir water chemistry, resultingin very high Na^+ e Cl^- levels.

To identify the main hydrogeochemical processes in the investigated reservoirs, the relationships between the main ions and the geochemical modeling employing PHREEQC were used. These methods have proven efficient in identifying geochemical sources and processes involved in the ionic composition of surface and groundwater (Sharma et al., 2012; Abdel Wahed et al., 2014; Han et al., 2014; Merchán et al., 2015; Singh et al., 2017; Guo et al., 2018; Liu et al., 2020c, Wisitthammasri et al., 2020).

In general, most Cl^- originates from atmospheric or seawater sources, and its primary lithogenic source is weathering halite and evaporites. The relationship between Na^+ and Cl^- has been used to assess the contribution of these sources, compared with the Na^+/Cl^- ratios in meq L^{-1} of halite (1.0) and marine aerosol (0.85). Abnormal concentrations can result from saline waste leaching and domestic and industrial waste (Singh et al., 2005; Sharma et al., 2012, Morán-Ramírez et al., 2016). The evaporation process also contributes to significant increases in Cl concentrations. Liu et al. (2020a) and Hardie & Eugster (1970) indicated that Na^+ and K^+ should behave similarly, and simply accumulate in solution during evaporation.

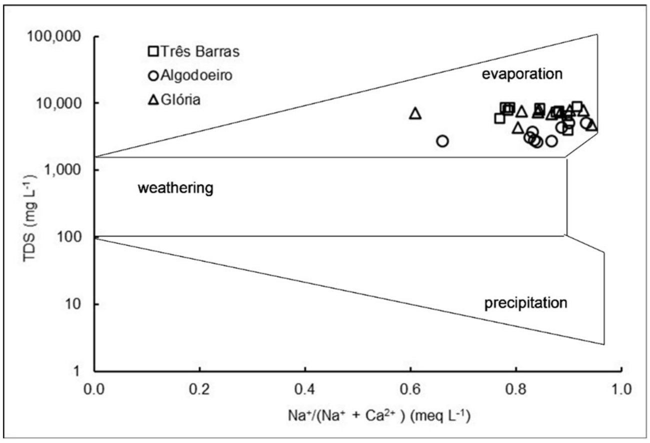

Figure 3. Gibbs diagram indicating the investigate reservoir samples.

Figure 4a shows the relationship of $Na^+ + K^+$ with Cl^- for the reservoir samples, where the 1:0.85 line was included, which corresponds to the relationship in atmospheric precipitation (Drever, 1982). Almost all samples were below the 1:0.85 line, indicating that Na^+ and K^+ concentrations were lower than expected if marine aerosol were the only source of these ions. Therefore, the ion exchange process may also be involved in the control of Na^+ and K^+ concentrations. According to Slama & Bouhlila (2017), ion exchanges with clay materials are usually observed when the water is being salinized.

In reverse ion exchange, the Ca^{2+} ions present in clay minerals are exchanged for the Na^+ and/or K^+ ions in the water (Equation 3), decreasing their concentrations in water and increasing Ca^{2+}. In saline water during ion exchange with clay minerals, K^+ is preferred over Na^+ in exchange sites and the exchangeable cation is always initially Ca^{2+} (Drever, 1982).

$$CaX_2 + 2\,Na^+ \rightarrow Ca^{2+} + NaX \tag{3}$$

The relationship between $(Na^+ + K^+) - Cl$ with $(Ca^{2+} + Mg^{2+}) - (SO_4^{2-} - HCO_3^-)$ was used to confirm the possibility of the ion exchange process. This relationship represents the amount of Na^+ and/or K^+, Ca^{2+} and/or Mg^{2+} gained or lost from other sources, except for the contribution of marine aerosol and/or halite, calcite, dolomite and gypsum. If ion exchange is a significant process, the relationship between these parameters should be linear, with the slope close to -1.0 (Farid et al., 2015; Jia et al., 2020; Wisitthammasri et al., 2020). The results were very close to a straight line with a slope of -1.001 (Figure 4b), indicating that ion exchange significantly affected reservoir water hydrochemistry.

Potential SO_4^{2-} sources include atmospheric precipitation, gypsum or anhydrite dissolution and pyrite oxidation, as well as some potential contribution from anthropogenic inputs (Gaillardet et al., 1999; Morán-Ramírez et al., 2016). The mean SO_4^{2-}/Cl^- ratios in meq L^{-1} were 0.040 at Três Barras, 0.095 at Algodoeiro and 0.101 at Gloria. At Algodoeiro and Glória, the ratios were equivalent to the marine aerosol ratio (0.104), thus suggesting that atmospheric precipitation should be the main source of SO_4^{2-} for the water in these reservoirs. At Lake Magadi, a saline lake in East Africa, progressive SO_4^{2-} removal during salinization evolution has been observed, attributed to the sulfate reduction process (Drever, 1982). It is possible, therefore, that this is the cause of the lower SO_4^{2-}/Cl^- ratio value at the Três Barras reservoir.

Weathering of carbonate and silicate minerals and the dissolution of evaporites are the main sources of dissolved ions in water. The HCO_3^-/Na^+ versus Ca^{2+}/Na^+ ratio has been employed to assess the relative importance of these sources to ionic water composition (Sharma et al., 2012; Morán-Ramírez et al., 2016).

Figure 4c suggests that water chemical composition is largely controlled by silicate weathering, with a limited contribution from carbonate dissolution. In an environment where the chemical water

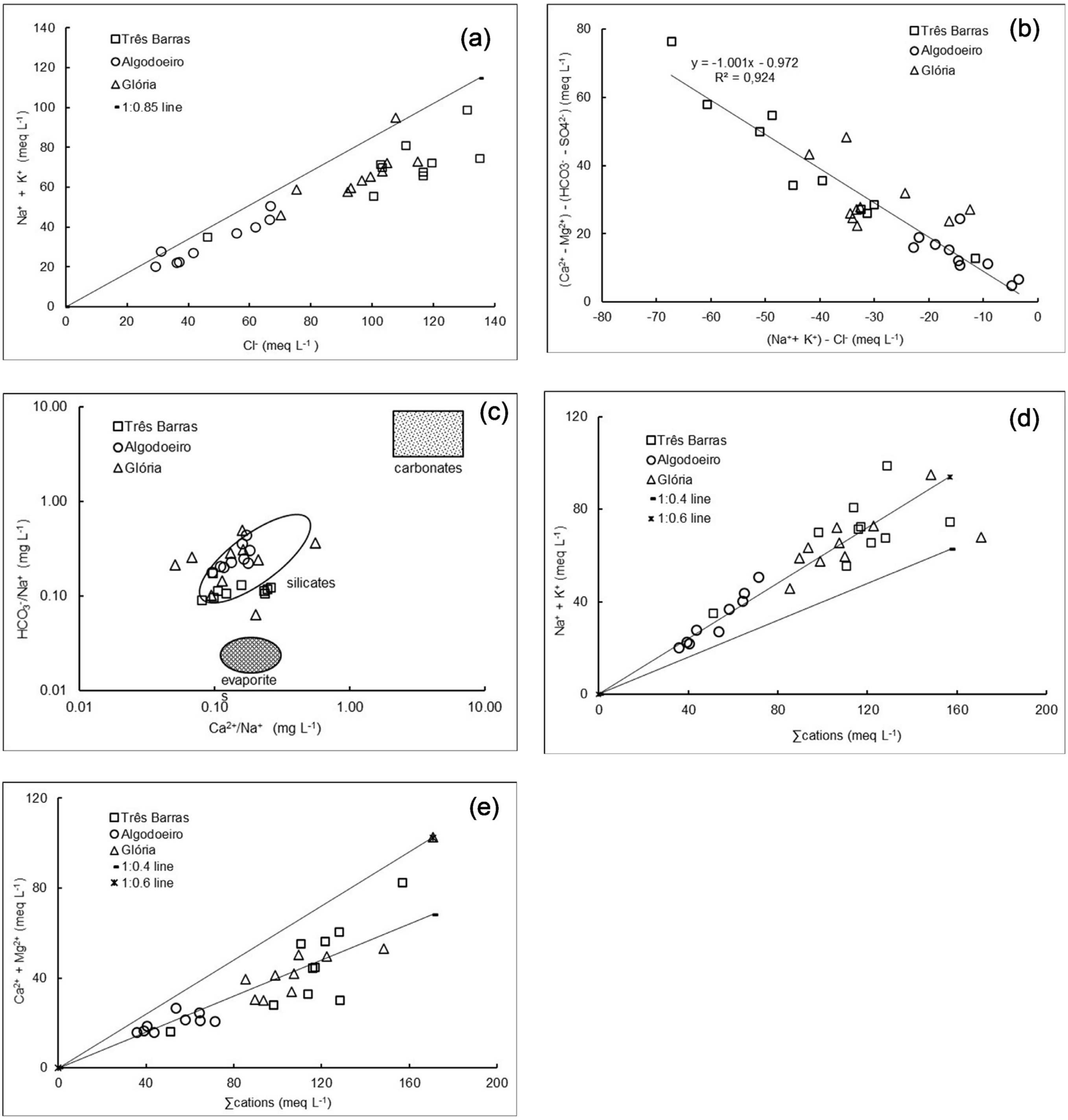

Figure 4. Dispersion graphs: (a) $Na^+ + K^+$ vs Cl^-; (b) $(Na^+ + K^+)$ - Cl vs $(Ca^{2+} + Mg^{2+})$ – $(SO_4^{2-}$ - $HCO_3^-)$; (c) HCO_3^-/ Na^+ vs Ca^{2+}/ Na^+; (d) Na^+ + K^+ vs ∑cations; (e) Ca^{2+} + Mg^{2+} vs ∑cations.

composition is mainly controlled by evaporation, as in the case of the investigated reservoirs (Figure 3), HCO_3^- is progressively removed from the water, preferentially precipitating as calcite (Drever, 1982), which corroborates the limited participation of carbonates in ionic water composition of. There is no evidence of the presence of evaporites in the reservoir region, thus, Na^+ and K^+ must be derived mainly from atmospheric sources and the weathering of silicates rich in sodium and potassium.

The dissolution or alteration of mineral silicates present in bedrock is more difficult to assess, as they degrade incongruously, generating solid phases (usually clays) together with the dissolved ionic species (Drever, 1982; Das & Kaur, 2001; Subramani et al., 2010).

Silicate weathering can be understood through the relationships between $(Na^+ + K^+)$ and $(Ca^{2+} + Mg^{2+})$ with the total cations (∑cations) generated in silicate degradation reactions

(Sharma et al., 2012; Wisitthammasri et al., 2020). Figures 4d and 4e indicate the participation of silicates in Na^+, K^+, Ca^{2+} and Mg^{2+} concentrations. The reservoir samples were distributed for $Na^+ + K^+$ close to the 1:0.6 line and for $Ca^{2+} + Mg^{2+}$ around the 1:0.4 line, which correspond to the $\left(Na^+ + K^+)|\sum cations\right)$ and $\left(Ca^{2+} + Mg^{2+})|\sum cations\, ratios\right)$, respectively, according to Equation 4 (Drever, 1982). This means that the CO_2-enriched waters from the reservoirs react with the silicates of the host rocks, specifically plagioclase ($Na_{0.62}Ca_{0.38}Al_{1,38}Si_{2.62}O_8$), feldspar ($KAlSi_3O_8$) and biotite ($KMg_3AlSi_3O_{10}(OH)_2$), leaching Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO_3^- and converting into kaolinite ($Al_2Si_2O_5(OH)_4$).

$$\begin{gathered}177\, Na_{0.62}Ca_{0.38}Al_{1.38}Si_{2.62}O_8 + 7.3\, KMg_3AlSi_3O_{10}\left(OH\right)_2 + \\ 13\, KAlSi_3O_8 + 412.5\, H_2O + 310\, CO_2 = 133\, Al_2Si_2O_5\left(OH\right)_4 + \\ 110\, Na^+ + 68\, Ca^{2+} + 22\, Mg^{2+} + 20\, K^+ + 270\, SiO_2 + 310\, HCO_3^-\end{gathered} \tag{4}$$

The evaluation presented herein for silicate weathering in the investigated three reservoirs is consistent with the results obtained by Sharma et al. (2012) for surface and groundwater in the Mahi River basin in western India. Based on HCO_3^-/Na^+ relationships and ($Na^+ + K^+$) and ($Ca^{2+} + Mg^{2+}$) versus ∑cations, the authors concluded that silicate weathering was the main source of Na^+, K^+, Ca^{2+}, Mg^{2+}. They also suggested that the poor correlations between HCO_3^- and Ca^{2+} and Mg^{2+} indicate the limited contribution of carbonates. They also highlighted that the local geology favors silicate weathering as the most likely cation and bicarbonate source.

Alves et al. (2021), when assessing reservoirs undergoing increasing salinization processes in northeastern Brazil, also concluded that atmospheric transport and silicate were the main geochemical processes responsible for the chemical characteristics of the waters of the investigated reservoirs, with a smaller contribution to carbonate dissolution.

Wisitthammasri et al. (2020) indicated that the fact that they did not observe a relationship between ($Ca^{2+} + Mg^{2+}$) with HCO_3^-, in agreement with the theoretical range predicted for carbonate dissolution, is an indication that water hydrochemistry in the Province of Saraburi/Thailand is consistent with silicate minerals. Therefore, they suggested that the chemical composition of groundwater in this area is influenced by the weathering of rocks containing minerals such as biotite, feldspar and quartz.

Geochemical modeling

Geochemical modeling was applied in the present study, as employed by Alves et al. (2021), between two water samples from each reservoir, selected considering that they are representative of the data set variability of each reservoir. Thus, the ionic composition of the sample with the lowest salinity (< TDS) was taken as a starting point for each reservoir and the ionic composition of the sample with the highest salinity (> TDS) was simulated using the PHREEQC (Parkhurst; Appelo, 2013), by removing moles of water, as a function of the evaporation factor.

To study the behavior of the main solutes during the water evaporation evolution from the investigated reservoirs, the main ion concentrations and the saturation indices (SI) were plotted against chloride. In general, ionic species concentrations and saturation indices are plotted against Cl^-, as chloride behaves conservatively once dissolved, and also because this indicates the degree of solute concentration in water, due to evaporation evolution (Banks et al., 2004; Smith; Compton, 2004). In relation to a specific mineral phase, an $SI < -0.05$ indicates an undersaturation state (with a tendency towards dissolution) and an $SI > 0.05$ corresponds to oversaturation (with a tendency towards precipitation), while an SI between - 0.05 and +0.05 denotes an equilibrium state, *i.e.*, saturation conditions (Parkhurst; Appelo, 2013).

Figures 5a, 5b, and 5c indicate the variations in saturation indices with respect to chloride. The initial water is oversaturated at all three reservoirs in relation to calcite and dolomite and undersaturated in relation to gypsum and halite. The SI calculated in the modeling for the Glória and Algodoeiro reservoirs (Figure 5a,c) evolved in a very similar way, with calcite and dolomite precipitation occurring in the initial phase and then remaining subsaturated and saturated, respectively. Kinetic factors should be responsible for maintaining dolomite saturation after precipitation (Banks et al., 2004). Halite and gypsum remain undersaturated, indicating a slight trend towards a decrease in SI with increasing salinization (increases in Cl^-), while for the initial oversaturation of calcite and dolomite was much lower ($SI<<1$) at the Três Barras reservoir (Figure 5e), and halite and gypsum showed a clear increase in SI with increasing salinization.

The variations in the concentrations of ionic species, calculated in the modeling in relation to chloride, are presented in Figures 5b, 5d, 5e and 5f. Na^+ and Cl^- are dominant in the initial and final water solutions and behave conservatively. Therefore, their concentrations increase in the same proportion and are controlled by evaporation (Huang et al., 2009). Regarding Ca^{2+} and Mg^{2+}, after an initial reduction due to carbonate precipitation, displayed an increasing increase in concentrations, with more pronounced increases for the Três Barras reservoir due to the higher evaporation factor (65%). Concerning HCO_3^-, this ion presented a high reduction at the beginning (199.5 to 23.73 mg L^{-1} at Glória, 263.1 to 46.20 mg L^{-1} in Algodoeiro and 212.9 to 56.72 mg L^{-1} at Três Barras), followed by a small decrease until reaching the final value.

Chemical Ca^{2+}, Mg^{2+} and HCO_3^- variations in the water of the reservoirs under evaporation are in agreement with that predicted by the Hardie-Eugster model. According to the model as modified by Drever (1982), chemical variations are explained in terms of successive chemical divisions. Chemical division occurs when less soluble mineral starts to precipitate, removing solutes and leading to changes in water composition. This, in turn, results in water concentration variations of the ions that compose the precipitate, leading to increased concentrations of ions present at higher concentration and decrease concentrations of ion present at lower concentrations in the solution. The Ca^{2+} and Mg^{2+} concentrations in meq L^{-1} in the initial waters of the reservoirs are higher than HCO_3^- and, as predicted by the Hardie-Eugster model, calcite and dolomite precipitation leads to increased Ca^{2+} and Mg^{2+} concentrations compared to HCO_3^-, whose concentration decreases over successive evaporations.

Regarding K^+ and SO_4^{2-}, these ions showed little variation with chloride. As they were present at the lowest concentrations

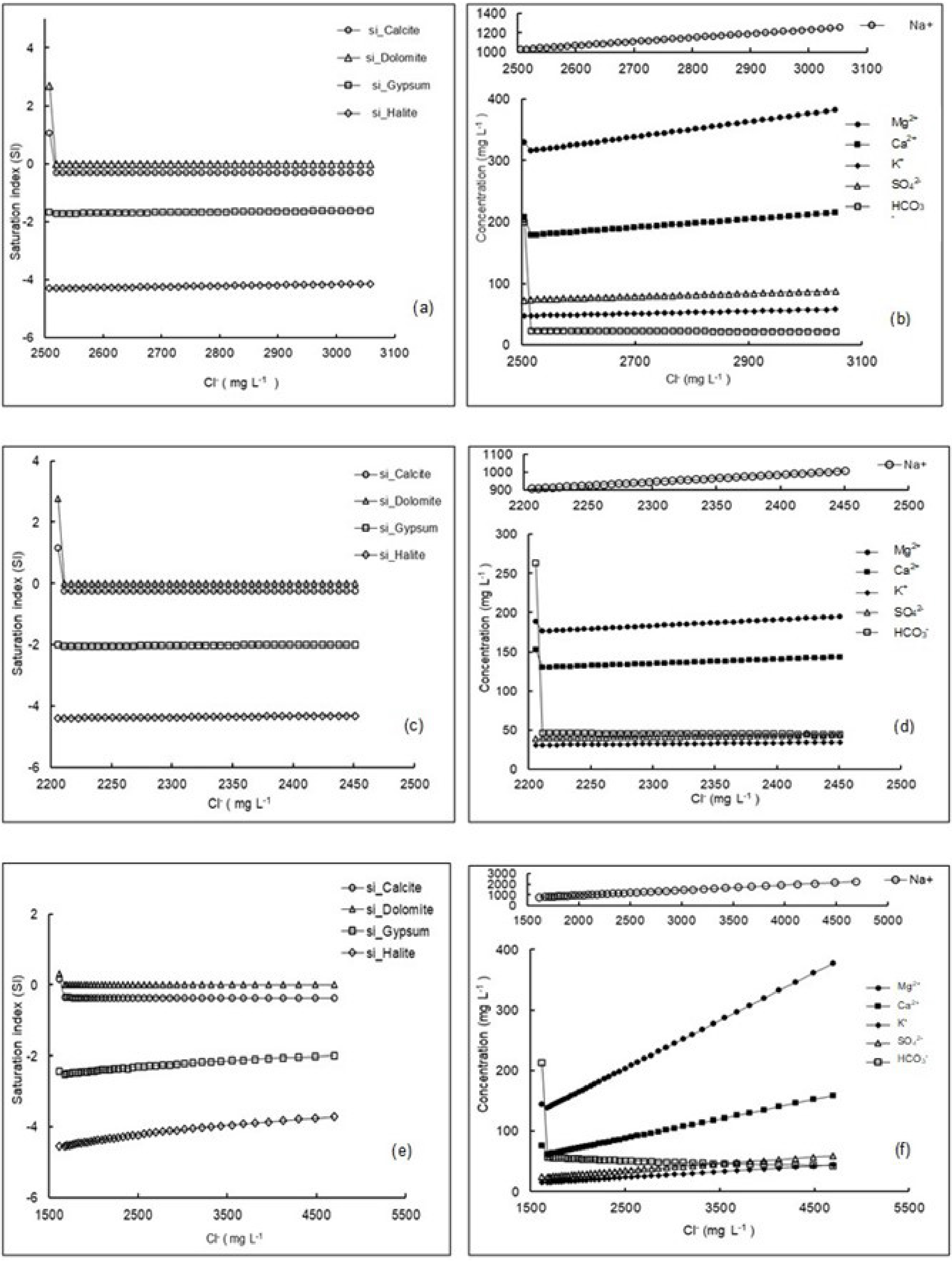

Figure 5. Evolution of mineral saturation indices and ionic concentrations during evaporation as indicated by PHREEQC modeling.

Table 4. Comparison between the actual water composition in the investigated reservoirs (final sample) and the evaporation modeling results.

Reservoir/	Três Barras 65% water removal		Algodoeiro 10% water removal		Glória 18% water removal	
Parameter	Final sample	Modeling result	Final sample	Modeling result	Final sample	Modeling result
pH	8.4	7.9	8.6	7.9	8.5	7.8
Na^+ (mg L^{-1})	2238	2264	1143	1007	1235	1255
K^+ (mg L^{-1})	54.30	43.95	36.13	34.67	153.5	57.93
Ca^{2+} (mg L^{-1})	179.6	158.8	110.4	143.2	198.2	214.9
Mg^{2+} (mg L^{-1})	251.0	377.5	182.8	194.7	374.9	381.6
SO_4^{2-} (mg L^{-1})	46.79	59.22	65.92	66.02	128.2	87.36
Cl^- (mg L^{-1})	4656	4694	2375	2450	3270	3054
HCO_3^- (mg L^{-1})	204.7	42.85	203.6	44.82	621.9	22.46

between cations and anions, respectively, these ions must, during evaporation, accumulate proportionally to their initial concentrations (Abdel Wahed et al., 2014).

Table 4 demonstrates that the modeling not only reproduces the trend observed in the actual hydrochemical data (Table 2), but also indicated ionic concentrations consistent with those observed for the actual reservoir samples (final sample). The difference between the actual values (final sample) and those calculated by the modeling for pH and most ions was less than ± 10%, indicating excellent agreement.

The highest deviation was observed for HCO_3^- at all three reservoirs, where real water concentrations were much higher than predicted by the modeling. Similar deviations were observed in the Khakassian/Siberia (Banks et al., 2004) and Qarun/Egypt (Abdel Wahed et al., 2014) lakes, attributed to the fact that calcite precipitates more slowly than HCO_3^- decreases during evaporation (Smith; Compton, 2004). Drever (1982) also points out that dissolution-precipitation chemistry is not only controlled by solubility, as considered in the applied modeling, but also by kinetics.

At the Três Barras reservoir, predicted Mg^{2+} concentrations were much higher than the real data. Banks et al. (2004) reported similar results for Lake Khakassian/Siberia, indicating that this may be due to the progressive dolomitization of precipitated calcite, ion exchange or silicate phase sorption.

At the Glória reservoir, simulated K^+ and SO_4^{2-} were over 30% below actual concentrations, suggesting the contribution of additional sources not considered in the modeling process, such as anthropogenic inputs (Abdel Wahed et al., 2014; Alves et al., 2021). The impact of anthropogenic activities may be assessed by the relationship between HCO_3^- and the sum of major cations ($\sum$cations = $[Na^+ + K^+ + Ca^{2+} + Mg^{2+}) - Cl^-]$. The Cl^- subtraction is used to eliminate the effect of salts such as NaCl and $CaCl_2$ so the relationship between HCO_3^- and $\sum$cations begins to represent only mineral dissolution, *i.e.,* carbonates and silicates (Kim, 2003; Barzegar et al., 2018). Samples located on the 1:1 line represent the distribution of ions originating only from carbonate and silicate weathering (Barzegar et al., 2018). Urban, industrial and agricultural wastes can contribute to ionic composition. When this occurs, the samples deviate from the 1:1 line. Figure 6 confirms the occurrence of anthropogenic impacts, mainly at the Glória reservoir, where a greater sample deviation from the 1:1 line is noted.

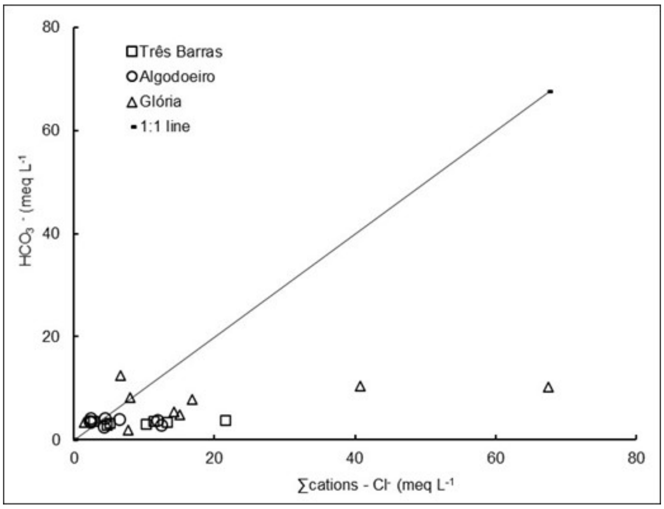

Figure 6. HCO_3^- and $\sum$cations – Cl^- scatter plot.

CONCLUSIONS

The geochemical processes that potentially control chemical water characteristics at the salinized reservoirs Algodoeiro, Glória and Três Barras, located in the state of Sergipe, Northeastern Brazil, were evaluated using the Gibbs diagram, ionic ratios and geochemical modelling.

The reservoir waters presented the same ionic abundance ($Na^+ > Mg^{2+} > Ca^{2+} > K^+$ e $Cl^- > SO_4^{2-} > HCO_3^-$), but distinct chemical compositions. Samples from the Algodoeiro reservoir are distinguished from the other reservoirs due to lower ionic concentrations and TDS values, while samples from the Três Barras reservoir presented higher TDS, Na^+, Mg^{2+}, Ca^{2+} and Cl^- values and lower K^+, HCO_3^- and SO_4^{2-} concentrations compared to the Glória reservoir.

Geochemical evolution was controlled by the evaporation-crystallization process, which may also suffer the influence of anthropogenic inputs. The geochemical processes involved in the chemical composition of water from reservoirs mainly include sea salt dissolution, silicate weathering, ion exchange and, to a lesser extent, carbonate dissolution.

The geochemical modeling confirmed that the evaporation-crystallization process led to an increase in Na^+, Mg^{2+}, Ca^{2+} and Cl^- concentrations and a reduction in HCO_3^- by the precipitation of calcite and dolomite. Furthermore, the simulated models reproduced the trend observed in the real hydrochemical data and demonstrated excellent agreement between the simulated and real ion concentrations for the most of the larger ions. The highest deviation was observed for HCO_3^-, whose actual concentrations were much higher than those predicted by the modeling, attributed to kinetic restrictions concerning calcite precipitation.

ACKNOWLEDGEMENTS

The authors would like to thank the National Council for Scientific and Technological Development (CNPq): This work is part of the project entitled “Hydrogeochemistry of processes that control the salinization of Sergipe reservoirs”, approved in the Universal Call 2018 and financed by CNPq. CAPES for the PNPD scholarship granted.

This study used the data generated in the “Monitoring of Superficial Springs and Reservoirs of the State of Sergipe” project. Thus, we would like to thank the Special Superintendence of Water Resources and the Environment (SERHMA/SEDURBS) and the Technological and Research Institute of Sergipe (ITPS).

REFERENCES

Abdel Wahed, M. S. M., Mohamed, E. A., El-Sayed, M. I., M’nif, A., & Sillanpää, M. (2014). Geochemical modeling of evaporation process in Lake Qarun, Egypt. *Journal of African Earth Sciences*, *97*, 322-330. http://dx.doi.org/10.1016/j.jafrearsci.2014.05.008.

Abdel Wahed, M. S. M., Mohamed, E. A., El-Sayed, M. I., M’nif, A., & Sillanpää, M. (2015). Hydrogeochemical processes controlling the water chemistry of a closed saline lake located in Sahara Desert: lake Qarun, Egypt. *Aquatic Geochemistry*, *21*(1), 31-57. http://dx.doi.org/10.1007/s10498-015-9253-3.

Agência Nacional de Águas – ANA. (2021). *Sistema de Acompanhamento de Reservatórios – SAR*. Brasília: ANA. Retrieved in 2021, January 25, from https://www.ana.gov.br/sar/nordeste-e-semiarido/sergipe

Alencar, N. R. O. (2020). *Processos hidrogeoquímicos envolvidos na salinização dos reservatórios Algodoeiro e Três Barras situados na região do baixo São Francisco no estado de Sergipe* (Dissertação de mestrado). Programa de Pós-graduação em Recursos Hídricos, Universidade Federal de Sergipe, São Cristóvão.

Alves, J. P. H., Fonseca, L. C., Chielle, R. S. A., & Macedo, L. C. B. (2018). Monitoring water quality of the Sergipe River basin: an evaluation using multivariate data analysis. *Revista Brasileira de Recursos Hídricos*, *23*(0), 1-12. http://dx.doi.org/10.1590/2318-0331.231820170124.

Alves, J. P. H., Lima, M. H. R., Dória, J. R., Silva, I. S., & Monteiro, A. S. C. (2021). Hydrogeochemical characterization of reservoir waters undergoing salinization processes in Northeastern Brazil. *Revista Brasileira de Recursos Hídricos*, *26*, 1-16. http://dx.doi.org/10.1590/2318-0331.262120210043.

American Public Health Association – APHA. (2012). *Standard methods for the examination of water and wastewater* (22nd ed.). Washington: APHA.

Banks, D., Parnachev, V. P., Frengstad, B., Holden, W., Karnachuk, O. V., & Vedernikov, A. A. (2004). The evolution of alkaline, saline ground- and surface Waters in the southern Siberian steppes. *Applied Geochemistry*, *19*(12), 1905-1926. http://dx.doi.org/10.1016/j.apgeochem.2004.05.009.

Barzegar, R., Moghaddam, A. A., Nazemi, A. H., & Adamowski, J. (2018). Evidence for the occurrence of hydrogeochemical processes in the groundwater of Khoy plain, northwestern Iran, using ionic ratios and geochemical modeling. *Environmental Earth Sciences*, *77*(16), 1-17. http://dx.doi.org/10.1007/s12665-018-7782-y.

Bomfim, L. F. C., Costa, V. G., & Benvenuti, S. M. P. (2002a). *Projeto cadastro da infra-estrutura hídrica do Nordeste: Estado de Sergipe. Diagnóstico do município de Itabaiana* (22 p.). Aracaju: CPRM. Retrieved in 2021, January 25, from https://rigeo.cprm.gov.br/handle/doc/2513

Bomfim, L. F. C., Costa, V. G., & Benvenuti, S. M. P. (2002b) *Projeto cadastro da infra- estrutura hídrica do Nordeste: Estado de Sergipe. Diagnóstico do Município de Gracho Cardoso* (19 p.). Aracaju: CPRM. Retrieved in 2021, January 25, from https://rigeo.cprm.gov.br/handle/doc/2493

Bouzourra, H., Bouhlila, R., Elango, L., Slama, F., & Ouslati, N. (2015). Characterization of mechanisms and processes of groundwater salinization in irrigated coastal area using statistics, GIS, and hydrogeochemical investigations. *Environmental Science and Pollution Research International*, *22*(4), 2643-2660. PMid:25196959. http://dx.doi.org/10.1007/s11356-014-3428-0.

Connor, J. D., Schwabe, K., King, D., & Knapp, K. (2012). Irrigated agriculture and climate change: the influence of water supply variability and salinity on adaptation. *Ecological Economics*, *77*, 149-157. http://dx.doi.org/10.1016/j.ecolecon.2012.02.021.

Das, B. K., & Kaur, P. (2001). Major ion chemistry of Renuka lake and weathering processes, Sirmaur disrict, Himachal Pradesh, India. *Journal of Environmental Geology*, *40*(7), 908-917. http://dx.doi.org/10.1007/s002540100268.

Delgado, C., Pacheco, J., Cabrera, A., Batllori, E., Orellana, R., & Bautista, F. (2010). Quality of groundwater for irrigation in tropical karst environment: the case of Yucatán, Mexico. *Agricultural Water Management*, *97*(10), 1423-1433. http://dx.doi.org/10.1016/j.agwat.2010.04.006.

Drever, J. I. (1982). *The geochemistry of natural waters: surface and groundwater environments* (3rd ed.). New Jersey: Prentice Hall.

El Yaouti, F., El Mandour, A., Khattach, D., Benavente, J., & Kaufmann, O. (2009). Salinization processes in the unconfined aquifer of Bou-Areg (NE Morocco): A geostatistical, geochemical, and tomographic study. *Applied Geochemistry*, *24*(1), 6-31. http://dx.doi.org/10.1016/j.apgeochem.2008.10.005.

Elsdon, T. S., De Bruin, M., Diepen, N. J., & Gillanders, B. M. (2009). Extensive drought negates human influence on nutrients and water quality in estuaries. *The Science of the Total Environment*, *407*(8), 3033-3043. PMid:19215967. http://dx.doi.org/10.1016/j.scitotenv.2009.01.012.

Farid, I., Zouari, K., Rigane, A., & Beji, R. (2015). Origin of the groundwater salinity and geochemical processes in detritaland carbonate aquifers: Case of Chougafiya basin (Central Tunisia). *Journal of Hydrology*, *530*, 508-532. http://dx.doi.org/10.1016/j.jhydrol.2015.10.009.

Fontes, A. S., Zucchi, M. R., Medeiros, Y. D. P., & Azevedo, A. E. G. (2015). Avaliação dos fatores intervenientes no processo de salinização em reservatórios superficiais do semiárido brasileiro. *Revista Brasileira de Recursos Hídricos*, *20*(3), 708-721. http://dx.doi.org/10.21168/rbrh.v20n3.p708-721.

Gaillardet, J., Dupré, B., Louvat, P., & Allègre, C. J. (1999). Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. *Chemical Geology*, *159*(1-4), 3-30. http://dx.doi.org/10.1016/S0009-2541(99)00031-5.

Gibbs, R. J. (1970). Mechanisms controlling world water chemistry. *Science*, *170*(3962), 1088-1090. PMid:17777828. http://dx.doi.org/10.1126/science.170.3962.1088.

Guo, J., Zhou, X., Wang, L., Zhang, Y., Shen, X., Zhou, H., Ye, S., & Fang, B. (2018). Hydrogeochemical characteristics and sources of salinity of the springs near Wenquanzhen in the eastern Sichuan Basin, China. *Hydrogeology Journal*, *26*(4), 1137-1151. http://dx.doi.org/10.1007/s10040-017-1692-z.

Guo, M., Zhou, X., Li, J., Wu, W., & Chen, Y. (2015). Assessment of the salinization processes in the largest inland freshwater lake of China. *Stochastic Environmental Research and Risk Assessment*, *29*(7), 1823-1833. http://dx.doi.org/10.1007/s00477-014-0995-z.

Hammer, O., Harper, D. A. T., & Ryan, P. D. (2001). *Paleontological statistic.* Oslo: University of Oslo. Retrieved in 2018, January 10, from http://folk.uio.no/ohammer/past

Han, D. M., Song, X. F., Currell, M. J., Yang, J. L., & Xiao, G. Q. (2014). Chemical and isotopic constraints on evolution of groundwater salinization in the coastal plain aquifer of Laizhou Bay, China. *Journal of Hydrology*, *508*, 12-27. http://dx.doi.org/10.1016/j.jhydrol.2013.10.040.

Hardie, L. A., & Eugster, H. P. (1970). The evolution of closed-basin brines. *Mineralogical Society of America - Special Papers*, *3*, 273-290.

Huang, X., Sillanpää, M., Gjessing, E. T., & Vogt, D. R. (2009). Water quality in the Tibetan Plateau: major ions and trace elements in the headwaters of four major Asian rivers. *The Science of the Total Environment*, *407*(24), 6242-6254. PMid:19783282. http://dx.doi.org/10.1016/j.scitotenv.2009.09.001.

Jia, H., Qian, H., Zheng, L., Feng, W., Wang, H., & Gao, Y. (2020). Alterations to groundwater chemistry due to modern water transfer for irrigation over decades. *The Science of the Total Environment*, *717*, 137170. PMid:32062271. http://dx.doi.org/10.1016/j.scitotenv.2020.137170.

Johansson, O., Aimbetov, I., & Jarsjö, J. (2009). Variation of groundwater salinity in the partially irrigated Amudarya River delta, Uzbekistan. *Journal of Marine Systems*, *76*(3), 287-295. http://dx.doi.org/10.1016/j.jmarsys.2008.03.017.

Kaushal, S. S., Duan, S., Doody, T. R., Haq, S., Smith, R. M., Johnson, T. A. N., Newcomb, K. D., Gorman, J., Bowman, N., Mayer, P. M., Wood, K. L., Belt, K. T., & Stack, W. P. (2017). Human-accelerated weathering increases salinization, major ions, and alkalinization in fresh water across land use. *Applied Geochemistry*, *83*, 121-135. PMid:30220785. http://dx.doi.org/10.1016/j.apgeochem.2017.02.006.

Khalil, B., & Ouarda, T. B. M. J. (2009). Statistical approaches used to assess and redesign surface water-quality monitoring networks. *Journal of Environmental Monitoring*, *11*(11), 1915-1929. PMid:19890548. http://dx.doi.org/10.1039/b909521g.

Kim, K. (2003). Long-term disturbance of groundwater chemistry following well installation. *Ground Water*, *41*(6), 780-789. PMid:14649861. http://dx.doi.org/10.1111/j.1745-6584.2003.tb02419.x.

Koh, D.-C., Ko, K.-S., Kim, Y., Lee, S.-G., & Chang, H.-W. (2007). Effect of agricultural land use on the chemistry of groundwater from basaltic aquifers, Jeju Island, South Korea. *Hydrogeology Journal*, *15*(4), 727-743. http://dx.doi.org/10.1007/s10040-006-0142-0.

Lerman, A. (2009). Saline lakes' response to global change. *Aquatic Geochemistry*, *15*(1-2), 1-5. http://dx.doi.org/10.1007/s10498-008-9058-8.

Liu, F., Zhao, Z., Yang, L., Ma, Y., Xu, Y., Gong, L., & Liu, H. (2020c). Geochemical characterization of shallow groundwater using multivariate statistical analysis and geochemical modeling in an irrigated region along the upper Yellow River, Northwestern China. *Journal of Geochemical Exploration*, *215*, 106565. http://dx.doi.org/10.1016/j.gexplo.2020.106565.

Liu, P., Hoth, N., Drebenstedt, C., Sun, Y., & Xub, Z. (2017). Hydro-geochemical paths of multi-layer groundwater system in coal mining regions: using multivariate statistics and geochemical modeling approaches. *The Science of the Total Environment*, *601–602*, 1-14. PMid:28551533. http://dx.doi.org/10.1016/j.scitotenv.2017.05.146.

Liu, X., Zhang, G., Zhang, J., Xu, Y. J., Wu, Y., Wu, Y., Sun, G., Chen, Y., & Ma, H. (2020a). Efects of irrigation discharge on salinity of a large freshwater lake: a case study in Chagan Lake, Northeast China. *Water*, *12*, 2112. http://dx.doi.org/10.3390/w12082112.

Marandia, A., & Shand, P. (2018). Groundwater chemistry and the Gibbs Diagram. *Applied Geochemistry*, *97*, 209-212. http://dx.doi.org/10.1016/j.apgeochem.2018.07.009.

Meireles, A. C. M., Frischkorn, H., & Andrade, E. M. (2007). Sazonalidade da qualidade das águas do açude Edson Queiroz, bacia do Acaraú, no Semiárido cearense. *Ciência Agronômica*, *38*(1), 25-31. Retrieved in 2020, December 11, from http://ccarevista.ufc.br/seer/index.php/ccarevista/article/view/145

Melo, A. P. S., Garcia, H. L., Mendonça, C. S., Barreto, V. L., & Garcia, C. A. B. (2018). Utilização do Índice de Qualidade de Água de Reservatório – IQAR para avaliação da qualidade da água dos reservatórios Algodoeiro e Glória. In L. M. Schiebelbein (Ed.), *Gestão de recursos hídricos e sustentabilidade* (pp. 66-76, Vol. 2). Ponta Grossa: Atena. https://doi.org/10.22533/at.ed.2541909018.

Merchán, D., Auqué, L. F., Acero, P., Gimeno, M. J., & Causapé, J. (2015). Geochemical processes controlling water salinization in an irrigated basin in Spain: identification of natural and anthropogenic influence. *The Science of the Total Environment*, *502*, 330-343. PMid:25262295. http://dx.doi.org/10.1016/j.scitotenv.2014.09.041.

Monteiro, A. S. C., Silva, E. L., Silva, R. R. M., & Alves, J. P. H. (2021). Mecanismos que controlam as características das águas dos reservatórios do estado de Sergipe, Nordeste do Brasil. *Scientia Plena*, *17*(01), 011701. http://dx.doi.org/10.14808/sci.plena.2021.011701.

Morán-Ramírez, J., Ledesma-Ruiz, R., Mahlknecht, J., & Ramos-Leal, J. A. (2016). Rockewater interactions and pollution processes in the volcanic aquifer system of Guadalajara, Mexico, using inverse geochemical modeling. *Applied Geochemistry*, *68*, 79-94. http://dx.doi.org/10.1016/j.apgeochem.2016.03.008.

Müller, B., & Gächter, R. (2011). Increasing chloride concentrations in Lake Constance: characterization of sources and estimation of loads. *Aquatic Sciences*, *74*(1), 101-112. http://dx.doi.org/10.1007/s00027-011-0200-0.

Nielsen, D. L., Brock, M. A., Rees, G. N., & Baldwin, D. S. (2003). Effects of increasing salinity on fresh water ecosystems in Australia. *Australian Journal of Botany*, *51*(6), 655-665. http://dx.doi.org/10.1071/BT02115.

Palácio, H. A. Q., Araújo Neto, J. R., Meireles, A. C. M., Andrade, E. M., Santos, J. C. N., & Chaves, L. C. G. (2011). Similaridade e fatores determinantes na salinidade das águas superficiais do Ceará, por técnicas multivariadas. *Revista Brasileira de Engenharia Agrícola e Ambiental*, *15*(4), 395-402. http://dx.doi.org/10.1590/S1415-43662011000400011.

Parkhurst, D. L., & Appelo, C. A. J. (Eds.). (2013). *Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations* (Techniques and Methods, No. 6-A43, 497 p.). Reston: U.S. Department of the Interior, U.S. Department of the Interior, U.S. Geological Survey. Retrieved in 2020, December 11, from http://pubs.usgs.gov/tm/06/a43

Peck, A. J., & Hatton, T. (2003). Salinity and the discharge of salts from catchments in Australia. *Journal of Hydrology*, *272*(1-4), 191-202. http://dx.doi.org/10.1016/S0022-1694(02)00264-0.

Santos, J. S., Oliveira, E., & Massaro, S. (2000). Avaliação da salinização de açudes no semiárido brasileiro por ICP-AES. *Química Nova*, *23*(4), 453-456. http://dx.doi.org/10.1590/S0100-40422000000400004.

Sharma, A., Singh, A. K., & Kumar, K. (2012). Environmental geochemistry and quality assessment of surface and subsurface water of Mahi River basin, western India. *Environmental Earth Sciences*, *65*(4), 1231-1250. http://dx.doi.org/10.1007/s12665-011-1371-7.

Shrestha, S., & Kazama, F. (2007). Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji River basin, Japan. *Environmental Modelling & Software*, *22*(4), 464-475. http://dx.doi.org/10.1016/j.envsoft.2006.02.001.

Singh, A. (2018). Salinization of agricultural lands due to poor drainage: a viewpoint. *Ecological Indicators*, *95*, 127-130. http://dx.doi.org/10.1016/j.ecolind.2018.07.037.

Singh, A. K., Mondal, G. C., Kumar, S., Singh, T. B., Tewary, B. K., & Sinha, A. (2008). Major ion chemistry, weathering processes and water quality assessment in upper catchment of Damodar River basin, India. *Environmental Geology*, *54*(4), 745-758. http://dx.doi.org/10.1007/s00254-007-0860-1.

Singh, A. K., Mondal, G. C., Singh, P. K., Singh, S., Singh, T. B., & Tewary, B. K. (2005). Hydrochemistry of reservoirs of Damodar River basin, India: weathering processes and water quality assessment. *Environmental Geology*, *48*(8), 1014-1028. http://dx.doi.org/10.1007/s00254-005-1302-6.

Singh, C. K., Kumar, A., Shashtri, S., Kumar, A., Kumar, P., & Mallick, J. (2017). Multivariate statistical analysis and geochemical modeling for geochemical assessment of groundwater of Delhi, India. *Journal of Geochemical Exploration*, *175*, 59-71. http://dx.doi.org/10.1016/j.gexplo.2017.01.001.

Singh, K. P., Malik, A., Mohan, D., & Sinha, S. (2004). Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India): a case study. *Water Research*, *38*(18), 3980-3992. PMid:15380988. http://dx.doi.org/10.1016/j.watres.2004.06.011.

Slama, F., & Bouhlila, R. (2017). Multivariate statistical analysis and hydrogeochemical modelling of seawater-freshwater mixing along selected flow paths: case of Korba coastal aquifer Tunisia. *Estuarine, Coastal and Shelf Science*, *198*, 636-647. http://dx.doi.org/10.1016/j.ecss.2016.10.005.

Smith, M., & Compton, J. S. (2004). Origin and evolution of major salts in the Darling pans, Western Cape, South Africa. *Applied Geochemistry*, *19*(5), 645-664. http://dx.doi.org/10.1016/j.apgeochem.2003.10.003.

Sousa, E. S., Pereira, F. S., Cruz, J. W. S., Lisboa, V. A. C., Rosa, M. L. S., & Conceição, H. (2017). Petrografia e química mineral do stock Gracho Cardoso, Domínio Macururé, Sistema Orogênico Sergipano. In *Anais do 27º Simpósio de Geologia do Nordeste*, João Pessoa, PB. Retrieved in 2021, October 12, from http://www.geologiadonordeste.com.br/safetyarea/v3.0/trabalhos/resumo_pdf/17.pdf

Souza Filho, F. D. A. D., & Campos, J. N. B. (2002). Um método paramétrico de avaliação do potencial de salinização de reservatórios aplicado a regiões semiáridas. *Revista Brasileira de Recursos Hídricos*, *10*(2), 5-14. https://dx.doi.org/10.21168/rbrh.v10n2.p5-14.

Subramani, T., Rajmohan, N., & Elango, L. (2010). Groundwater geochemistry and identification of hydrogeochemical processes in a hard rock region, Southern India. *Environmental Monitoring and Assessment*, *162*(1-4), 123-137. PMid:19247793. http://dx.doi.org/10.1007/s10661-009-0781-4.

Swinton, M. W., Eichler, L. W., & Boylen, C. W. (2015). Road salt application diferentially threatens water resources in Lake George, New York. *Lake and Reservoir Management*, *31*(1), 20-30. http://dx.doi.org/10.1080/10402381.2014.983583.

Tweed, S., Grace, M., Leblanc, M., Cartwright, I., & Smithyman, D. (2011). The individual response of saline lakes to a severe drought. *The Science of the Total Environment*, *409*(19), 3919-3933. PMid:21752428. http://dx.doi.org/10.1016/j.scitotenv.2011.06.023.

Vallejos, A., Daniele, L., Sola, F., Molina, L., & Pulido-Bosch, A. (2020). Anthropic-induced salinization in a dolomite coastal aquifer: hydrogeochemical processes. *Journal of Geochemical Exploration*, *209*, 106438. http://dx.doi.org/10.1016/j.gexplo.2019.106438.

Wisitthammasri, W., Chotpantarat, S., & Thitimakorn, T. (2020). Multivariate statistical analysis of the hydrochemical characteristics of a volcano sedimentary aquifer in Saraburi Province, Thailand. *Journal of Hydrology: Regional Studies*, *32*, 100745. http://dx.doi.org/10.1016/j.ejrh.2020.100745.

Zhang, Y., Xu, M., Li, X., Qi, J., Zhang, Q., Guo, J., Yu, L., & Zhao, R. (2018). Hydrochemical characteristics and multivariate statistical analysis of natural water system: a case study in Kangding County, Southwestern China. *Water*, *10*(1), 80. http://dx.doi.org/10.3390/w10010080.

Zhu, B., Wang, X., & Rioual, P. (2017). Multivariate indications between environment and ground water recharge in a sedimentary drainage basin in northwestern China. *Journal of Hydrology*, *549*, 92-113. http://dx.doi.org/10.1016/j.jhydrol.2017.03.058.

Authors contributions

Adnívia Santos Costa Monteiro: Software, methodology.

Eveline Leal da Silva: Investigation.

Nívia Raquel Oliveira Alencar: Investigation.

Crislaine Melo Cardoso: Investigation.

Igor Santos Silva: Software.

Roseane dos Santos Nascimento: Software.

José do Patrocinio Hora Alves: Project administration Management and Coordination responsibility for the research activity planning and execution; validation verification, whether as a part of the activity or separate, of the overall replication/ reproducibility of results/experiments and other research outputs, writing- original draft preparation

Editor-in-Chief: Adilson Pinheiro

Associated Editor: Ibraim Fantin da Cruz