



Research Article

Hydrogeochemical Characteristics of Groundwater in the Prefecture of Bassar, Togo

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Abstract

This study aims to assess the factors and geochemical processes controlling groundwater quality in the prefecture of Bassar. It is a major yam tubers and pre-colonial West African iron production center in Togo but with limited investigations on groundwater chemistry. Conventional hydrochemical techniques with geochemical mass balance calculations, intervariables correlation, and factor analysis with principal component methods were applied to a chemical database of major ions and heavy metals concentrations of twenty borehole water samples. These groundwater samples were collected during the dry season and analyzed following AFNOR standard methods for the examination of water. The results showed fresh and circumneutral groundwater types with pH values between 6.7 and 7.5 with an average of 7.1 and EC between 280 and 1148 $\mu\text{S}/\text{cm}$ and an average of 691 $\mu\text{S}/\text{cm}$. All the hydrochemical parameters comply with the WHO drinking water guideline value except Arsenic content for 5 % of the samples, suggesting potential health risks for residents relying on raw groundwater for drinking purposes. Anions and cations' contributions to groundwater mineralization are in the order of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ and $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$, respectively. The main hydrochemical facies were mixed cations- HCO_3^- water types, followed by accessory Ca-HCO_3 , Mg-HCO_3 , Ca-Mg-Cl , and Mg-Na-HCO_3 , under the control of water-rock interaction mechanisms and human activities influence from agriculture practices. The geochemical processes are silicate minerals hydrolysis, carbonate, and soil salts dissolution, sorption, and cations exchange with the thermodynamic equilibrium of groundwater with kaolinite, muscovite, K-feldspar, and smectites such as Mg-montmorillonite solid phases. Fe/Mn-(hydr)oxide phases in the aquifer matrix exert significant control on the mobility of As and Sb originating from geogenic sources in the study area. This study provides insight into the factors and geochemical processes controlling the groundwater quality, as a baseline tool for water security concerning major and trace constituents in the Bassar prefecture.

Keywords

Arsenic, Cations Exchange, Groundwater, Hydrochemistry, Silicates, Togo

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1. Introduction

Groundwater constitutes an essential natural resource in the life of men, animals, and plants and, therefore, in the balance of ecosystems. Having it available sufficiently and of good quality contributes to maintaining human health and socio-economic development [1]. Global water use continues to increase due to rapid population growth. Thus, we are witnessing the overexploitation of aquifer systems with withdrawals above current recharge rates in parts of the world [2, 3]. This sometimes leads to water shortage problems. Beyond the issues of quantities, anthropogenic factors such as urbanization with the discharge of wastewater, stock farming, agriculture with the use of fertilizers, and mining also generate problems of groundwater contamination and salinization [4-7]. Thus, faced with climatic hazards, available water resources are threatened and pose increasingly complex problems under the influence of combined natural and anthropogenic factors [8-11].

Like many other developing countries, Togo faces numerous environmental challenges regarding water resources in terms of quality and quantity [12]. Indeed, water resources in Togo are subject to climate change's impacts and anthropogenic activities such as agriculture, urbanization, and mining [13-15]. Surface water appears more vulnerable to these impacts [15, 16]. With the help of donors, the Togolese Government initiate various village water programs to improve the supply of drinking water in rural and sometimes peri-urban areas of the country [17]. Unfortunately, studies on water quality and aquifer functioning do not accompany these projects to improve aquifer system development and exploitation strategies.

Nevertheless, few research activities have shown that anthropogenic pollution strongly controls groundwater quality degradation due to domestic and urban wastes, septic tanks, and inadequate sanitation systems. This water quality deterioration is not limited to urban areas [14, 18, 19] but also to rural areas because of agricultural and pastoral activities and the poor practice of hygiene and sanitation rules around water points [20-22]. Certain areas of the country still exist where groundwater's hydrogeochemical characterization and quality assessment are lacking or limited. This is the case in Bassar's prefecture, which represents the central zone of iron exploitation and yam production in Togo. It has not benefited from studies to understand the geochemical process of hydrochemical evolution except for a few works focusing on heavy metal contamination around the mining zone [15, 23]. Then, this study was conducted by considering major ions and trace elements chemistry in the whole prefecture of Bassar, which is mainly rural and where water supply relies on groundwater resource exploitation. The main objective of this study is to improve knowledge regarding groundwater quality in the Bassar prefecture. This involves explicitly characterizing the physicochemical quality of groundwater in Bassar's prefecture and assessing the associated major factors and geo-

chemical processes.

2. Study Area

The prefecture of Bassar is located between 9°00'N to 9°40'N and 0°12'E to 1°00'E (Figure 1). The geomorphology, with altitudes between 119 and 722 m and an average of 340 m above sea level, is characterized by the plain zone located towards the West and the mountainous zone, the Atakora range, towards the East [24]. This configuration explains the diversity of plant cover, rainfall, and socio-economic activities. The prefecture of Bassar is located in the tropical climatic zone characterized by two well-defined seasons: one humid and rainy, extending from April to October for an average annual rainfall of 1200 mm, and the other hot and dry, which spans from November to March with an average yearly temperature of 28 °C [21]. The main crops in Bassar prefecture are yams, maize, millet, sorghum, groundnuts, soya, cotton, cowpeas, and rice, with high application of synthetic and organic fertilizers.

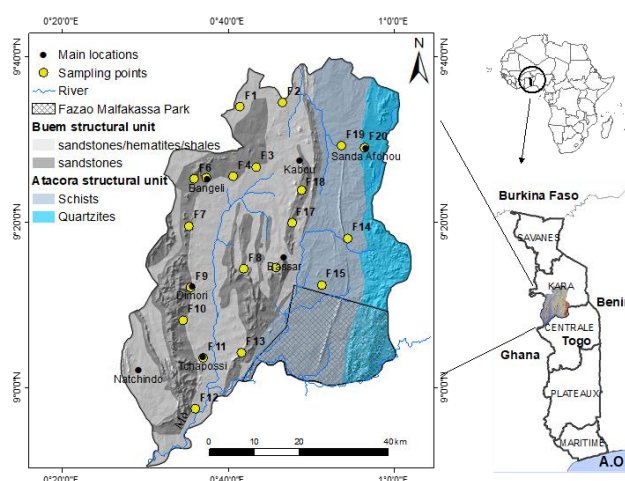


Figure 1. Map showing the study area's geological setting and sampling points.

The groundwater available in the Bassar prefecture is stored in two main geological units (Figure 1). The Atakora structural units are composed of schist, micaschist, and quartzites associated with calcareous-dolomitic cipolins, and the metasediments rocks of the Buem structural units are formed of clays, argillites, sandstones, and schists [24-26]. The Buem sandstone and shale aquifers are of variable hydrogeological interest, with an average flow rate of 10 m³/h. The boreholes are relatively deep, with an average static level of 12 m bgl, the first water inflow often between 30 and 36 m bgl, the percentage of successful boreholes about 90 %, and water of relatively good quality [26]. The schist and quartzite basement aquifer of the Atakora structural unit is of moderate

hydrogeological interest. Their productivity is lower than that of the Buem sandstone and shale aquifer, with a drilling success rate of about 60 % [26].

3. Material and Methods

Twenty (20) boreholes used for drinking water supply were sampled at the end of the dry season 2021, considering their spatial representativeness in the study area. During field work, a HANNA®-type multimeter was used to measure the field's pH (± 0.1), electrical conductivity ($\pm 2\%$, $\mu\text{S}/\text{cm}$), and temperature ($\pm 0.1\text{ }^\circ\text{C}$) in groundwater. The samples were analyzed in the laboratory for major ions (calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulfate, and nitrate) according to the standard methods of the French Association for Standardization [27, 28]. Samples for Pb, Cr, Cu, Co, Cd, As, Zn, Fe, Mn, Ni, Sb, Sr, and Si were pre-acidified with HNO_3 solution (trace metal grade acid) before the analyses, using an inductively coupled plasma-optical spectrometry (ICP-OES) technology device by coupling an inductively coupled argon plasma with a spectrometer. The analyses were performed at the GEGENAA laboratory, University of Reims Champagne-Ardenne, France. For quality control, each sample analysis was repeated three times before considering the mean concentration, and the analytical precession was checked by verifying the standards and blanks.

The descriptive statistics method was used to get an overall idea of the physicochemical parameters of groundwater in the study area. Factor analysis was done using the principal component method to identify factors controlling groundwater chemistry. The approach followed the description provided by King et al. [29] and Patel et al. [30]. Descriptive analysis, correlation analysis, ionic ratio, saturation indices, and bivariate plots were used to study the hydrochemical characteristics and geochemical processes [30, 31]. The Piper diagram [32] was used to identify hydrochemical facies. In terms of the proportions of major anions and cations, it allowed a global overview of the main trends in water types. The Gibbs diagram [33] was used to appreciate the mechanisms controlling groundwater chemistry, including the influence of precipitation chemistry, water-rock interactions,

and evaporation phenomena. The saturation index with respect to a mineral is defined as $\text{SI} = \log(\text{IAP}/K_s)$, where IAP is the ionic activity product of the mineral and K_s is the equilibrium solubility constant of the mineral. Silicate minerals stability diagrams were also applied to assess the thermodynamic equilibrium conditions of groundwater. The geochemical modeling program “The Geochemist’s Workbench 2023”, was implemented with the thermodynamic Thermodem database focused on low-temperature water-rock interactions to calculate the groundwater thermodynamic equilibrium conditions at the temperature of $25\text{ }^\circ\text{C}$ and the pressure of 1 atm [34].

4. Results and Discussions

4.1. Hydrogeochemical Characteristics

Temperature and pH

Groundwater temperature ranged from 26.5 to $31.3\text{ }^\circ\text{C}$ with a mean of $28.6\text{ }^\circ\text{C}$ (Table 1). There is no WHO guideline for drinking water, but it is known that cool water is generally more reliable than warm water. Temperature impacts several physical and biogeochemical processes [35], particularly parameters such as pH and dissolved gas [36]. Groundwater pH is crucial in determining its quality and suitability for various uses. pH range of 6 to 8.5 is considered acceptable for most purposes. The pH in groundwater samples varied from 6.7 to 7.5 with a mean value of 7.1 (Table 1), indicating circumneutral nature. All samples complied with the WHO permissible pH range in drinking water, suggesting an acceptability for drinking and other domestic and socioeconomic purposes. Other investigations around iron mines in the northern part of the study area [15] and in Ghana’s part of the Buem structural unit [37] have reported cases of acidic groundwater out of the permissible range. In the Oti basin, west of the study area, in Ghana, average pH values around 7.6 were reported and explained by carbonate and hydroxide minerals in sandstone rocks, [38]. The interplay of acidic pH factors and geogenic alkalinity sources may explain the trend to circum-neutral groundwater in the study area.

Table 1. Descriptive statistics.

	Min	Max	Average	St.Dev	WHO standards	% out of the limit
Temperature ($^\circ\text{C}$)	26.5	31.3	28.6	1.5	-	
pH	6.7	7.5	7.1	0.3	6.5-8.5	0
EC ($\mu\text{S}/\text{cm}$)	280	1148	691	231	-	
TDS (mg/L)	168	883	538	170	100	0
Ca^{2+} (mg/L)	25.6	101.6	49.2	22.5	100	
Mg^{2+} (mg/L)	14.1	56.9	37.4	10.6	50	

	Min	Max	Average	St.Dev	WHO standards	% out of the limit
Na ⁺ (mg/L)	1.7	88.6	36.3	22.6	150	0
K ⁺ (mg/L)	0.7	5.2	3.1	1.3	12	0
HCO ₃ ⁻ (mg/L)	65.9	656.0	357.0	123.0	>30	0
Cl ⁻ (mg/L)	10.7	142.0	41.0	33.8	250	0
SO ₄ ²⁻ (mg/L)	0.2	17.0	6.2	5.3	400	0
NO ₃ ⁻ (mg/L)	0.3	25.7	7.3	6.4	50	0
SiO ₂ (mg/L)	17.7	61.1	37.6	9.6	-	-
As (µg/L)	< LD	20.8	2.7	4.6	10	5
Cu (µg/L)	< LD	54.5	6.0	13.1	2000	0
Fe (µg/L)	< LD	120.6	39.7	36.6	300	0
Mn (µg/L)	< LD	34.1	6.0	9.7	80	0
Pb (µg/L)	3.9	9.2	5.9	1.5	10	0
Sb (µg/L)	< LD	2.2	0.8	0.8	20	0
Sr (µg/L)	< LD	1170.0	365.6	350.8	-	-
Zn (µg/L)	< LD	38.6	7.7	11.6	5000	0

Electrical conductivity (EC) and total dissolved solids (TDS)

The EC values ranged from 280 to 1148 µS/cm and averaged at 691 µS/cm and the TDS between 168 and 883 mg/L with an average of 538 mg/L (Table 1). These values suggest moderate mineralization on average. All the samples collected complied with the WHO standards for TDS (1000 mg/L). Previous studies around the study area in the Kara Region, Togo [15, 39], and Volta Region, Ghana [37] revealed fresh water in nature in Bassar Prefecture, except for scarce hotspots of high mineralization. EC and TDS provide a first glance at the level of minerals dissolution or weathering effects on groundwater. The degree of mineralization from fresh to very saline water types may show diverse stages of hydrochemical evolution related to both natural and anthropogenic factors [40]. In the study area region, groundwater mineralization generally increases from highland quartzites and shist domain in the Easter Atacora structural unit toward the Buem formations and to the lower land metasediments in the West towards Ghana [21, 37].

Anions contents

Table 1 shows that the contents HCO₃⁻ varied from 65.9 mg/L to 656 mg/L for an average of 353.63 mg/L. The recorded chloride levels vary between 10.7 mg/L and 142 mg/L, averaging 36.4 mg/L. Sulfate levels vary between 0.23 mg/L and 16.98 mg/L, with an average of 6.18 mg/L and a difference of 5.35 mg/L. The most common values are lower than 10 mg/L, suggesting the early stage of the chemical evolution of groundwater. The nitrate values varied from 0.3 to 27.5 mg/L, averaging 7.3 mg/L. These results are consistent with

other investigations in the Kara Region, which show low groundwater pollution caused by anthropogenic nitrate [39]. Generally, nitrate concentration is lower than 10 mg/L in groundwater free from human activities' influence, while the greater values are attributable to the significant effects of human activities [41]. However, all samples comply with the WHO guideline value of 50 mg/L. Anions contribution to groundwater mineralization is in the order of HCO₃⁻ > Cl⁻ > SO₄²⁻ > NO₃⁻.

Cations and silica contents

Calcium levels range from 25.6 mg/L to 101.6 mg/L, averaging 46.5 mg/L. Magnesium concentrations averaged 37.42 mg/L and varied from 14.09 mg/L to 56.86 mg/L. The lower standard deviation of magnesium (Table 1) showed lower dispersion than other cations. The presence of Mg²⁺ could be considered fundamental in groundwater from the study area. The minimum and maximum sodium concentrations are 1.7 mg/L and 88.6 mg/L, respectively, with an average of 36.3 mg/L. Potassium concentrations were the lowest and ranged between 0.7 mg/L and 5.2 mg/L, with an average concentration of 3.15 mg/L. Cations contribution to groundwater mineralization is in the order of Ca²⁺ > Mg²⁺ > Na⁺ > K⁺. The low concentrations of potassium and ions order align with previous studies in similar geological settings in the country [42-44]. These results contrast those in the Bono East Region, Ghana, also dominated by silicate-bearing rocks and sandstones where EC is lower than 175 µS/cm, with potassium as the most dominant cation and magnesium as the lowest [45]. A higher application of synthetic NPK fertilizers was identified as the source of high potassium in groundwater, while the

intensification of water-rock interaction processes is conducive to the increase of Ca^{2+} , Mg^{2+} , and Na^+ contents in groundwater [45, 46]. Silica content varied from 17.7 to 61.1 mg/L with a mean value of 37.6 mg/L. These relatively high concentrations are consistent with the silicate minerals dominating in the study area. The high range of silica contents suggests various controlling factors, such as the extent of rock-water interaction and the impact of anthropogenic activities [31].

Heavy metals and metalloid contents

Among the trace elements assessed, Cd, Co, Cr, and Ni were found below their detection limits. Cu, Fe, Mn, Pb, Sb, Sr, and Zn were detected with mean values of 6.0, 39.7, 6.0, 5.9, 0.8, 362.6, and 7.7 $\mu\text{g/L}$. The contents of these trace elements were consistent with their various recommended WHO limits (Table 1), and the values appear much lower than those obtained in surrounding mining and urban areas in the Kara Region, probably due to fewer anthropogenic impacts [15, 47]. Unexpectedly, groundwater iron content is relatively low compared to the northern part, although the study area is historically an iron production province. The former iron mining site near the canton of Bangeli in the north of the study area may represent a groundwater iron hotspot, probably due to contamination and remobilization processes associated with excavation operations [15]. Groundwater pH and redox conditions are determinant factors that control iron and other heavy metals mobilization from soil and aquifer matrix. In addition to these conditions, high groundwater iron concentrations are associated with a more humid climate and elevated soil organic carbon [48]. The arsenic content varied from the detection limit to 20.8 $\mu\text{g/L}$ with an average of 2.7 $\mu\text{g/L}$ and was the contaminant limiting groundwater use for drinking purposes for 5 % of samples in the study area (Table 1). In the northern iron mining vicinities, As content was lower than 2 $\mu\text{g/L}$ [15] while in the eastern urban Kara, concentrations were as high as 48.25 $\mu\text{g/L}$ with up to 25 % out of the [35] permissible level of 10 $\mu\text{g/L}$ [47]. Arsenic is a toxic contaminant that contributes to the incidences of cancer, diabetes, and skin diseases in exposed populations worldwide [49, 50]. In the river basins underlain mostly with crystalline rocks in Ghana, 7.86 % of samples exceeded 10 $\mu\text{g/L}$, and hotspots occurred in urban districts in gold-mining areas [49]. High arsenic contamination provinces are depicted in the south and Southeast Asian countries due to geogenic contamination [48]. These results suggest that the Kara region should be considered for a comprehensive investigation of public health concerns of arsenic and co-contaminants since they pose carcinogenic hazards even at lower concentrations.

Hydrochemical facies and mechanisms

The analysis of the Piper diagram (Figure 2) reveals the dominance of mixed cations- HCO_3^- water types, followed by accessory Ca-HCO_3 , Mg-HCO_3 , Ca-Mg-Cl , and Mg-Na-HCO_3 in the study area. These hydrochemical facies might be due to silicate and carbonate rocks characterizing the geological settings of the study area (Figure 1). Chloride

water type in such geological domain is known to be derived from human activities impact, while sodium ion enrichment results from the groundwater chemistry evolving along the topographic flow path through Na-bearing minerals such as Na-feldspar weathering and cation exchange [30, 45].

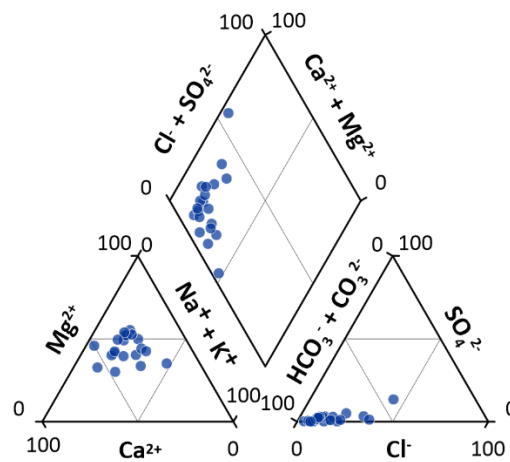


Figure 2. Piper diagram.

The Gibbs diagram is used to distinguish the contribution of the leading natural processes to the mineralization of groundwater [30]. Figure 3 shows that water-rock interaction processes are the main hydrochemical mechanisms controlling groundwater chemistry.

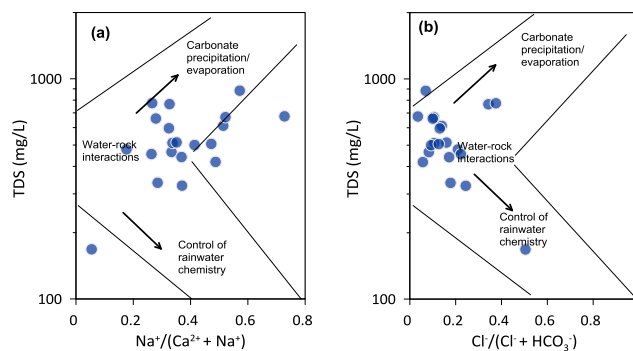


Figure 3. Gibbs Diagram.

The controls of rainwater chemistry, evaporation, and carbonate precipitation also occur to a certain extent in limited samples. Rainwater control indicates probably recently infiltrated waters from recharge areas with a limited mixing process. The Sudan-Guinean climatic conditions with annual rainfall around 1200 mm/year are not favorable to evaporation control compared to regions with arid and semi-arid climatic conditions [46, 51]. However, the precipitation of carbonate minerals such as dolomite and calcite may occur depending on the high bicarbonate content and calcium and magnesium inputs. The saturation indices varied from -1.26 to 0.40 with

an average of -0.13 for calcite and from -2.41 to 1.08 with an average of 0.03 for dolomite.

4.2. Statistical Analysis

Inter-variables correlations

The correlation plot in Figure 4 gives the Pearson correlation coefficients between different parameters at a confidence level of 95 %. There were significant positive correlations ($r > 0.6$, $p < 0.05$) between conductivity (CE) and bicarbonate, magnesium, calcium, and sodium ions. This indicates that groundwater alkalinity, hardness, and sodium contribute significantly to water mineralization. All these ions showed significant inter-correlations, suggesting a concomitant input of these ions from similar sources or processes.

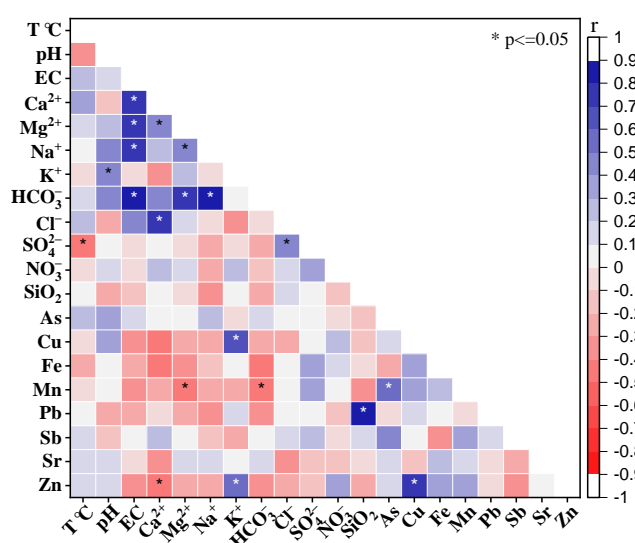


Figure 4. Inter-variables Pearson's correlations plot.

The correlations of EC with salinity and anthropogenic impact indicators (Cl^- , SO_4^{2-} , and NO_3^-) are weak. However, chloride, sulfate, and nitrate are positively correlated with

each other (Figure 4) as they originate from similar routes related to anthropogenic impacts, such as fertilizers, agriculture practices, livestock farming, and household wastes [52]. The positive correlations of calcium with nitrate and chloride indicate the contribution of anthropogenic sources to calcium content. These results indicate various sources and processes in groundwater mineralization [31]. Silica and Pb present a significant correlation, probably due to the geogenic release of Pb into groundwater through silicate minerals weathering. Heavy metal ions such as Pb (II) and precipitated hydroxide can undergo adsorption processes onto minerals such as silica and be released together into groundwater [53].

Arsenic is correlated with Mn and Sb. Arsenic and antimony are metalloids exhibiting similar geochemical behavior and are often found in the same mineral associations [54]. Their correlation with Mn may result from their co-occurrence in sulfides, Fe, and Mn ores in the Bassar region, a major pre-colonial West African iron production center [55]. Fe, Mn, and Sb showed a correlation trend but not significant with SO_4^{2-} and Zn (Figure 4), suggesting probably similar sources from sulfides oxidation. Zn, Cu, and potassium showed positive and significant correlations with each other suggesting similar sources. Potassium is also correlated with pH. Positive but weak correlations connect nitrate with Zn, Cu, and potassium, suggesting that anthropogenic influence enhances their contents in groundwater. In addition to K-bearing minerals such as K-feldspar and biotite weathering, potassium fertilizers such as NPK may contaminate groundwater with K and micronutrients above groundwater background levels. Long-term fertilizer and manure application may build up high levels of micronutrients such as Zn and Cu in the soil and unsaturated zone and contribute to groundwater contamination [56, 57].

Factor analysis

The factor analysis results are presented in Table 2, showing seven principal components with an eigenvalue higher than one. These components explained a total of 87.27% of the variability in the dataset.

Table 2. Factor analysis results.

Variables	PC1	PC2	PC3	PC4	PC5	PC6	PC7
T °C	0.04	0.01	0.17	0.90	-0.07	0.09	0.11
pH	0.56	0.46	-0.19	-0.39	0.14	0.14	-0.11
EC	0.92	-0.17	0.23	0.11	0.09	-0.03	0.07
Ca^{2+}	0.42	-0.35	0.68	0.27	-0.02	-0.08	0.24
Mg^{2+}	0.82	0.10	0.27	0.16	0.00	-0.23	0.05
Na^+	0.83	-0.16	-0.21	-0.01	0.19	0.20	-0.11
K^+	0.21	0.87	-0.15	-0.07	-0.18	-0.12	-0.09
HCO_3^-	0.95	-0.08	-0.08	0.09	0.13	-0.08	0.10

Variables	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Cl ⁻	0.04	-0.23	0.86	0.07	-0.12	0.31	0.06
SO ₄ ²⁻	-0.16	-0.04	0.59	-0.66	0.02	0.14	0.08
NO ₃ ⁻	-0.06	0.47	0.61	-0.07	0.14	-0.49	-0.14
SiO ₂	-0.11	-0.10	0.04	0.00	-0.97	-0.04	0.04
As	0.51	0.04	0.05	0.29	0.20	0.59	0.25
Cu	-0.24	0.89	-0.07	-0.12	0.05	0.22	0.08
Fe	-0.34	0.16	0.10	-0.35	0.06	0.37	-0.62
Mn	-0.18	0.21	0.16	0.00	-0.09	0.90	-0.10
Pb	-0.21	0.08	0.01	0.06	-0.92	0.07	0.09
Sb	-0.05	-0.09	0.15	-0.07	-0.09	0.09	0.91
Sr	0.33	-0.30	0.01	0.54	0.10	0.36	-0.20
Zn	-0.35	0.78	-0.06	0.24	0.20	0.15	-0.31
Eigenvalue	5.23	3.29	2.19	2.07	1.90	1.56	1.20
Explained Variance (%)	26.16	16.47	10.96	10.37	9.52	7.78	6.01
Cumulative Variance (%)	26.16	42.63	53.59	63.97	73.48	81.27	87.27

Variables loading most strongly on the first component (PC1) include EC, Mg²⁺, Na⁺, and HO₃⁻ while pH and Ca²⁺ load weakly. This component explained 26.16% of the dataset variance and reflects silicates and carbonate minerals control on groundwater mineralization in the study area dominated by quartzites, schists, and quartzite sandstones (Figure 1). The PC2 explained 16.47% of the total variance and loads strongly on Zn, Cu, and K⁺, weakly on pH, and NO₃⁻. It loads weakly and negatively on Ca²⁺. The elements K, Cu, and Zn are known to undergo sorption processes within aquifers under typical natural conditions depending on the sorbing solid phase (clay, organic matter, and metal oxides and hydroxides) and the fluctuating acidity of the groundwater [58]. In shallow groundwater, nitrate-related biochemical processes are also associated with species controlling groundwater pH [59]. Therefore, PC2 could be defined as the control of agriculture contamination from agrochemicals and manure on cations exchange processes in the savannah and agriculture-dominated lands of the study area. PC3 accounted for 10.96% of the total variability in the dataset, with high loading on calcium, chloride, nitrate, and sulfate and weakly on chloride, reflecting human activities' influence, particularly agriculture practices on groundwater [45]. Under anthropogenic impact, calcium ions adsorbed on the soil and aquifer matrix can be exchanged with the protons released in part by the transformation of ammonium into nitrate. Consequently, nitrate can be leached and released with calcium and ammonium conservative

co-contaminants (Cl⁻ and SO₄²⁻) into groundwater. PC3 may reflect groundwater recharge from areas affected by agricultural and other anthropogenic activities. PC4 presented high loads on temperature and Sr and negative loads on SO₄²⁻. It accounts for 10.37% and opposes strontium content with groundwater salinization at prevailing temperature conditions. Silicates such as feldspar weathering and carbonate dissolution, along with cations exchange, enrich strontium content in groundwater, while additional salts dissolution are key factors of the regression of strontium content due to the lower solubility of its salts [60]. Potential mineral sources of Sr, such as carbonates and associated evaporites, commonly occur within sandstone aquifer sediments in the study area and nearby [37, 45, 61]. Variables loading most strongly on the PC5 are SiO₂ and Pb, accounting for 9.52% of the total variance. This association probably underscores the role of the volcanic series, which includes olivine basalt, diorite, and some rhyolite in the study area [61]. PC6 explained 7.78 % of the variance and showed high loadings on As and Mn and low loadings on Fe and Sr. PC7 accounted for 6.01 % of the total variability in the dataset, with high loading on Sb and negative loading on Fe. [45]. PC6 and PC7 probably pointed out the impact of Fe/Mn-(hydr)oxide formation as well as sulfidic and hematitic jasperoids of the study area [61] in governing environmental reactions such as adsorption, and the redox transformations of As and Sb [62].

4.3. Geochemical Processes

Binary plots (Figure 5) were used to assess geochemical processes contributing to water mineralization.

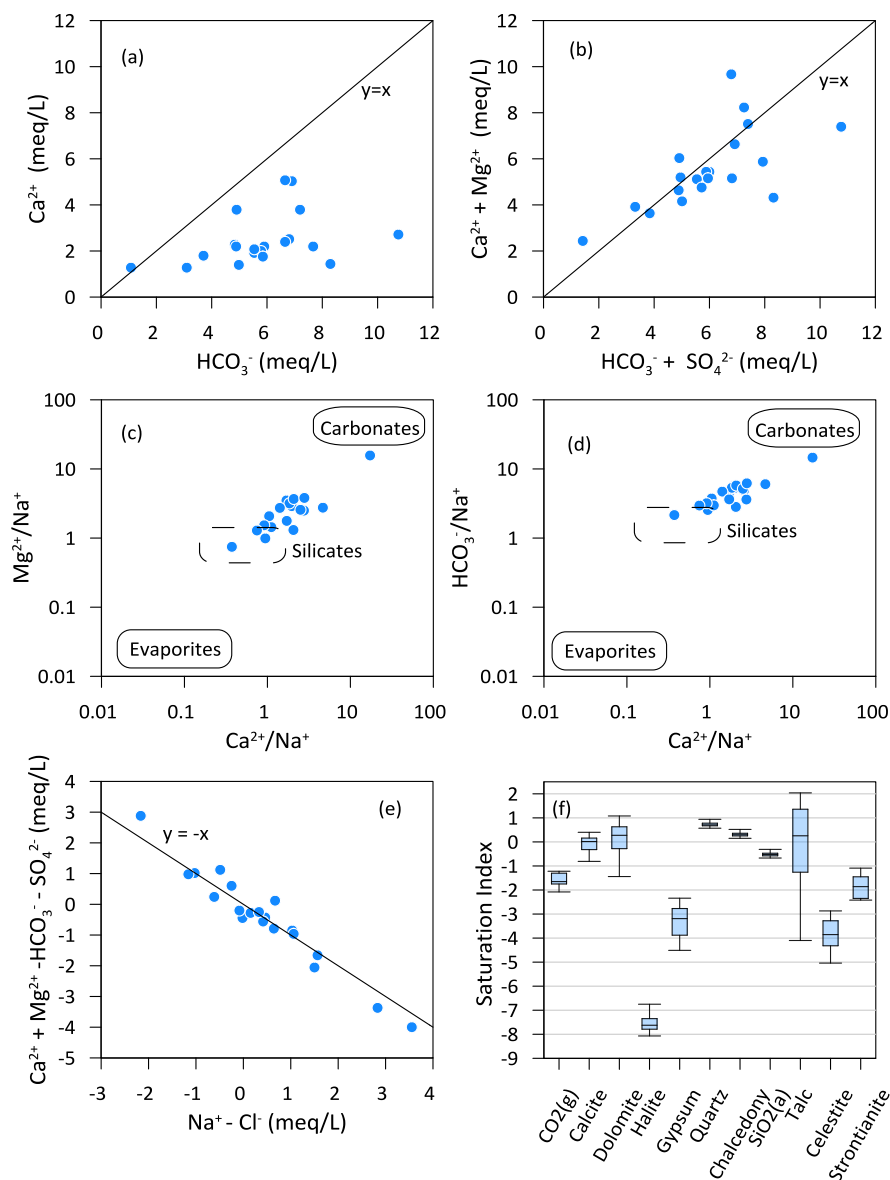


Figure 5. Bivariate plots showing (a to e) the relationship between selected parameters and (f) the saturation indices of selected minerals.

Figure 5a shows an excess of HCO_3^- over Ca^{2+} , and Figure 5b the dispersion of points not falling on the dissolution line $y = x$ in the plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs $(\text{HCO}_3^- + \text{SO}_4^{2-})$. This indicates that the dissolution of carbonate minerals does not mainly control groundwater mineralization. Gaillardet diagrams [60, 63] showing the relationship between HCO_3^- , Mg^{2+} , and Ca^{2+} weighted by Na^+ can help distinguish the control of evaporites, carbonates, and silicates on groundwater chemistry. Figure 5c and 5d reveal the control of silicate minerals and the contribution from carbonate minerals dissolutions. This is consistent with quartzites, schists, and sandstone rocks dom-

inating the study area and shows that cations and bicarbonate mainly originate from the alteration of silicate minerals such as plagioclases, alkali feldspars, and ferromagnesian minerals such as biotites, amphiboles, and pyroxenes [25, 61]. In the study area, the partial pressure varies from $10^{-2.1}$ atm at $10^{-1.2}$ atm with an average of $10^{-1.6}$ atm. These very high values indicate the control of root CO_2 on the chemical alteration of silicate minerals.

The diagram $[(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]$ vs. $(\text{Na}^+ - \text{Cl}^-)$ is used to highlight the cations exchange processes, often taking the form of aligning the points along the line with the

equation $y = -x$ [31, 60]. Figure 5e shows a linear distribution of points falling along the line with slope -1. This suggests cation exchange between Na^+ and Ca^{2+} or Mg^{2+} within groundwater and aquifer matrix. Such a process may render reduced calcium in favor of sodium in groundwater. Secondary minerals phase precipitation may also reduce calcium and magnesium content in groundwater. Figure 5f shows that over 50 % of the samples are saturated (Saturation index > 0) concerning calcite, dolomite, and talc. Gypsum, halite, celestite, and strontianite are undersaturated (Saturation index < 0) (Figure 5f), showing that the dissolution of chloride and sulfate salts or minerals can proceed in the aquifer systems. At the same time, the supply of Ca^{2+} and Mg^{2+} can be mutated by processes such as cation exchange and carbonate precipitation. Samples are oversaturated regarding quartz and chalcedony while under-saturated regarding amorphous silica (Figure 5f). This means further silica dissolution or silicate weathering is required to reach thermodynamic equilibrium [64]. The sili-

cate minerals stability diagrams (Figure 6) show that the samples plotted mainly in kaolinite, muscovite, Mg-montmorillonite, and K-feldspar stability fields. Variations in thermodynamic equilibrium conditions suggest various stages of hydrogeochemical evolution under water-rock interactions. The evolution of groundwater chemistry depends on its equilibrium with these primary and secondary silicate minerals. Depending on recharge, flow rate, and species activity, they can undergo solubility/precipitation processes. Meanwhile, the hydrolysis of other silicate minerals, such as albite, anorthite, plagioclases, amphibole, and biotite, and the dissolution of associated carbonates are ready to occur. Groundwater samples positioned in equilibrium or near equilibrium with the montmorillonite phase (Figure 6a, b, and c), a smectite clay mineral, support the occurrence of cations exchange in the study area. Smectites are swelling clay minerals commonly encountered in soil and aquifer matrices with a high potential to sorb inorganic cations of natural waters [65].

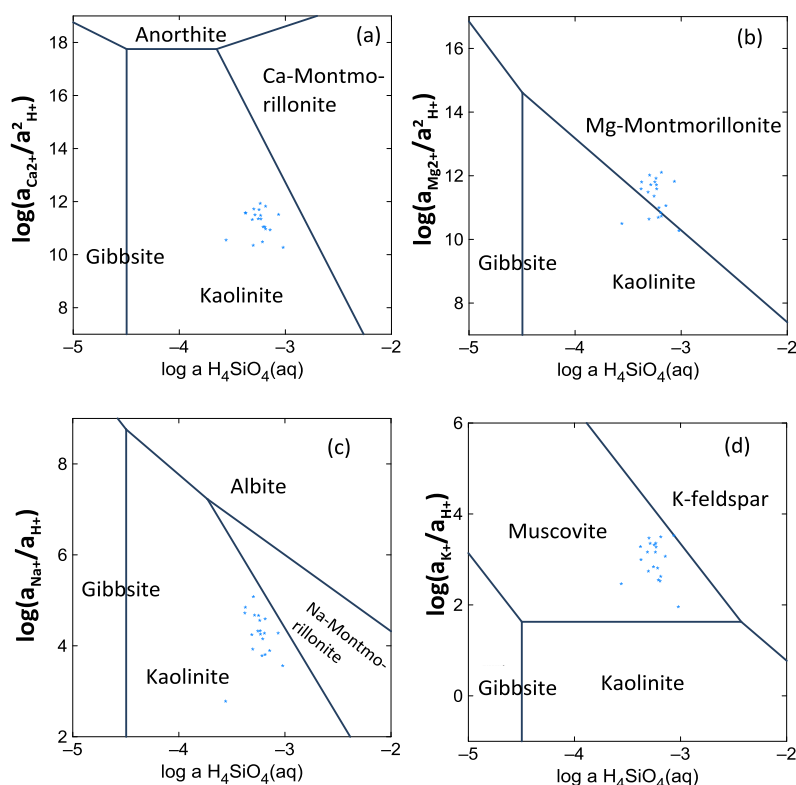


Figure 6. Silicates stability diagrams of $\text{Na}_2\text{O-K}_2\text{O-MgO-CaO-Al}_2\text{O}_3\text{-H}_2\text{O-SiO}_2$ systems for different silicate mineral phases at 25 °C and 1 atm, with sample points.

5. Conclusion

Groundwater in the prefecture of Bassar was found soft and circumneutral during this study. All the chemical parameters comply with the WHO standards except arsenic in 5 % of groundwater samples. Anions and cations' contributions to

groundwater mineralization are in the order of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ and $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ respectively. Toxic elements such as As, Pb, and Sb were above the detection limit and derived from geogenic sources. This may pose serious human health risks for residents and require attention for drinking water security in the study area. Nitrate concentrations were lower than the WHO permissible limit in drinking water

but reflected the influences of human activities, particularly agricultural practices. A combination of hydrochemical methods and multivariate statistical analysis has improved knowledge of the leading geochemical processes responsible for groundwater mineralization in the prefecture. The factor analysis identified seven factors explaining 87.27% of the total variance in the dataset. The factors were related to silicate rocks weathering and carbonate minerals dissolution, sorption and cations exchange processes, anthropogenic impact in soils, application of agrochemicals and manure, and toxic trace elements mobilization. A broad range of thermodynamic equilibrium conditions with minerals such as calcite, dolomite, gypsum, halite, celestite, strontianite, talc, quartz, chalcedony, amorphous silica, Kaolinite, montmorillonite, and K-feldspar reflected various stages of hydrogeochemical evolution of groundwater. Groundwater quality monitoring and effective and affordable water treatment technologies are required to improve strategies for properly managing groundwater resources and water security in the Bassar prefecture.

Abbreviations

EC	Electrical Conductivity
TDS	Total Dissolved Solids
WHO	World Health Organization

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Conflicts of Interest

The authors declare no conflicts of interest.

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