

Hydrochemical Assessment of Groundwater Quality from Fractured Basement Aquifers in the South-central of Burkina Faso, West Africa

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Received March 28, 2025; Revised April 30, 2025; Accepted May 07, 2025

Abstract: In central southern Burkina Faso, as elsewhere in the country, groundwater resources are the reliable source of drinking water. During its residence time in the rocks, the groundwater interacts with them and its chemical composition is considerably modified. Methods like major ions geochemistry, the assessment of water quality indices, and the application of geostatistical analysis have been utilized to define the hydrogeochemical processes governing groundwater quality. For this study, 249 groundwater samples were taken from manual boreholes. The findings indicated that the groundwaters ranged from circumneutral to alkaline, with predominant concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- . According to the calculated groundwater quality indices, water from the majority of the boreholes was suitable for domestic uses. However, a few boreholes had high concentrations of F^- and Fe_T that exceeded the World Health Organization recommended guideline value for drinking water. The elevated F^- concentrations were probably due to the weathering of the granitic rocks, while the Fe_T concentrations appeared to come from the water pumps installed on these boreholes. Bivariate plots indicated that geochemical processes like silicate weathering, mineral dissolution and precipitation, ion exchange, and evapotranspiration were the key factors affecting solute acquisition in groundwater. Furthermore, desorption and ion exchange in alkaline pH conditions could enhance F^- enrichment in groundwater. Zones with low ionic strength and electrical conductivity have been identified as groundwater recharge zones, which should be protected and subject to a regular monitoring program. This study results could help professionals in the field to implement appropriate groundwater quality management strategies.

Keywords: fractured basement aquifers, spatial assessment, groundwater hydrochemical evolution, kriging, Burkina Faso

Cite This Article: Césard Millogo, Aboubakar Sako, Blehiman Sagnon, and Samuel Nakolendoussé, "Hydrochemical Assessment of Groundwater Quality from Fractured Basement Aquifers in the South-central of Burkina Faso, West Africa." *Applied Ecology and Environmental Sciences*, vol. 13, no. 1 (2025): 34-43. doi: 10.12691/aees-13-1-5.

1. Introduction

The geochemical signatures of groundwater are influenced by various natural and anthropogenic factors. They are generally governed by the nature of geochemical reactions, the solubility of salts, the weathering of rocks, the groundwater flow rate, crystallisation by water evaporation, the contribution of atmospheric precipitation and anthropogenic activities [1] [2,3] [4,5].

Interaction with CO_2 , SO_2 , and NO_x causes rainwater to become acidic, and its chemistry is modified through a series of microbial-mediated redox processes within the regolith. These processes manage the carbon levels in groundwater and modify the distribution of its key ions

and trace elements. [6,7].

The extended residence time of groundwater in aquifers, combined with seasonal variability in precipitation and evapotranspiration, leads to continuous changes in its chemical composition due to interactions with the surrounding rocks [8,9,10,11,12,13]. In addition, land development and deforestation can also influence groundwater chemistry [14,15,16]. For these reasons, hydrogeochemistry is extensively employed to evaluate lithological influences on groundwater chemistry worldwide [17,18,19]. The study area is situated on a crystalline basement mainly consisting of several generations of granitoids (early or late) containing substantial minerals like micas and amphibole that are rich in F and Fe. Iron is the second most abundant and heaviest metal in the Earth's crust [20,21]. The element is the most

common dissolved chemical in groundwater [22]. Due to water-rock interactions, large amounts of F and Fe can be released into the aquifer [23]. Other possible sources of fluoride loadings in groundwater include the disposal of domestic and industrial waste, as well as the use of fertilizers and pesticides in agriculture. [24,25,26].

Iron is a necessary element found in almost all living organisms. Its deficiency leads to anemia [27]. There is no standard for the maximum amount of iron permitted in drinking water [28]. However, when its concentration in water exceeds 0.3 mg/L, iron can alter the taste and colour of water, and stain washed clothes and household appliances [29,30]. Excessive exposure to iron can elevate the risk of developing conditions such as Parkinson's disease, Huntington's disease, cardiovascular issues, hyperkeratosis, diabetes mellitus, pigmentation changes, Alzheimer's disease, as well as kidney, liver, respiratory, and neurological problems [31]. Irregular rainfall limits the amount of surface water, leading people to rely on more mineralised groundwater for drinking water. This exposes them to diseases caused by excessive concentrations of Fe and F.

Recently, hundreds of thousands of boreholes have been drilled in rural and peri-urban areas of Burkina Faso to provide people with drinking water. However, these boreholes are operated without taking into account the effects of natural geogenic and anthropic sources of toxic chemicals, which can compromise groundwater quality. To monitor and alleviate the impacts of such geogenic and anthropic pollution, and develop a sustainable and integrated groundwater management plan, it is essential to understand the current status of the chemical constituents regulating groundwater quality [32,33,34].

Traditionally, the concentrations of the various quality parameters in water intended for human consumption are compared with the recommendations in the guidelines. Parameters whose concentrations exceed the limit values set by national standards or those of the World Health Organisation (WHO) are considered potentially harmful to the ecosystem and human health. While this method offers insights into water quality, it does not convey information on temporal trends in overall water quality [35].

Alternatively, the water quality index (WQI) is used to assess the potability of water. This method, used by [36,37], provides a more comprehensive evaluation of a more global assessment of drinking water quality. This numerical method combines a wide range of groundwater quality parameters into a single value, producing a score that reflects the status of groundwater quality at a specific spatiotemporal scale. [38,39].

Graphical methods, such as dispersion and ion concentration diagrams, are commonly employed to evaluate groundwater quality from various sources. To our knowledge, no study on geochemical characterization using the Water Quality Index (WQI) and geostatistics has been conducted in the central-southern region of Burkina Faso. This study hypothesized that elevated concentrations of parameters like TH, Fe_T and F^- are primarily influenced by the in-situ weathering of crystalline basement rocks, with a lesser impact from anthropogenic activities. The study aimed to explore the mechanisms affecting groundwater chemistry in the region. The results will aid water resource managers in monitoring groundwater

quality in south central Burkina Faso.

2. Presentation of Study Site

2.1. Environmental Setting

Our study area is located in south-central Burkina Faso, more precisely in the commune of Toécé and the surrounding area (Figure 1). The climate is Sudanian and Sahelian type characterized by alternating dry and rainy seasons. Average temperatures range between 25 and 40°C. The hottest months are October, March, and April, whereas August and December are the coldest. Rainfall is unevenly distributed in time and space, with an annual average of around 800 mm. Isohyets are moving further south as a result of increasingly low rainfall [40]. The hydrographical network is dense and the area straddles two watersheds. The area is predominantly agricultural, with subsistence rainfed crops, orchards, market gardening, etc.

The farmland is dotted with vegetation in places. The presence of water, albeit temporary, encourages irrigation, especially at the start of the dry season. Livestock farming is also practised on the extensible land. All these activities increase the pressure on water resources and can have an impact on their quality.

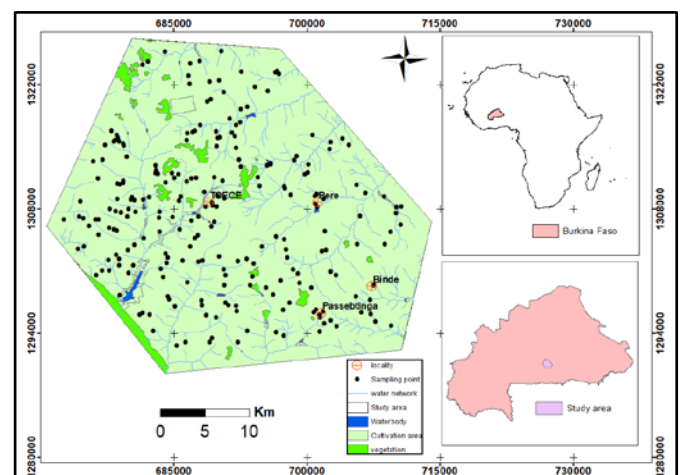


Figure 1. Presentation of the study area

2.2. Geological and Hydrogeological Settings

The study area is based on a crystalline foundation of granitoids, which constitute the majority of the outcrops (Figure 2). These granitoids are oriented NE-SW, consistent with the schistosity of the surrounding greenstone belts. There are two generations of granitoids present. The first generation, referred to as early granitoids, is characterized by a low degree of weathering and is affected by numerous fractures. In these formations, the success rate of drilling is relatively high and can reach up to 70%, with significant flow rates sometimes exceeding 10 m³/h. The second generation is more recent and less fractured, with a thin weathered layer. The failure rate of water wells in these granitoids is high. Late magmatic phenomena are marked by the intrusion of dolerites in the form of NNE-SSW oriented dykes, discontinuous over several tens of kilometers. They are located in the

southern and southwestern parts of the study area. These dark, equigranular rocks, with a fine to medium grain, locally exhibit varying degrees of weathering into rounded forms. These rounded forms are covered with a thin yellowish weathering film [41,42]. Advanced lateritization affects all the terrains. The granitoids generally contain significant minerals (quartz, feldspars, micas, amphiboles, etc.). Due to weathering, many chemical elements from these minerals end up in the water, altering its chemical composition.

The porosity of laterites and the lithostructural discontinuities, mainly oriented NE-SW, serve as the preferred pathways for meteoric waters during infiltration. These features can also be preferential routes for accidental or diffuse pollution that may occur in the area. Alluvium composed of gravel, sand, and clay is found in rivers or along riverbanks, sometimes extending over considerable distances. The aquifers within these alluvial deposits are utilized by farmers during the dry season for irrigating their crops.

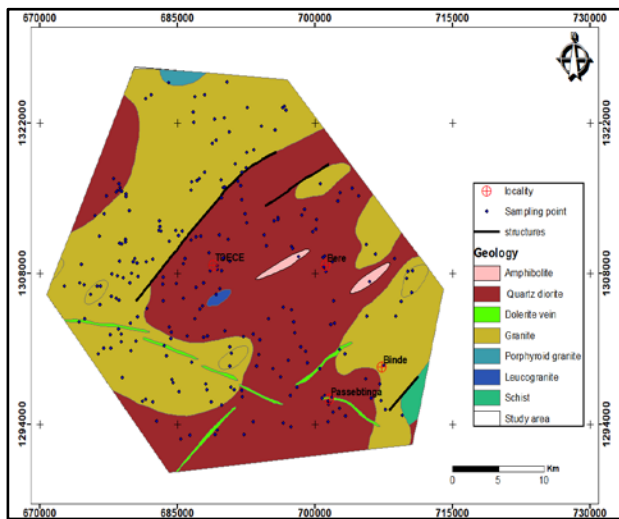


Figure 2. Simplified geological map of the study area

3. Material and Methods

3.1. Sample Collection and Analysis

For this study, 249 groundwater samples were taken from boreholes tapping fractured crystalline aquifers in the study area. To confirm that the borehole samples accurately reflected groundwater rather than water that had lingered in the boreholes for a period, we operated the boreholes for a few minutes (10-15 minutes) prior to collecting the samples (weber,1992). To avoid the influence of microorganism activity, each sample was passed through a 0.2 μm filter capsule into two sets of pre-conditioned polyethylene bottles. One set was acidified ($\text{pH} < 2$) with ultra-pure HNO_3 to keep the ions in solution and was then used for the analysis of major cations and trace elements, while the concentrations of major anions were determined in a set of non-acidified samples. The pH, temperature, electrical conductivity (EC) and turbidity were measured in field with a calibrated meter.

Once the samples were received at the Geochemistry Laboratory of the BUMIGEB in Ouagadougou, the

concentrations of Ca^{2+} and Mg^{2+} were measured by titration using 0.05 N EDTA and 0.01 N EDTA, respectively. The concentrations of HCO_3^- and Cl^- were determined by titration with H_2SO_4 and AgNO_3 , respectively. Sodium and K^+ concentrations were measured using flame photometry (APHA 1995), while F^- , SO_4^{2-} , NO_3^- , and PO_4^{3-} concentrations were determined by UV-Vis spectrophotometry. Total hardness (TH) was assessed by the EDTA complexometric titration method (WHO 1999). Total iron (Fe_T) concentrations were measured using an atomic absorption spectrometer (AA 7000, Perkin Elmer 2380). The analytical accuracy was verified by calculating Ionic Balance Error (IBE) as follows (Eq. 1):

$$\text{IBE} (\%) = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}} \times 100 \quad (1)$$

Generally, the value of IBE should be less than $\pm 5\%$, and certainly less than $\pm 10\%$ [43]. In this study, all samples were IBE values less than $\pm 10\%$. In this study, samples with Ion Balance Errors exceeding $\pm 10\%$ were excluded from the dataset. Approximately 70% of the samples had IBE values within the $\pm 10\%$ range, indicating that charge imbalances would not have a significant impact on the results. The remaining dataset was sufficiently large for geostatistical modelling of groundwater quality.

3.2. Water Quality Index (WQI)

The WQI for each sample was computed based the WHO standard guidelines for drinking water (WHO 2011). The WQI was based on twelve parameters: pH, TDS, TH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , and F^- . Each parameter was assigned a weight (w_i) from 1 to 5, according to its potential impact on human health. NO_3^- , F^- , SO_4^{2-} , and TDS were given the highest weights, while HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , and Cl^- received the lowest weights (Table 1). The relative weights (W_i) for each parameter were calculated as described in Equation 2.

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (2)$$

where W_i represents the relative weight, w_i is the weight of each parameter and n is the total number of parameters. The quality rating scale (q_i) was also calculated by dividing the concentration of each parameter (C_i) by its corresponding WHO guideline value (S_i) for drinking water (Eq. 3):

$$q_i = \frac{C_i}{S_i} \times 100 \quad (3)$$

Before calculating WQI, a sub-index (SI_i) of each parameter was determined using the following equations (Eq. 4–5):

$$SI_i = q_i \times W_i, \quad (4)$$

$$\text{WQI} = \sum SI_i \quad (5)$$

The computed WQI values categorize groundwater into five distinct classes [44,45] (1) excellent water ($\text{WQI} <$

50); (2) good water (WQI = 50–100); (3) poor water and (5) water unsuitable for human consumption (WQI > 300) (Table 2).

Table 1. Parameters for calculating the water quality index

Parameter	Unit	Who (Si)	Weight (wi)	Relative weight (Wi)
pH	mg/L	8.5	4	0.114
TDS	mg/L	600.0	4	0.114
TH	mg/L	500	2	0.057
Ca ²⁺	mg/L	75	2	0.057
Mg ²⁺	mg/L	50	2	0.057
Na ⁺	mg/L	200	2	0.057
K ⁺	mg/L	12	2	0.057
HCO ₃ ⁻	mg/L	120	1	0.029
Cl ⁻	mg/L	250	3	0.086
SO ₄ ²⁻	mg/L	250	4	0.114
F ⁻	mg/L	1.5	4	0.114
NO ₃ ⁻	mg/L	10	5	0.143
			35	1.00

Table 2. Statistical of physico-chemical parameters of the groundwater samples.

Parameter	Unit	N	Min	Max	Mean	Median	Std. D	Skewness	Kurtosis
pH		249	4.50	7.90	6.43	6.40	0.52	0.21	0.71
IS		249	0.00	0.01	0.00	0.00	0.00	2.72	13.69
pCO ₂	atm	249	0.00	3.05	0.10	0.06	0.21	11.22	151.66
TDS	mg/L	249	89.70	625.83	175.96	160.77	74.04	2.97	12.97
EC	μS/cm	249	130.00	907.00	255.02	233.00	107.31	2.97	12.97
TH	mg/L	249	40.00	400.00	104.38	96.00	45.01	2.55	11.98
Ca ²⁺	mg/L	249	9.62	138.87	28.67	22.44	16.44	2.47	10.77
Mg ²⁺	mg/L	249	0.00	26.21	8.37	8.72	5.70	0.35	-0.01
Na ⁺	mg/L	249	3.05	23.73	8.16	7.03	3.59	1.10	1.49
K ⁺	mg/L	249	0.00	8.14	4.28	4.16	1.08	0.35	1.23
HCO ₃ ⁻	mg/L	249	65.88	610.00	142.33	134.20	58.71	3.46	21.25
Cl ⁻	mg/L	249	0.00	29.94	3.65	1.50	6.28	2.39	4.59
SO ₄ ²⁻	mg/L	249	0.00	44.25	4.53	3.28	5.13	2.81	15.56
NO ₃ ⁻	mg/L	249	0.00	76.66	6.71	1.40	13.31	3.21	11.26
F ⁻	mg/L	249	0.04	2.08	0.37	0.22	0.36	1.96	3.77
PO ₄ ³⁻	mg/L	249	0.00	1.77	0.15	0.07	0.23	3.32	15.84
Fe _T	mg/L	249	0.00	23.44	1.07	0.48	2.06	6.48	59.80
Mn	mg/L	249	0.00	0.41	0.01	0.00	0.04	5.99	45.74
WQI	mg/L	249	16.22	133.61	34.68	28.68	20.05	2.76	8.84

Std. D: Standard deviation

3.3. Hydrogeochemical Modelling

To determine the main geochemical reactions influencing groundwater chemistry, hydrogeochemical modeling serves as a crucial analytical tool [46]. In this study, Visual MINTEQ (version 4) was employed to compute the values of the saturation index (SI), ionic strength (IS), and partial pressure of CO₂ (pCO₂).

4. Results and Discussion

4.1. Groundwater Constituents

4.1.1. Physico-chemical Parameters

The results of the physico-chemical parameter measurements in the groundwater samples are shown in the table below (Table 2). Among these parameters, pH is crucial in regulating the biogeochemical processes

occurring in groundwater [47,48]. Whereas a high pH may not directly influence human health, it can significantly alter the taste of drinking water. The pH of the groundwater sampled ranged from 4.5 to 7.9 with an average $\pm$ standard deviation of 6.43 ± 0.52 , which indicating the neutral nature of the groundwater. This also suggests that dissolved carbonates were mainly in the form of HCO₃⁻. The concentration of EC provides a general trend of the groundwater mineralisation, and it ranged from 130 to 907 μ S/cm with an average of 255.02 ± 107.31 μ S/cm. The generally low mineralization rates can be linked to the scarce presence of evaporite minerals in the local geological formations, as higher groundwater mineralization typically occurs in evaporitic formations [49]. Groundwater is considered fresh water when TDS ranges from 0 to 1000mg/L [50]. Total dissolved solids were low and varying from 89.7 to 625.83 mg/L (average = 175 ± 74 mg/L), suggesting that the groundwater is fresh due to the dilution effects of recharge rainwater or minimal mineral dissolution [50].

4.1.2. Groundwater Recharge Areas

Irrespective of the geological context, groundwater mineralisation can vary from one place to another depending on the nature of the mixture of soils and resources residence time, which are directly related to the strength of the ions. Positive values of SI indicate that the water is supersaturated concerning the mineral phase, negative values signify undersaturation and zero indicates equilibrium [37]. The IS of the groundwater sampled ranged from 0.0017 to 0.0127 with an average $\pm$ standard deviation of 0.0036 ± 0.0013 , which indicating the saturated nature of the groundwater.

Groundwaters with low ionic strength (i.e., <0.005) indicate a high rate of freshwater inflow into the aquifer (i.e., recharge areas), whereas, groundwaters with high ionic strength suggest less freshwater inflow, designating those areas as discharge zones [51].

The modelled log pCO₂ values were relatively higher than atmospheric log pCO₂ (-3.75) and ranged from -2.89 and 0.48 (Figure 3), suggesting that the aquifer system is open to the soil CO₂.

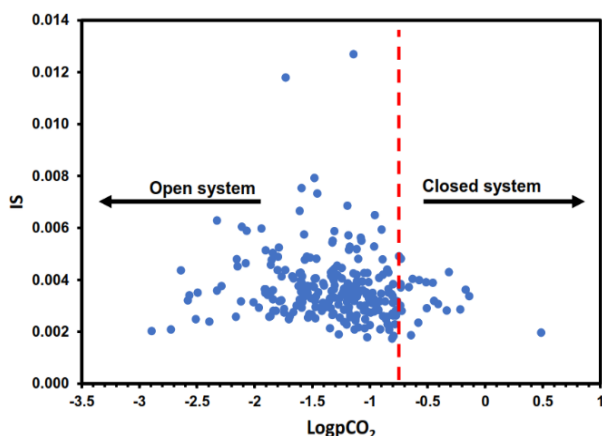


Figure 3. Bivariate plot between logpCO₂ and ionic strength of the groundwater samples

Many boreholes have high log pCO₂ values (~ -0.75) and are considered to be in a closed system which is characterised by a long residence time favouring the prolongment of water-rock interactions [36,37]. We can therefore conclude that the majority of drilling water is concentrated in the mixing zone and in the closed system. This could be explained by the fact that our study area straddles watersheds, which is not very conducive to groundwater recharge. Nonetheless, continued research to gain a better understanding of the sources and mechanisms of groundwater recharge is essential for better management of water resources.

4.1.3. Groundwater Cation Content

The dominant cations in the samples were Ca²⁺ and Mg²⁺ and followed by Na⁺ and K⁺. The order of abundance is: Ca²⁺ > Mg²⁺ > Na⁺ > K⁺. Calcium concentrations varied from 9.62 to 138.87 mg/L (average = 28.67 ± 16.44 mg/L), whereas, those of Mg²⁺ ranged from <1 to 26.21 mg/L (average = 8.37 ± 5.7 mg/L) reflecting weathering of silicate minerals. As a result, TH, that is mainly regulated by Ca²⁺ and Mg²⁺ concentration, varied from 40 to 400 mg CaCO₃/L with an average value of 104.38 ± 45 CaCO₃/L under WHO reference value (500

mg CaCO₃/L) for drinking water. Around 20% and 5% of the sample were classified as being “hard” and “very hard” waters, respectively [52]. The groundwater with TH greater than 80 mg CaCO₃/L ($\sim 80\%$) are unsuitable for domestic uses because they coagulate soap lather [53]. Additionally, long-term consumption of hard water may contribute to cardiovascular diseases and prenatal mortality [54].

Sodium concentrations ranged from 3.05 to 23.73 mg/L (average = 8.16 mg/L). Due to its limited mobility during chemical alterations K⁺ concentrations in groundwater are relatively low compared with Na⁺ concentrations [55], and ranged from <1 to about 8.14 mg/L (average = 4.25 ± 1.08 mg/L).

4.1.4. Groundwater Anion Content

The anion HCO₃⁻ was the most dominant anion in groundwater, with concentrations varied from 65.88 to 610 mg/L (average 142.33 ± 58.71 mg/L). The order of abundance is: HCO₃⁻ > NO₃⁻ > SO₄²⁻ > F⁻ > PO₄³⁻. The high HCO₃⁻ concentrations in groundwater can be attributed to CO₂ inputs from precipitation, as well as to the dissolution of carbonates in the soil and the weathering of primary silicate minerals [56]. The high CO₂ pressure resulting from the mineralisation of organic matter may be a driving force behind the high HCO₃⁻ concentrations in some groundwater samples. Groundwater mineralisation (i.e. EC) shows a strong correlation with HCO₃⁻ concentrations (Figure 4).

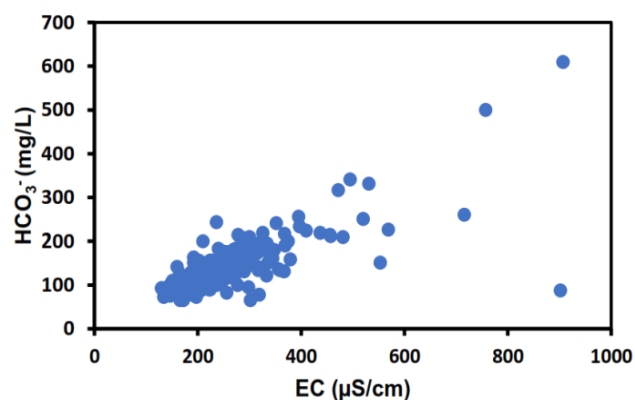


Figure 4. Linear correlation between EC and HCO₃⁻

Consequently, the EC of groundwater samples can be used as an indicator to assess the extent of interactions between water and rock.

Sulphate concentrations varied from <1 to 44.25 mg/L (average = 4.53 ± 5.13 mg/L), contributing to TZ⁻ concentrations. In natural waters with sufficient salinity, SO₄²⁻ concentrations generally range from 2 to 80 mg/L [57]. All the samples therefore have SO₄²⁻ concentrations within the natural range for fresh groundwater. However, the significant standard deviation and high skewness indicate considerable spatial variation and potential anthropogenic or localized weathering contributions of sulfide minerals to SO₄²⁻ concentrations in groundwater [58].

NO₃⁻ concentrations in excess of WHO standards were found in 16% of boreholes. Although the abundance of NO₃⁻ in groundwater is mainly linked to various anthropogenic sources [59,60] non-anthropogenic processes such as enrichment by evaporation, nitrogen

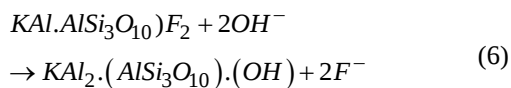
fixation by organisms or water-rock interactions have also been identified as potential sources of NO_3^- concentrations in groundwater in semi-arid environments [61,62,63].

Chloride is typically found in low concentrations within rock-forming minerals, and its levels in groundwater are mainly due to atmospheric inputs or seawater intrusion. [64]. Cl^- concentrations varied from <1 to 29.94 mg/L. All the samples had chloride concentrations well below the WHO standard.

Phosphate was only detected in 167 samples (i.e., 67.07%) with concentrations varying from <1 to 1.77 mg/L (average = 0.15 ± 0.23 mg/L).

Fluoride concentrations above 0.7 mg/l in drinking water are considered beneficial to human health, as they protect against dental caries. Nevertheless, very high concentrations of F^- in groundwater can lead to tooth discolouration and skeletal fluorosis [28]. Fluoride concentrations in water samples groundwater samples ranged from < 0.04 to 2.08 mg/L (average = 0.37 ± 0.36 mg/L). Fluoride concentrations of 0.7 mg/L, 1.5 mg/L and greater than 1.5 mg/L were found in 81,92 and 1.60 % of the samples, respectively. This indicates a low risk of endemic dental caries and, to a lesser extent, dental mottling and the occurrence of skeletal fluorosis in the region [65,66,67].

Ranges of high F^- concentrations (i.e. <1.5) occur in close proximity to basement late granitic rocks that contain common fluoride-bearing minerals such as fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), cryolite (Na_3AlF_6) and topaz ($\text{Al}_2(\text{SiO}_4)\text{F}_2$) [68,69]. With the same valency and ionic radius as F^- , OH^- can also replace F^- in biotite (Eq. 6), leading to high concentrations of F^- in alkaline groundwater:



Total iron concentrations varying from <1 to 23.3 mg/L (average = 1.07 ± 2.06 mg/L). A total of 144 samples were concentration greater than 0.3mg/L. Elevated iron levels in water can negatively impact municipal uses, industrial machinery, agriculture, and human health. Children and newborns are particularly more vulnerable to the effects of this contaminant compared to adults [70].

Iron concentrations are variable throughout the study area and do not appear to be related to lithology. A correlation between anthropogenic nitrate and Fe_T shows a total absence of correlation, with a weak coefficient of determination of 0.0064. This implies a non-anthropogenic origin. This shows that the origin of Fe_T in these boreholes is linked to the drainage pumps, which oxidise and promote the dissolution of Fe.

4.2. Overall Groundwater

The calculated WQI ranges from 16 to 146.33 (average = 35.37 ± 22.29). According to the results, the quality of the groundwater sampled ranged from "excellent" ($\text{WQI}=1-25$) to "unfit" for consumption ($\text{WQI}>150$). Based on the calculated WQI, 87.14%, 12.85% and 2.81% of the groundwater samples had a WQI below 50, above 50 and above 100, respectively.

4.3. Groundwater Hydrochemical Evolution

Chemical weathering of bedrock is one of the main processes governing the geochemical cycle of the main ions in the aquifer system [71]. Therefore, understanding the geochemistry and quality of groundwater necessitates a detailed examination of major ions such as K^+ , Na^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , HCO_3^- , NO_3^- and Cl^- . These ions can be utilized to categorize groundwater types, as well as to assess mixing, evaporation, and chemical weathering. Based on the molar ratios of the Ca/Na versus HCO_3/Na diagram [72,73], silicate weathering is the main lithogenic contributor to Ca^{2+} and Mg^{2+} loadings in the groundwater system, followed by carbonate dissolution (Figure 5).

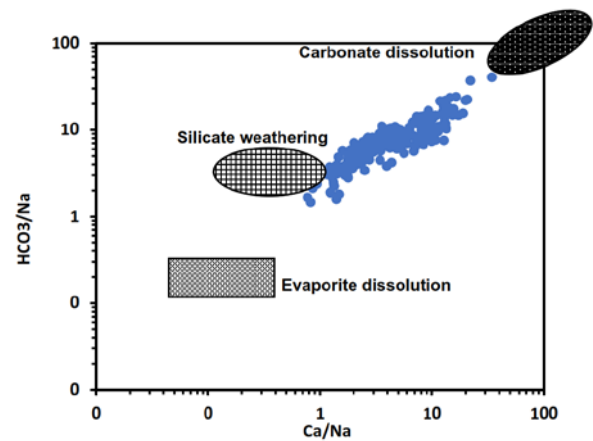
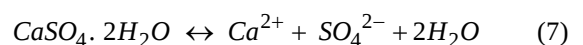


Figure 5. Bivariate plots of HCO_3/Na vs. Ca/Na of the groundwater samples

Additional evidence for this is provided by high Na/Cl ratios (> 1) of the majority of the samples on Na/Cl vs. Cl^- (Figure 6a) indicating that Na^+ levels in the groundwater were mainly influenced by silicate weathering [74]. A few samples showed Na/Cl ratios that projected on the 1:1 equiline, suggesting that halite dissolution partially contributed to Na^+ loadings in these boreholes. The dominance of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ over $(\text{HCO}_3^- + \text{SO}_4^{2-})$ on the scatter plot of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ vs $(\text{Ca}^{2+} + \text{Mg}^{2+})$ (Figure 6b) clearly indicates the presence of significant feldspar mineral weathering and ion exchange, whereas samples plotted close to the 1:1 equiline indicated dissolution of calcite, dolomite and gypsum [75,76].

Groundwater chemistry could be influenced by geochemical processes such as evapotranspiration, which increases its mineral concentration. Therefore, if evapotranspiration is the primary process, the Na/Cl ratio should remain stable as electrical conductivity increases [77]. In this study, a set of samples displayed a horizontal trend in the Na/Cl vs EC scatterplot (Figure 6c), indicating that, alongside silicate weathering, evapotranspiration also contributed to Na concentrations in the groundwater system.

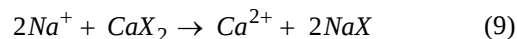
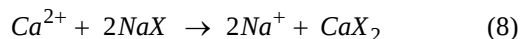
The Ca^{2+} vs. SO_4^{2-} scatter plot (Figure 6d) had been used to identify the sources Ca^{2+} and SO_4^{2-} in groundwater [78]. If the ions Ca^{2+} and SO_4^{2-} originated from gypsum weathering, the molar ratio of Ca^{2+} to SO_4^{2-} would be 1:1 as indicated by the following reaction (Eq. 7):



On the other hand, in this study there is no determined relationship between Ca^{2+} and SO_4^{2-} concentrations, implying that these two ions do not originate from the dissolution of gypsum. The slight excess of SO_4^{2-} over Ca^{2+} on the Ca^{2+} vs SO_4^{2-} graph can be attributed to the ion exchange process, while the excess of Ca^{2+} is linked to the alteration of the silicates. Additionally, the oxidation of sulfide minerals may also contribute to SO_4^{2-} loadings in groundwater. The weathering of calcite, dolomite, pyroxene and amphibole could contribute to the source of Ca^{2+} and HCO_3^- in groundwater. The scatter plot of Ca^{2+} versus HCO_3^- shows that some samples are represented above the 1:1 equilibrium, suggesting that Ca^{2+} concentrations exceed those of HCO_3^- , and indicating that anorthite and dolomite alteration are not occurring in these samples (Figure 6e). In contrast, few groundwater samples were plotted along the 1:1 equilibrium, indicating that the main source of Ca^{2+} and HCO_3^- in these samples is calcite weathering.

In addition, the $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. Na^+ scatter plot was employed to assess the extent of the ion exchange process. On the basis of this diagram, groundwater samples are projected above (i.e. reverse ion exchange; Eq. 8) and below 1:1 equilibrium (i.e. direct exchange; Eq.9),

suggesting that both direct and reverse ion exchange take place in the groundwater system. Nevertheless, direct exchange dominates in view of the number of samples below 1:1 equilibrium (Figure 6f):



Through direct ion exchange, Ca^{2+} and Mg^{2+} are released into groundwater while Na^+ or K^+ are retained by the aquifer materials. Conversely, Na^+ or K^+ are released into groundwater through reverse ion exchange while Ca^{2+} and Mg^{2+} are adsorbed onto the aquifer matrix [79]. It can be asserted that under the neutral pH conditions of the examined groundwater, reverse ion exchange occurs within the aquifer matrix. The key geochemical processes that influence the chemistry of groundwater include ion exchange, evapotranspiration, and the weathering of silicates. Moreover, the study area, which partially overlaps with the region's urban centers (i.e., the districts of Kombissiri, Toecé, Beré, Bindé, Guiba, Manga, and Nobéré), is therefore vulnerable to changes in groundwater quality.

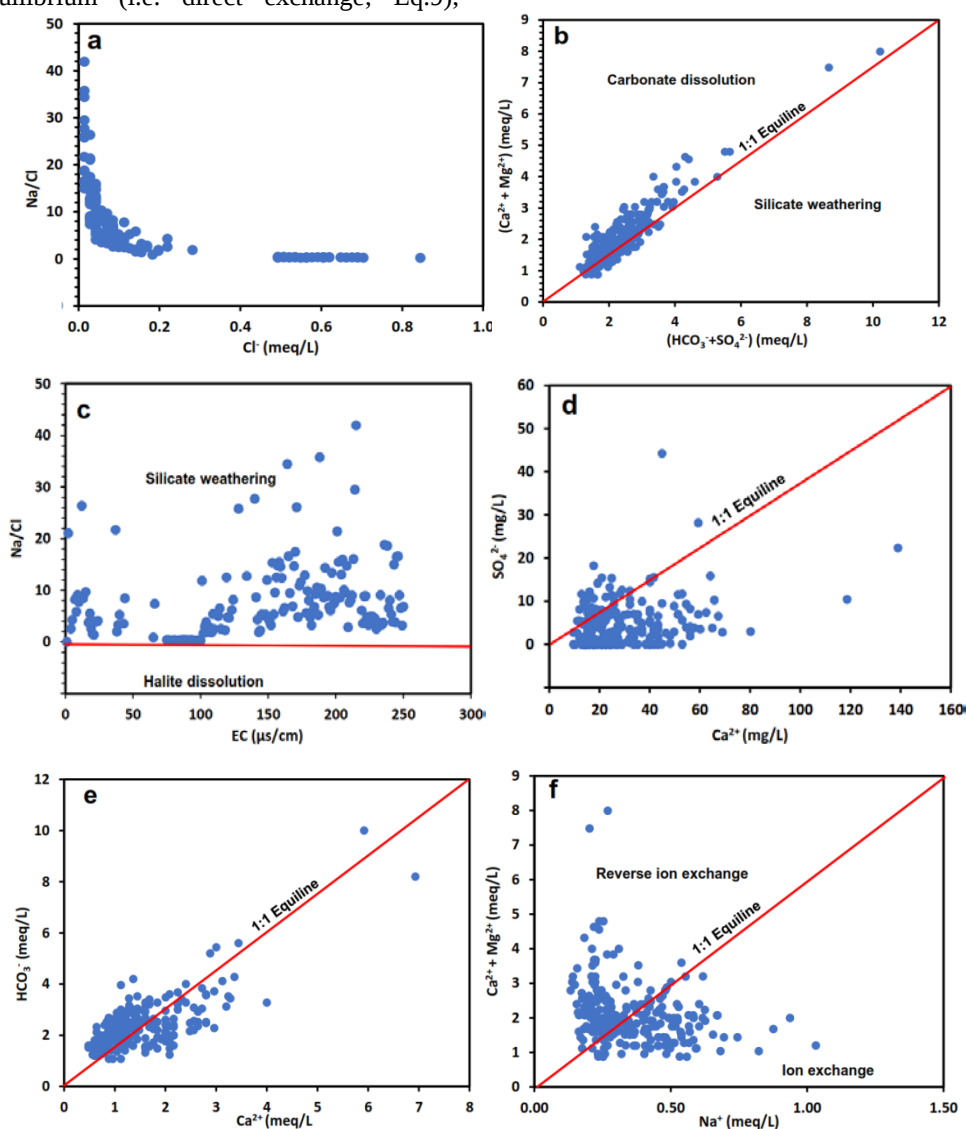


Figure 6. Scatter plots showing relationships between major ions in the groundwater samples

Table 3. Summary of saturation indices of selected mineral phases in the groundwater

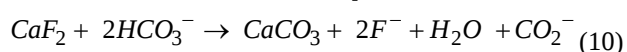
Mineral phase	Chemical formula	N	Min	Max	Mean	Median	Std.D	Skewness	Kurtosis
Aragonite	CaCO ₃	249	-4.04	0.57	-1.60	-1.62	0.71	0.12	0.37
Calcite	CaCO ₃	249	-3.90	0.71	-1.43	-1.47	0.69	0.20	0.30
Dolomite	CaMg (CO ₃) ₂	211	-7.94	0.40	-2.84	-2.93	1.00	0.21	0.36
Fluorite	CaF ₂	244	-4.07	-0.78	-2.64	-2.78	0.67	0.61	-0.27
Gypsum	CaSO ₄ .2H ₂ O	198	-5.94	-2.03	-3.32	-3.20	0.63	-1.54	3.50
FCO ₃ -Apatite	Ca ₁₀ (PO ₄) ₅ (CO ₃)F	133	-21.36	13.66	0.64	0.54	5.68	-0.46	0.93
Hydroxyapatite	Ca ₁₀ (PO ₄) ₆ (OH) ₂	166	-17.29	4.15	-3.47	-3.52	3.54	-0.47	0.71

4.4. Saturation Indices

Only 2.01 and 2.41% of the water samples were supersaturated (SI>0) with respect to aragonite and calcite, respectively. This points out partial sequestration/precipitation of Ca²⁺ and set free of Na⁺ in the groundwater system. Values of IS_d (IS_{dolomite}) ranged from -8.21 to 0.12 (average = -3.58 ± 1.34) with less than 1% of samples supersaturated relative to dolomite, reflecting additional Ca²⁺ sequestration. Groundwater samples undersaturated in calcite, aragonite, and dolomite may be attributed to insufficient mineral sources or a limited contact time between the groundwater and the aquifer, potentially influenced by infiltrated rainwater. The values of IS_g (IS_{gypsum}) range from -5.94 to -2.03 (-3.32 ± 0.63), as indicated in Table 3. All samples were undersaturated with respect to gypsum (SI_g < 0), reflecting the absence of gypsum in crystalline bedrocks.

Saturation index values for the fluorite mineral (CaF₂) ranged from -4.07 to -0.78 (average = -2.64 ± 0.67). All samples (100%) were highly undersaturated with respect to CaF₂, indicating of continuous dissolution of CaF₂ in the aquifer. An increase in pCO₂, whether from atmospheric inputs or microbial respiration, lowers the pH of groundwater. This process enhances the hydrolysis of aluminosilicate minerals, resulting in the production of HCO₃⁻.

The subsequent precipitation of CaCO₃ reduces HCO₃⁻ concentrations, thereby promoting the dissolution of CaF₂ and F⁻ enrichment, as shown in Eq.10:



In the same way, a reduction in pCO₂ during degassing leads to higher concentrations of pH and HCO₃⁻ [79]. This may result in an anion exchange between F⁻ and OH⁻, as well as the dissolution of CaF₂, thereby raising F⁻ levels in groundwater. Additionally, evapotranspiration and reverse cation exchange processes could lower Ca²⁺ levels in groundwater, thereby inhibiting the precipitation of CaF₂. On the other hand, supersaturation and the possible precipitation of FCO₃-apatite and hydroxyapatite (Table 3) in some groundwater samples may restrict F⁻ concentrations in groundwater.

5. Conclusion

Sampling of groundwater from boreholes for a wide range of chemical parameters, determination of water quality index values and geostatistical techniques were applied to assess the quality of groundwater for drinking

purposes in the basement aquifers of the southern region of Burkina Faso. Most of the boreholes analysed have chemical parameters whose values are below WHO standards.

Some boreholes had high concentrations of F⁻ and Fe_T. Alteration of silicates and carbonate, evapotranspiration and ion exchange appear to be the main hydrogeochemical processes controlling groundwater chemistry. Although NO₃⁻ and Cl⁻ concentrations are below the guideline values for drinking water, geostatistical modelling indicates that their levels are largely influenced by anthropogenic activities.

The presence of iron in borehole water is linked to the nature of the pumps, which are mainly made of oxidisable steel.

The results also indicated those certain high concentrations of F⁻ in groundwater may be linked to the precipitation of Ca²⁺ and exchange between OH⁻ and F⁻ on minerals containing fluorite. Based on the results of the study, particular attention should be paid to boreholes located in recharge areas due to possible anthropogenic pollution and discharge areas, where interactions between water and rock are relatively long, due to geogenic pollution.

Abbreviations

BUMIGEB: Bureau des Mines et de Géologie du Burkina
 EDTA: Ethylenediaminetetraacetic Acid
 IBE: Ionic Balance Error
 SI: Saturation indices
 UV: Ultraviolet
 WHO: World Health Organization
 WQI: Water Quality Index

Use of AI Tools Declaration

No artificial intelligence (AI) tools were used in this work.

ACKNOWLEDGEMENTS

The authors would like to thank all those who contributed in any way to the success of this work.

Conflict of Interest

There is no conflict of interest in this article.

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