

Hydrochemical Assessment of Groundwater Quality in the City of Manga and the Surrounding Area, Burkina Faso, West Africa

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Abstract: The population of the city of Manga and the surrounding area is supplied with drinking water by boreholes exploiting the fractured rock aquifer. However, these boreholes are often managed without considering the impact of natural geogenic and anthropogenic sources of toxic chemicals, which can threaten groundwater quality. Major ion geochemistry, water quality index calculations have been used to understand the hydrogeochemical processes controlling water quality. To carry out this study, 94 water samples from wells were collected and analyzed. Physicochemical parameters indicate neutral and soft waters due to low mineralization. The dominant ions are Ca^{2+} , Mg^{2+} , and HCO_3^- . Most of the analyzed samples are considered excellent according to the WQI. Analysis using bivariate diagrams revealed that the main factors affecting solute acquisition in groundwater are silicate weathering, mineral dissolution and precipitation, ion exchange, and evapotranspiration. This study enabled us to assess the hydrochemical quality of the water and gain a better understanding of the physico-chemical processes controlling the mineralization of groundwater in the study area. It will therefore be a decision-making tool for sustainable water management.

Keywords: groundwater, hydrochemical evolution, saturation indices, WQI, Manga, Burkina Faso

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1. Introduction

Anthropogenic and natural factors such as the nature of geochemical reactions, salt solubility, rock weathering, groundwater flow, evaporation-induced crystallization, and the contribution of atmospheric precipitation govern the geochemical signatures of groundwater [1,2,3,4,5] [6,7,8,9]. Atmospheric gases such as CO_2 , SO_2 , and NO_x cause rainwater to become acidic. Once the rainwater interacts with the regolith, microbial-mediated redox processes further modify its chemistry. These processes influence both the carbon content of groundwater and the distribution of its major ions and trace elements [10,11].

The extended residence time of groundwater in aquifers, coupled with seasonal variations in precipitation and evapotranspiration, results in ongoing changes to its chemical composition through interactions with the surrounding rocks [12,13,14,15,16,17].

Additionally, deforestation, human activities, and their spatial distribution can also affect groundwater chemistry

[18,19,20]. This has led researchers to use hydrogeochemistry to assess the lithological contributions to groundwater chemistry on a global scale [21,22,23]. The study area is essentially underlain by crystalline basement rocks, composed of volcano-sedimentary, plutonic rocks represented by granitoids. These rocks are made up of various minerals whose alteration would release several chemical elements into solution.

Recently, numerous boreholes have been drilled in rural and peri-urban areas of Manga city to supply drinking water. However, these boreholes are often managed without considering the impact of natural geogenic and anthropogenic sources of toxic chemicals, which can threaten groundwater quality. To effectively monitor and address these pollution sources and to develop a sustainable and integrated groundwater management plan, it is crucial to understand the current status of the chemical constituents that influence groundwater quality [24,25].

Typically, the concentrations of various quality parameters in water intended for human consumption are compared with the standards set by the WHO. Parameters exceeding these WHO limits are considered potentially harmful to both the ecosystem and human health.

Although this method offers insight into water quality, it does not provide information on spatial or temporal trends in overall water quality [26].

The WQI is also used to assess water potability. This method, utilized by [27,28,29], provides a more comprehensive evaluation of water quality for consumption purposes. This numerical approach consolidates a wide range of groundwater quality parameters into a single value, generating a score that describes the condition of groundwater quality over a specific spatial and temporal scale [30,31].

To our knowledge, no geochemical characterization study using the WQI has been conducted in the city of Manga and its surroundings. As part of the drinking water supply plan for the city of Manga, a number of high-flow boreholes need to be drilled. Given the various anthropogenic activities associated with natural hydrochemical processes, water quality could be affected. Hydrogeochemical analyses were used to test this hypothesis and achieve the study's objectives. The results will help water resource managers monitor the quality of groundwater in the city of Manga and its surroundings.

2. Study Area

2.1. Environmental Setting

The study was conducted in the watershed draining the city of Manga and its surrounding area, the capital of the Zoundwéogo province (Central-South region) in Burkina Faso (Figure 1)

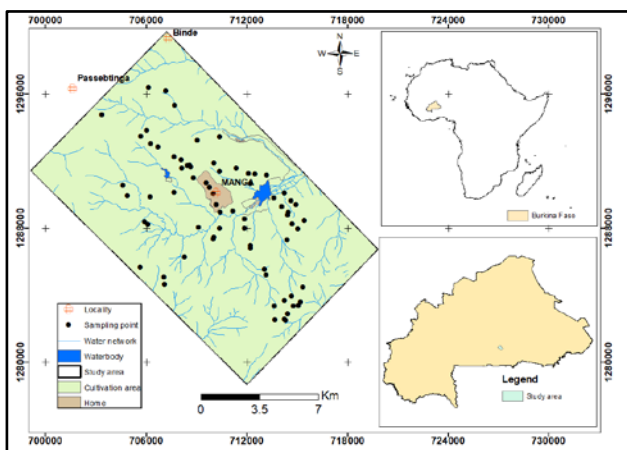


Figure 1. Geographical location of the groundwater sampling sites and land occupation map showing major regional watercourses in study area

The municipality falls within the Sudanian and Sahelian type climatic zone, characterized by annual rainfall ranging between 600 and 900 mm, with a rainy season lasting 4 to 5 months from May to October [32] and a very long dry season of 7 to 8 months. Precipitation is irregular both spatially and temporally, with an annual average of 800 mm. Minimum temperatures range between 21°C and 22°C, while maximum temperatures range between 30°C and 35°C. Hydrologically, the municipality of Manga is part of the Nakambé watershed, one of the major basins in the country.

The majority of the population in the municipality is

engaged primarily in agriculture and livestock farming, with agricultural production heavily dependent on climatic variability. These climatic uncertainties, along with ongoing degradation of soils, vegetation cover, and water resources, limit agricultural yields. Cultivated lands require fertilizers, and most farmers use pesticides, organic fertilizers, and chemical fertilizers to boost yields. Additionally, population pressure and rampant urbanization are making soils impervious and limiting groundwater recharge. These factors are likely to impact groundwater quality.

2.2. Geological and Hydrogeological Settings

The study area is primarily underlain by crystalline basement rocks, composed of volcanic-sedimentary and plutonic rocks represented by granites, tonalites, and quartz diorites, as well as late magmatic phenomena marked by the emplacement of dolerite dykes [32,33] (Figure 2).

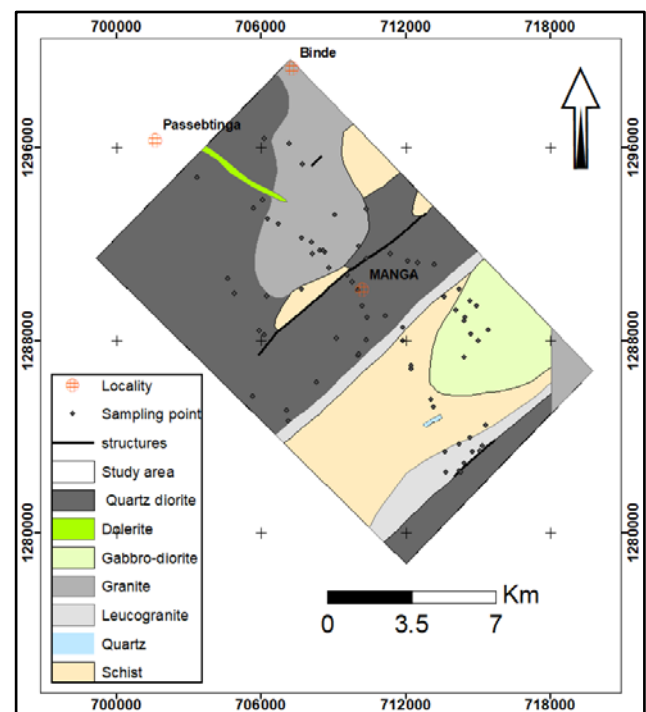


Figure 2. Simplified geological map of the study area

These geological formations form altered and fractured aquifers [34]. The recent model of basement aquifers, proposed by several authors [35,36,37] distinguishes three (03) "layers" from bottom to top based on hydrogeological properties: (1) the top of the fractured basement, where fractures are tectonic in origin, generally sub-vertical, and act as major drains at depth; (2) an intermediate layer (the fractured zone). This is particularly developed in granite formations, where it can reach thicknesses of several tens of meters. This zone is characterized by primarily horizontal fractures; (3) finally, the upper layer, which corresponds to the weathered part of the rock. Depending on the depth and degree of weathering, two compartments are distinguished: the upper, the alloterites, and the lower, the isaloterites. The alloterites generally have relatively low permeability due to their high clay content but possess high capacitive function.

These geological formations contain disseminated and vein-type sulfur minerals, which generally constitute gold metallotectics. Oxidation of these sulfur minerals through chemical weathering or exposure to air during gold extraction can generate acidic leachate, rich in SO_4^{2-} , promoting rock dissolution and the mobility of trace elements in the environment, potentially reaching groundwater.

The discontinuity of aquifers and the distance from groundwater sources are responsible for the drying up of traditional wells during the dry season, especially those not near watercourses. Consequently, water supply relies on boreholes, typically using manual pumps in rural areas. In principle, these structures should be less vulnerable, but due to population pressure and increased use of chemicals, the search for water points is conducted along fractures, which are the preferred recharge zones of the aquifer. While these recharge zones are crucial for the availability and sustainability of the water resource, they are also sources of anthropogenic pollutants due to the transport of microorganisms, pesticides, chemical fertilizer effluents, and heavy metals.

3. Material and Methods

3.1. Sample Collection and Analysis

To carry out this study, 94 groundwater samples were taken from boreholes tapping fractured crystalline aquifers in the watershed draining the city of Manga. To ensure that the borehole samples were indeed representative of groundwater and not of water that had been in the boreholes for some time, we put the boreholes into production for a few minutes (10-15 minutes) before the samples were taken. To avoid the effects of microorganism activity on groundwater chemistry, each sample was pumped through a 0.2 μm filter capsule into two sets of pre-conditioned polyethylene bottles. One set was acidified ($pH < 2$) 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 physico-chemical parameters such as pH, temperature, electrical conductivity (EC) and turbidity were measured in field under minimum atmospheric contact, using 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 in the groundwater samples were measured using an atomic absorption spectrometer (AA 7000, Perkin Elmer 2380). The analytical accuracy was cross-checked by calculating IBE as follows (Eq. 1):

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

In general, the value of IBE should be less than $\pm 5\%$, and certainly less than $\pm 10\%$ [38]. In this study, all samples were IBE values less than $\pm 10\%$. In this study, samples with IBE 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 significantly affect the results. The remaining dataset was sufficiently large for geostatistical modelling of groundwater quality.

3.2. Water Quality Index

The WQI for each sample was computed using 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 (wi) 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).

Table 1. Weight, relative weight and the WHO's standards used to calculate groundwater quality index

Parameters	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

The relative weights (Wi) for each parameter were calculated as described in Equation 2.

$$Wi = \frac{wi}{\sum_{i=1}^n wi} \quad (2)$$

where Wi is the relative weight, wi is the weight of each parameter and n is the number of the parameters. The quality rating scale (qi) was also computed by dividing the concentration of each parameter (Ci) by its corresponding WHO guideline value (Si) for drinking water (Eq. 3):

$$qi = \frac{Ci}{Si} \times 100 \quad (3)$$

Before computing WQI, a sub-index (Sli) of each parameter was calculated as follows (Eq. 4–5):

$$Sli = qi \times Wi \quad (4)$$

$$WQI = \sum Sli \quad (5)$$

The calculated WQI values group groundwater into five different classes [39,40]: (1) excellent water (WQI < 50); (2) good water (WQI = 50-100); (3) poor water (WQI = 100-200); (4) very poor water (WQI = 200-300); and (5) water unsuitable for human consumption (WQI > 300) (Table 2).

Table 2. Univariate statistical summary of physico-chemical Parameters of the groundwater samples

Parameter	Unit	N	Min	Max	Mean	Median	Std. D	Skewness	Kurtois
pH		94	6.20	8.00	7.32	7.40	0.39	-0.83	6.20
IS		94	6.20	8.00	7.32	7.40	0.39	-0.83	0.70
pCO ₂	atm	94	0.00	0.01	0.01	0.01	0.00	0.33	-0.41
TDS	mg/L	94	0.00	2.10	0.04	0.01	0.22	9.63	93.18
EC	µS/cm	94	109.02	745.89	296.06	279.80	115.89	0.89	1.42
TH	mg/L	94	158.00	1081.00	429.07	405.50	167.95	0.89	1.42
Ca ²⁺	mg/L	94	44.00	324.00	187.96	180.00	70.32	0.15	-0.64
Mg ²⁺	mg/L	94	18.44	96.19	48.42	46.49	17.30	0.56	-0.02
Na ⁺	mg/L	94	0.00	57.78	16.40	13.33	13.31	1.22	0.91
K ⁺	mg/L	94	2.30	11.96	8.00	8.93	2.24	-0.67	-0.79
HCO ₃ ⁻	mg/L	94	1.98	11.56	5.32	4.79	2.14	0.95	0.56
Cl ⁻	mg/L	94	85.40	463.60	238.49	229.36	86.42	0.33	-0.32
SO ₄ ²⁻	mg/L	94	0.00	7.49	1.07	0.00	1.81	1.93	3.36
NO ₃ ⁻	mg/L	94	0.00	76.58	12.58	9.79	12.53	1.92	6.29
F ⁻	mg/L	94	0.00	10.94	1.27	0.00	2.61	2.11	3.50
PO ₄ ³⁻	mg/L	94	0.00	0.71	0.08	0.06	0.08	5.14	35.57
Fe _T	mg/L	94	0.00	1.77	0.09	0.05	0.20	6.53	50.27
WQI	mg/L	94	0.00	16.55	0.62	0.26	1.79	7.80	68.22

Std. D: Standard deviation

3.3. Hydrogeochemical Modelling

Hydrogeochemical modelling is a crucial analytical tool for identifying the primary geochemical reactions that control groundwater chemistry. To identify the main geochemical reactions controlling groundwater chemistry, hydrogeochemical modelling is an important analytical tool that can be utilized [41]. In this study, Visual MINTEQ (version 4) was used to calculate 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 Table 2 presents the results of the measurements of physico-chemical parameters in the groundwater samples. Among these parameters, pH plays a central role in regulating the biogeochemical processes that take place in groundwater [42,43]. Although a high pH cannot have a direct impact on human health, it can profoundly affect the taste of drinking water. The pH of the groundwater sampled ranged from 6.20 to 8 with an average \pm standard deviation of 7.32 ± 0.39 , which indicating the neutral nature of the groundwater. This also suggests that dissolved carbonates were mainly in the form of HCO₃⁻. The EC concentration ranged from 158 to 1081 µS/cm with an average of 429.07 ± 167.95 µS/cm. The overall low mineralisation rates can be attributed to the low content of evaporite minerals in the local geological formations as high groundwater mineralisation generally occurs in evaporites formations [44]. Groundwater is considered fresh water when TDS ranges from 0 to

1000mg/L. Total dissolved solids were low and ranged from 109.02 to 745.89 mg/L (average = 296.06 ± 115.89 mg/L), indicating that the groundwater is fresh due to the dilution effects of recharge rainwater on the groundwater, or limited mineral dissolution [45].

4.1.2. Groundwater Recharge Areas

Groundwater mineralization can vary across different locations, influenced by soil composition and the residence time of resources, regardless of the underlying geology. The Saturation Index (SI) reflects these variations: positive values indicate that the water is supersaturated with respect to the mineral phase, negative values signify undersaturation, and a value of zero represents equilibrium [28]. The IS of the groundwater sampled ranged from 0.002 to 0.012 with an average \pm standard deviation of 0.006 ± 0.0021 , which indicating the saturated nature of the groundwater.

The groundwaters which have a low ionic strength (i.e., <0.005) are indicative a high rate of inflow of freshwater into the aquifer (i.e., recharge areas), whereas, high ionic strength groundwaters indicate less inflow of freshwater, and the areas are considerate to be discharge areas [46].

Sometimes the pCO₂ can be used to determine recharge zones, residence time and, more importantly, water-rock interactions [47,48]. The modelled log pCO₂ values were relatively higher than atmospheric log pCO₂ (-3.75) and ranged from 0.0014 and 2.09 (Figure 3), suggesting that the aquifer system is open to the soil CO₂. Many boreholes have high log pCO₂ values (~ -1.5) and are considered to be in a closed system which is characterised by a long residence time favouring the prolongment of water-rock interactions [27,28]. We can therefore conclude that the majority of drilling water is concentrated in the mixing zone and in the open system. Consequently, understanding the sources and mechanisms of

groundwater recharge in this semi-arid climate zone is essential for regional water resource management.

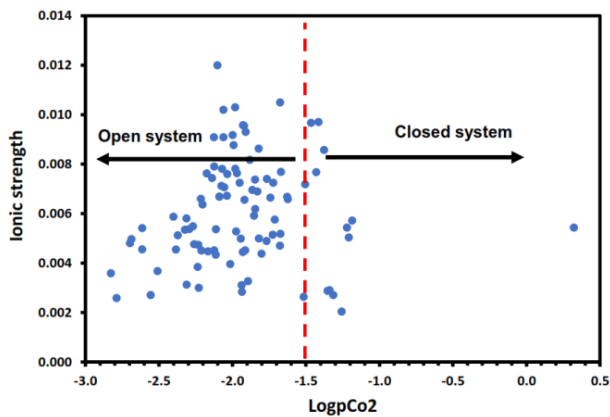


Figure 3. Bivariate plot between $\log p\text{CO}_2$ and ionic strength of the groundwater samples illustrating mostly a short residence time of the groundwater

4.1.3. Groundwater Cation Content

The ions Ca^{2+} and Mg^{2+} were the dominant cations in the samples and were followed by Na^+ and K^+ . The order of abundance is: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. Calcium concentrations varied from 18.44 to 96.19 mg/L (average = 48.42 ± 17.30 mg/L), whereas, those of Mg^{2+} ranged from <1 to 57.78 mg/L (average = 16.40 ± 13.31 mg/L) reflecting weathering of silicate minerals and calcite dissolution. As a result, TH, that is mainly regulated by Ca^{2+} and Mg^{2+} concentration, varied from 44 to 324 mg CaCO_3/L with an average value of 187.96 ± 70.30 CaCO_3/L under WHO reference value (500 mg CaCO_3/L) for drinking water. Around 45% and 12% of the sample were classified as being “hard” and “very hard” waters, respectively [49]. The groundwater with TH greater than 80 mg CaCO_3/L (~92%) are unsuitable for domestic uses because they coagulate soap lather [50]. Also, long term consumption of hard waters could trigger cardiovascular diseases and prenatal mortality [51].

Sodium concentrations ranged from 2.30 to 11.96 mg/L (average = 8 mg/L). Because of its low mobility during chemical alterations K^+ concentrations in groundwater are relatively low compared with Na^+ concentrations [52], and ranged from 1.98 to about 11.96 mg/L (average = 5.32 ± 2.14 mg/L).

4.1.4. Groundwater Anion Content

The anion HCO_3^- 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: $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{PO}_4^{3-} > \text{F}^-$. The high HCO_3^- concentrations in groundwater can be attributed to CO_2 inputs from precipitation, as well as to the dissolution of carbonates in the soil and the weathering of primary silicate minerals [53]. The high CO_2 pressure caused by the mineralisation of organic matter may be a driving force behind the high HCO_3^- concentrations in some groundwater samples. Groundwater mineralisation (i.e. EC) is strongly correlated with HCO_3^- concentrations (Figure 4). Consequently, the EC of groundwater samples

can be used as an indicator to assess the extent of interactions between water and rock.

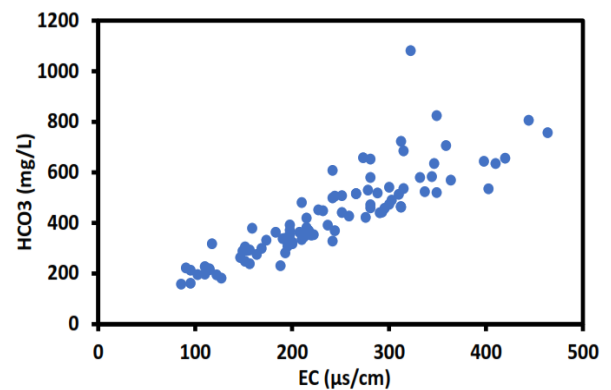


Figure 4. Scatter plot indicating a linear trend between EC and HCO_3^-

Sulphate concentrations varied from <1 to 76.58 mg/L (average = 12.58 ± 12.53 mg/L), contributing to TZ concentrations. In natural waters with sufficient salinity, SO_4^{2-} concentrations generally range from 2 to 80 mg/L [54]. All the samples therefore have SO_4^{2-} concentrations within the natural range for fresh groundwater. However, the high standard deviation and high skewness observed reflect extensive spatial variation and possible anthropogenic or localised weathering contributions of sulphide minerals to SO_4^{2-} concentrations in groundwater [55].

NO_3^- concentrations in excess of WHO standards were not found in boreholes. Although the abundance of NO_3^- in groundwater is mainly linked to various anthropogenic sources [56,57] 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 [58,59,60].

Chloride is generally present in low concentrations in rock-forming minerals, and its concentration in groundwater is mainly attributed to atmospheric inputs or seawater [61]. Cl^- concentrations varied from <1 to 7.49 mg/L. All the samples had chloride concentrations well below the WHO standard.

Phosphate was only detected in 85 samples (i.e., 90.42%) with concentrations varying from <1 to 1.77 mg/L (average = 0.09 ± 0.20 mg/L).

Fluoride concentrations above 0.7 mg/l in drinking water are considered beneficial to human health, as they protect against dental caries. However, excessive concentrations of F^- in groundwater can lead to tooth discolouration and skeletal fluorosis [62]. Fluoride concentrations in water samples groundwater samples ranged from 0 to 0.71 mg/L (average = 0.08 ± 0.08 mg/L). This suggests that the risk of exposure to disease caused by high fluoride levels is very low.

Total iron concentrations varying from <1 to 15.16 mg/L (average = 0.62 ± 1.79 mg/L). A total of 42 samples were concentration greater than 0.3 mg/L. Increased iron content in water has adverse effects on municipal uses, industrial machinery, agriculture and human health. Compared with adults, children and newborns are more sensitive to the effects of the contaminant [63].

4.2. Overall Groundwater

The calculated WQI ranges from 17.95 to 51.06 (average = $32.7635.37 \pm 7.53$). According to the results, the quality of the groundwater sampled ranged from "excellent" (WQI=1-25) to "unfit" for consumption (WQI>150). Based on the calculated WQI, 90.42%, 8.51% and 1.06% of the groundwater samples had a WQI below 25, above 25 and above 50, respectively. It is interesting to note that most groundwater samples were of excellent quality.

4.3. Groundwater Hydrochemical Evolution

Chemical weathering of bedrock is one of the main processes controlling the geochemical cycle of the main ions in the aquifer system [64]. Therefore, understanding the geochemistry and quality of groundwater requires a thorough interpretation of major ions such as K^+ , Na^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , HCO_3^- , NO_3^- and Cl^- . These ions can be used to classify groundwater types, mixing, evaporation and chemical weathering. According to the bivariate mixing plots of Ca/Na versus HCO_3^-/Na and Ca/Na versus Mg/Na [65,66], carbonate dissolution is the main lithogenic contributor to Ca^{2+} and Mg^{2+} loadings in the groundwater system, followed by silicate weathering (Figure 5a, b).

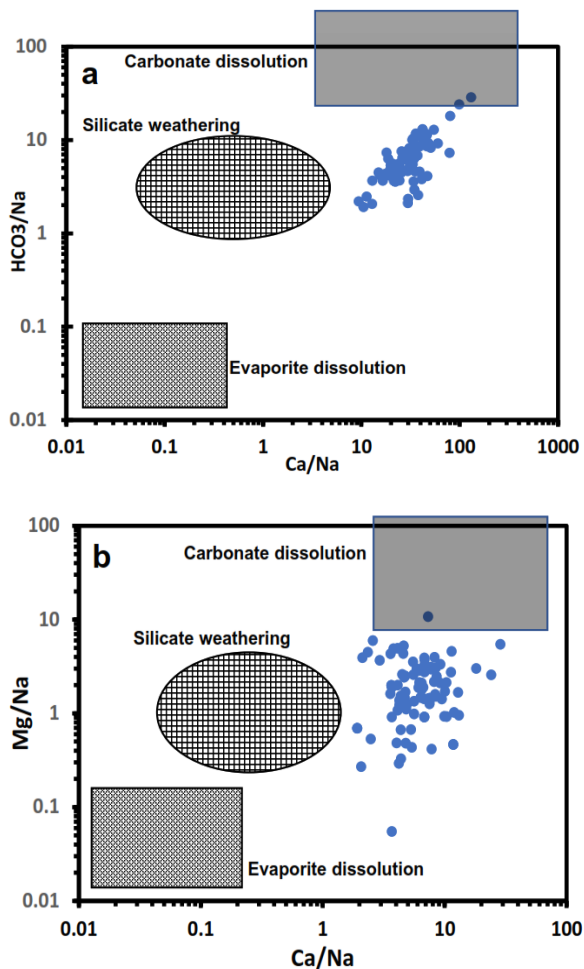
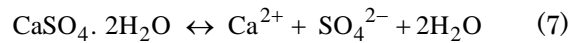


Figure 5. a bivariate plot of Ca/Na vs HCO_3^-/Na , b Ca/Na versus Mg/Na of the groundwater samples, showing the effect of water-rock influence on the groundwater chemistry

A ratio of less than 1 indicates the dissolution of dolomite, while a ratio greater than 1 indicates the dissolution of calcite [67,68]. Of the 94 wells, 80 have Ca/Mg ratios greater than 1 (Figure 6a), suggesting a predominant contribution of calcite to the abundance of Ca^{2+} and Mg^{2+} in the water chemistry of the wells. Chemical weathering and dissolution of minerals in the aquifer are generally triggered by carbonic acid (H_2CO_3) derived from atmospheric or biological CO_2 inputs.

The dominance of $(Ca^{2+} + Mg^{2+})$ over $(HCO_3^- + SO_4^{2-})$ on the scatter plot of $(HCO_3^- + SO_4^{2-})$ vs $(Ca^{2+} + Mg^{2+})$ (Figure 6b) clearly pointed out the existence of few dominant feldspar mineral weathering and ion exchange, whereas samples plotted close to the 1:1 equiline indicated dissolution of calcite, dolomite and gypsum [69,70].

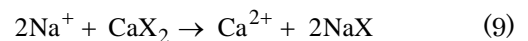
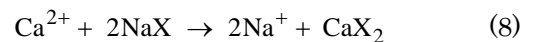
The Ca^{2+} vs. SO_4^{2-} scatter plot (Figure 6c) had been used to identify the sources Ca^{2+} and SO_4^{2-} in groundwater [71]. If the ions Ca^{2+} and SO_4^{2-} originated from gypsum weathering, the molar ratio of Ca^{2+} to SO_4^{2-} would be 1:1 according to the following reaction (Eq. 7):



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 mainly linked to the dissolution of calcite, dolomite and aragonite. Oxidation of sulphide minerals could also be a source of SO_4^{2-} loadings in groundwater.

The weathering of calcite, dolomite, pyroxene and amphibole could be 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, indicating that Ca^{2+} concentrations are higher than those of HCO_3^- and that anorthite and dolomite alteration isn't taking place in these samples (Figure 6d). In contrast, few groundwater samples were plotted along the 1:1 equilibrium, suggesting that the main source of Ca^{2+} and HCO_3^- in these samples is calcite weathering.

In addition, the $Ca^{2+} + Mg^{2+}$ vs. Na^+ scatter plot was used 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 6e):



Thus, through direct ion exchange, Ca^{2+} and Mg^{2+} are released into the groundwater and Na^+ or K^+ are retained by the aquifer materials. On the other hand, Ca^{2+} and Mg^{2+} are adsorbed onto the aquifer matrix and Na^+ or K^+ are released into the groundwater by reverse ion exchange [72,73]. It can be concluded that under the neutral pH conditions of the groundwater studied, reverse ion exchange takes place on the aquifer matrix. Ion exchange,

evapotranspiration, calcite and aragonite dissolution and silicate weathering are the main geochemical processes controlling groundwater chemistry. Additionally, the study area includes an urban center, the city of Manga. This makes it vulnerable to changes in groundwater quality.

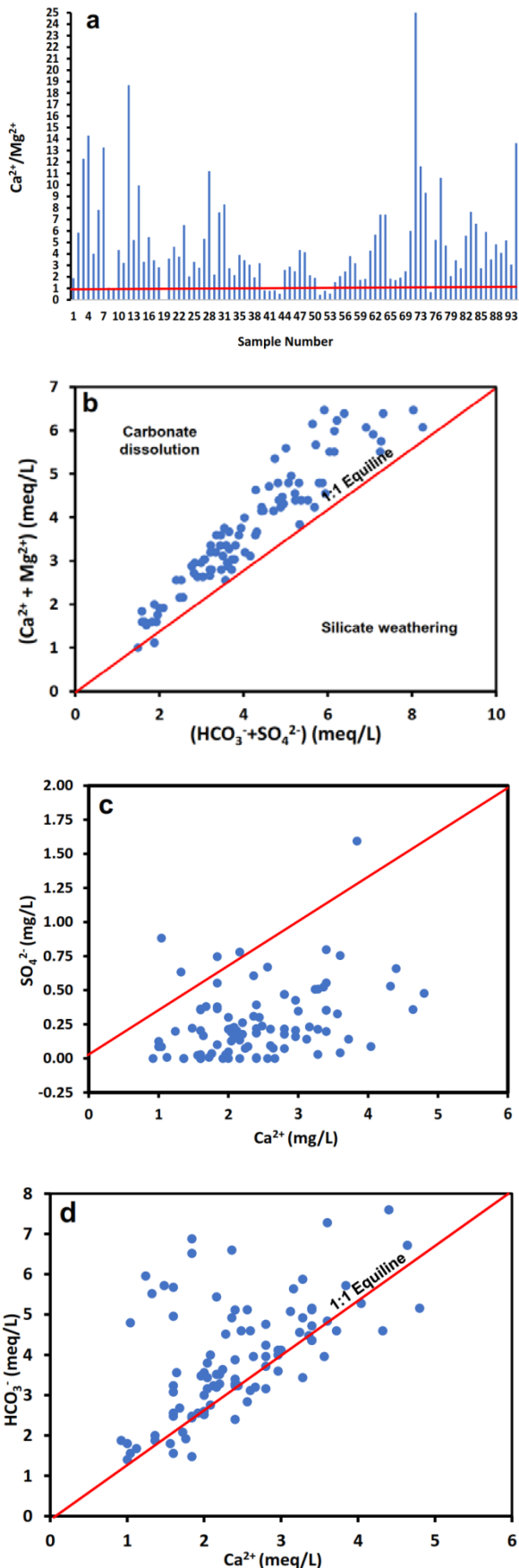


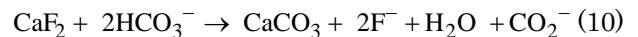
Figure 6. Scatter plots showing relationships between major ions in the groundwater samples

4.4. Saturation Indices

Around 31 and 48 % of the samples were supersaturated (SI > 0) with respect to aragonite and calcite, respectively. This indicates partial sequestration/precipitation of Ca²⁺ and release of Na⁺ in the groundwater system. Values of IS_d (IS_{dolomite}) ranged from -18.27 to 1.48 (average = -0.79 ± 2.14) with around 20% of samples supersaturated relative to dolomite, reflecting additional Ca²⁺ sequestration. The undersaturated groundwater samples with respect to calcite, aragonite and dolomite may be related to insufficient mineral sources or a short contact time of the groundwater with the aquifer, which may be influenced by infiltrated rainwater. With IS_g (IS_{gypsum}) values ranging from -9.11 to 1.58 (-2.73 ± 0.99; Table 3). Except one sample, 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 -14.71 to -1.37 (average = -3.81 ± 1.36). All samples (100%) were highly undersaturated with respect to CaF₂, indicating of continuous dissolution of CaF₂ in the groundwater system. An increase in pCO₂ due to atmospheric inputs or microbial respiration reduces the pH of the groundwater. This leads to hydrolysis of the 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:



Similarly, a decrease in pCO₂ during degassing results in an increase in pH and HCO₃⁻ concentrations [74]. This can lead to an exchange of anions between F⁻ and OH⁻ and the dissolution of CaF₂, thus increasing F⁻ concentrations in groundwater. Evapotranspiration and reverse cation exchange could also reduce Ca²⁺ concentrations in groundwater, thus preventing CaF₂ precipitation.

On the other hand, supersaturation and the possible precipitation of FCO₃-apatite and hydroxyapatite (Table 3) in some groundwater samples are likely to limit F⁻ concentrations in groundwater.

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
Anhydrite	CaSO ₄	83	-8.94	-1.97	-3.04	-2.92	0.82	-4.81	32.78
Aragonite	CaCO ₃	93	-2.07	0.66	-0.26	-0.16	0.54	-1.28	1.94
Calcite	CaCO ₃	94	-8.94	0.80	-0.21	-0.01	1.06	-6.29	50.60
Dolomite	CaMg (CO ₃) ₂	89	-18.27	1.76	-0.79	-0.42	2.14	-6.35	51.01
Fluorite	CaF ₂	92	-14.71	-1.38	-3.82	-3.59	1.37	-5.66	44.44
Gypsum	CaSO ₄ ·2H ₂ O	81	-9.11	1.59	-2.74	-2.65	0.99	-2.47	25.09
FCO3-Apatite	Ca ₁₀ (PO ₄) ₅ (CO ₃)F	81	-108.80	16.20	4.60	6.48	13.32	-7.90	67.62
Hydroxyapatite	Ca ₁₀ (PO ₄) ₆ (OH) ₂	84	-43.67	6.88	-0.22	0.57	5.34	-6.68	53.81

5. Conclusion

Groundwater sampling in boreholes for various chemical parameters, along with the assessment of water quality index values, has been conducted to evaluate the quality of groundwater for consumption in the aquifers beneath Manga city and its surrounding area. The primary hydrochemical processes influencing groundwater chemistry appear to be the alteration of silicates and carbonates, evapotranspiration, and ion exchange. A strong correlation between total iron and sodium concentrations suggests that their presence in the groundwater system mainly stems from natural geogenic processes, including chemical weathering and desorption in alkaline pH conditions. Most of the analyzed boreholes showed chemical parameters below WHO standards. Notably, over 90% of the groundwater samples were classified as excellent quality, with a water quality index below 25. Given this context, it is essential to monitor groundwater closely, as it is primarily in an open system where surface pollutants could infiltrate due to recharge.

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

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