

Hydrogeochemical Assessment of Groundwater in the Precambrian Rocks, South Eastern Desert, Egypt

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Abstract

This work refers to the characterization of the hydrochemistry of the southern part of the Eastern Desert in Egypt, on the basis of physico-chemical properties of groundwater occurring in the fractured Precambrian rocks inland and in sedimentary formations on the coastline of the Red Sea. Thirty-five groundwater samples have been collected from the study area for hydrochemical investigations to understand the sources of dissolved ions and assess the chemical quality of the groundwater. Several methods were used to interpret the hydrochemical data, *i.e.* graphical methods, principal components analysis, ions exchanges indices and saturation indices of various minerals. The results show that the major ionic relationships are $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$ and that groundwater chemical characteristics are controlled by natural geochemical processes but also, to a lesser extent, by anthropogenic activities. Natural minerals dissolution, ion exchanges and evaporation play a prominent role in the ion enrichment of groundwater. A comparison of groundwater quality in relation to WHO water quality standards proved that most of the water samples are not totally suitable for drinking water purpose.

Keywords

Eastern Desert, Pre-Cambrian Rocks, Groundwater, Hydrochemistry, Principal Components Analysis, Egypt

1. Introduction

Groundwater resource assessments and sustainability considerations are of utmost importance in the arid and

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semiarid regions, where water is commonly of critical economical and social significance. Egypt is facing this situation. In this country water needs are dramatically increasing, demanded by a rapidly growing population, increased urbanization, higher standards of living and agricultural policy. The World Bank describes Egypt as a country being under water stress. Limited natural fresh water resources in the Eastern Desert of Egypt call for evaluation of water resources in the area. The Eastern Desert represents 22% of the total area of the country. It houses both residential areas, commercial and industrial zones, as well as tourist villages. Groundwater is a significant and crucial resource in many areas in Egypt and it commonly plays a key role as a water supply for drinking, irrigation and industries. It represents a vital resource in the Eastern Desert due to the unavailability of other sources.

Despite importance of groundwater in the study area, little is known about the natural phenomena that govern the chemical composition of groundwater or anthropogenic factors that presently affect them. The chemical composition of groundwater is controlled by many factors that include composition of precipitation, geological structure and mineralogy of the watersheds and aquifers, and geochemical processes within the aquifer [1]. The interaction of all factors leads to various water types. Thus the purpose of the present study is to determine the current hydrochemical status of the southeastern desert groundwater and understand the mineralization processes. Major chemical ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , NO_3^- , SO_4^{2-}) were analyzed for this purpose. Samples were collected in 35 wells distributed all over the study area. The interpretation of hydrochemical data was made using various methods (Piper diagram, principal component analysis, base exchanges index, bi-elements scatter diagrams, saturation indices, and mapping). The objective aims at improving the knowledge of geochemical evolution of groundwater in this arid and semi-arid region, leading to sustainable development and effective management of groundwater resource.

2. Location of the Study Area

The Eastern Desert covers about 220,000 km² and is located between the Red Sea and the Nile Valley. It extends from latitude 22 N and 29 N or Egypt's borders with Sudan in the South, to the Delta in the North [2]. It forms around 22% of Egypt's surface area, and extends on average over 1100 km from North to South, and 225 km from East (Nile Valley) to West (Red Sea). But it was undeveloped due to the limited availability of water [3]. The Eastern Desert consists of high rugged mountains parallel to the coast and flanked to the north and west by dissected sedimentary plateau [4]. The study area (Figure 1) is located in the Southern part of the Eastern Desert (South Eastern Desert) and extends from El-Baramia area in Idfu-Marsa Alam road to Marsa Alam-Abu Ghuson on the Red Sea coast. The study area covers an area about 16800 km² and is limited by longitudes 33°50' - 35°45'E and latitudes 24°00' - 25°15'N.

The Eastern Desert is located in the extremely arid provinces in Egypt. Temperature ranges from 21°C to 41°C. Rainfall is considerably variable from one season to another. The average annual rainfall ranges from 3 to 50 mm/year on the southern part of the desert.

3. Geological and Hydrogeological Setting

The Eastern Desert is geologically composed mainly of sedimentary and Pre-Cambrian crystalline rocks. The crystalline rocks of the Pre-Cambrian basement complex form massive formations extending parallel to the Red Sea graben and consist mainly of metamorphic and igneous rocks [4] [5]. The sedimentary rocks are found on the coastal plain and overlain the Pre-Cambrian basement rocks. They consist of Quaternary alluvial sediments and Tertiary formations (sandstones interbedded with clays, evaporites intercalated with clay and sand) [6] [7]. The quaternary aquifer in the Eastern Desert is represented by wadi sediments and alluvial plains [2].

The groundwater occurrence in fractured igneous and metamorphic water bearing formations in the Eastern Desert of Egypt is controlled by the presence, width and direction of the joints, fractures, faults and dykes and thickness of weathering zones [8] [9]. The hydrogeological rock units in South Eastern Desert are classified into Red Sea Coastal aquifers formed by coastal Quaternary and Miocene formations, and fractured Pre-Cambrian basement aquifer composed of meta-volcanics, basic-ultrabasic rocks, granites and metasediments (schists and gneisses) (Table 1 and Figure 1). Embaby *et al.* [10] using geophysical methods, concluded that the structure of the study area can be schematized with three main layers, *i.e.* the wadi deposits 15 - 60 m thick, the fractured basement rock 20 - 100 m thick and massive basement rocks 40 - 250 m thick.

At the scale of the Eastern Desert, fractured Precambrian formations can be considered as a continuous medium.

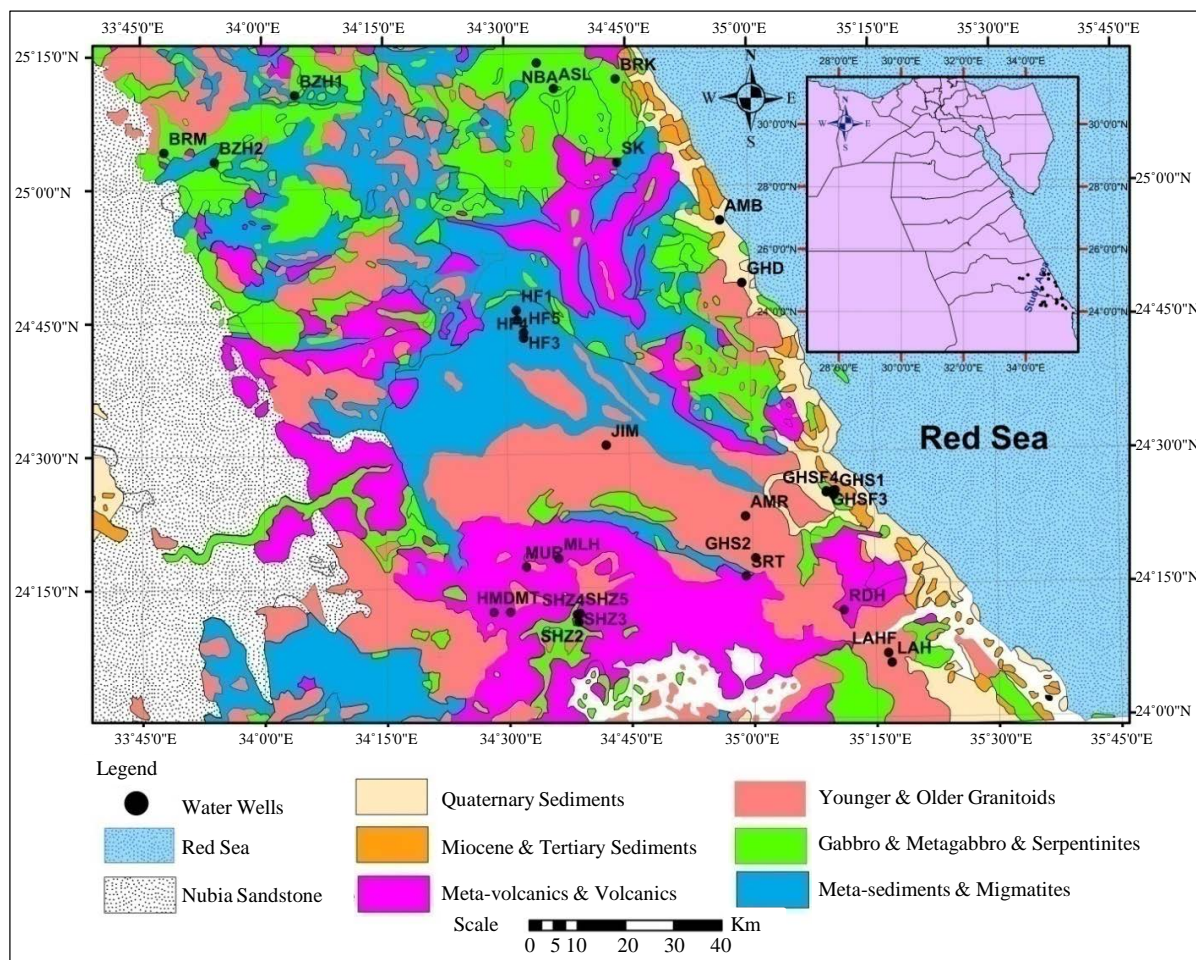


Figure 1. Simplified geological map of the study area and groundwater samples locations (modified from Aswan geological map, 1979).

A piezometric map (**Figure 2**) throughout the study area has thereby been established. It highlights a groundwater divide line from South to the North. To the west of this line, groundwater flows to the Nile. To the east the flow is towards the Red Sea. Recharge takes place from the occasional rainfalls. The mountainous zones probably act as preferential recharge zones.

4. Sampling and Analytical Procedure

A sampling network was set up to allow collection of representative data of the variability in space of the groundwater quality. This network consisted of 35 wells and covers the whole area (**Figure 1**). The rocks types of the aquifers where the wells were drilled are shown in **Table 1**.

Water samples were collected during two field campaigns, June 2013 and March 2014 in wells that form the observation network, because of great difficulties to access to the sites. Groundwater samples were filtered and collected in 0.5 L polyethylene bottles. All samples were stored in ice-boxes and then in a refrigerator in Egypt, before being sent to Poitiers in France. The analyses focused on the most common and most abundant ions in groundwater. The analyses were performed at the University of Poitiers for alkalinity and Cl^- using titration methods, and at the University of Pau, using an ICP-MS (Inductively Coupled Plasma Mass Spectrometry) for other cations and anions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , NO_3^- , SO_4^{2-} , Br^-). Note that for dosing Cl^- by titration with AgNO_3 , to avoid interference with sulfates, one to two drops of hydrogen peroxide (H_2O_2) at 30% were added while maintaining agitation. Temperature and pH were measured in the field. The ion-balance error computation, taking the relationship between the total cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and the total anions (NO_3^- ,

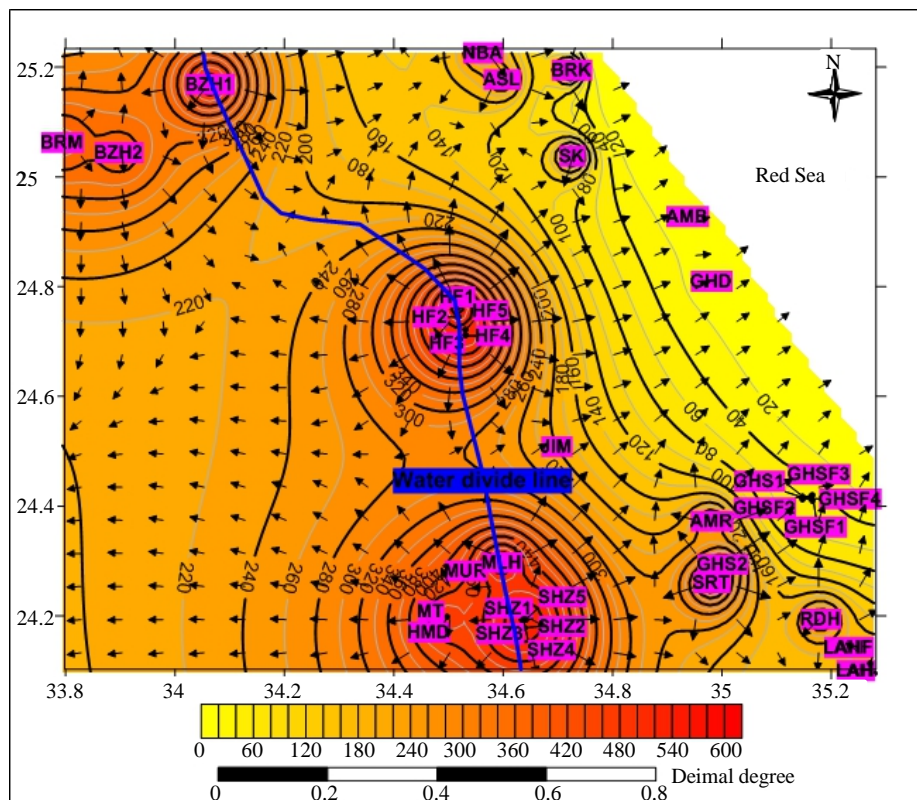


Figure 2. Piezometric map of the study area.

Table 1. Aquifer rock types and groundwater samples.

No.	Aquifer rock units	Wells No.	Wells locations
1	Meta-volcanic (Meta-andesite, meta-basalt)	1, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 26	Sukkari, El-Shazly ₁₋₅ , Abu Himimid, Miteiwit, Murirah, Malahaia and El-Barramia
2	Basic-ultrabasic (Gabbro, serpentinites, Meta-gabbro-diorite complex)	25, 26x and 30	Abu Ghuson-2, Sartut and El-Nabaa
3	Granitoids (Younger and older granite rocks)	13, 14, 15, 24, 27, 28, 29, 31, 32, 33, 34 and 35	El-Jimal, Beizah _{1,2} , El-Sheikha Amira, Hafafit _{3,5} , El-Asly, Lahmi, Lahmi-FAO, El-Reidah and Barikah
4	Meta-sediment (Schists, gneisses)	2 and 3	Hafaifit ₁₋₂
5	Quaternary (Alluvium, recent sediments)	16, 17, 19, 20, 21 and 22	Ambaout, Ghadir, Abu Ghuson FAO _{1,4}
6	Miocene (Coral reefs, sandstones, carbonate, evaporites)	18	Abu Ghuson-1

SO_4^{2-} , HCO_3^- and Cl^-) for each water sample, is observed to be within the range of acceptability ($\pm 5\%$) used in most laboratories [11], for all water samples. The hydrochemical data are given in Table 2.

5. Major Ions Chemistry

Table 3 shows the summary statistics for each water quality parameter. The pH ranges between 7.2 and 8.3. The average pH is 7.7, which indicates that the eastern desert groundwater is slightly alkaline. The lower pH values are located at the eastern part of the study area and reflect the connection between marine water and the sampled wells. The higher pH values of the western part of the study area may indicate preferential recharge areas. The groundwater temperature does not vary much and is included between 28°C and 29°C. The TDS (Total Dissolved Solids) ranges from 947 mg/l to 13,504 mg/l with a mean of 5974 mg/l. These figures show that the groundwater mineralization varies greatly on the study site.

Table 2. Hydrochemical data of the South Eastern Desert groundwater samples. TDS and ions concentrations are in mg/l. Hardness is in French degree (°F).

Sample	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Br ⁻	pH	Hardness
SK	2656.0	188.1	94.0	613.0	7.0	414.8	812.4	763.4	0.8	7.7	86
HF1	2880.0	27.3	56.0	872.0	29.0	503.3	627.7	949.1	1.0	7.9	30
HF2	3104.0	73.5	80.0	977.0	24.0	553.9	664.7	1149.7	1.1	7.5	51
SHZ1	5017.6	547.7	104.0	1248.0	8.0	244.0	1415.5	2122.7	3.7	7.8	179
SHZ2	10304.0	699.3	115.0	2977.0	47.0	230.0	3631.1	3374.1	10.6	7.7	222
SHZ3	6848.0	657.6	135.0	1800.0	13.0	161.7	1883.2	3122.7	4.9	7.5	220
SHZ4	4115.2	511.2	91.0	996.0	3.0	137.3	1132.4	1922.1	3.4	7.6	165
SHZ5	12864.0	1009.3	77.0	3582.0	36.0	101.9	5194.3	3248.4	14.7	7.7	284
HMD	2592.0	194.9	38.0	727.0	5.0	274.5	555.8	1122.7	2.5	7.9	64
MT	3532.8	261.9	74.0	982.0	5.0	291.6	997.0	1257.4	3.1	7.6	96
MUR	3328.0	252.3	78.0	880.0	6.0	268.4	726.2	1556.8	1.7	7.6	95
MLH	3648.0	541.8	131.0	653.0	6.0	259.3	1083.2	1491.0	1.2	7.3	189
JIM	947.2	96.7	31.5	171.9	4.5	158.6	270.8	197.6	0.4	7.8	37
BZH1	13504.0	825.6	1062.0	2879.0	76.0	109.8	5378.9	4676.5	5.6	7.8	643
BZH2	9408.0	859.4	402.0	2314.0	34.0	536.8	2954.1	4089.7	12.5	7.2	380
AMB	7872.0	1014.9	426.0	1252.0	57.0	96.4	3200.3	2248.4	8.3	7.8	428
GHD	7616.0	906.4	336.0	1044.0	39.0	78.1	3483.4	754.5	22.3	7.5	364
GHS1	10944.0	1550.3	343.0	1834.0	27.0	123.2	5366.6	1284.4	30.9	7.5	528
GHSF1	5331.2	609.2	180.0	1106.0	12.0	103.7	2412.5	838.3	7.9	7.7	226
GHSF2	9216.0	920.6	304.0	1814.0	32.0	125.1	4480.4	805.4	7.4	7.5	355
GHSF3	5504.0	615.5	181.0	1112.0	14.0	311.1	2486.4	772.4	8.4	7.9	228
GHSF4	10368.0	1136.0	344.0	2071.0	13.0	97.6	4665.0	1769.4	13.0	7.4	425
AMR	1881.6	130.2	30.2	427.9	7.7	225.7	637.5	296.4	0.6	8.0	45
GHS2	3788.8	461.6	177.0	689.0	13.0	413.6	1329.3	1065.8	1.2	7.6	188
SRT	5171.2	1014.3	28.0	967.0	41.0	62.8	1944.8	1829.3	3.9	8.1	265
BRM	3219.2	186.7	107.0	927.0	24.0	707.6	366.0	1892.2	0.8	8.3	91
HF3	2540.8	121.7	81.0	706.0	16.0	329.4	430.8	1248.5	0.7	7.8	64
HF4	3180.8	74.9	101.0	1012.0	39.0	359.9	787.8	991.0	1.0	8.1	60
HF5	8448.0	235.9	221.0	2778.0	102.0	1345.4	2117.1	3517.9	3.4	8.3	150
NBA	5056.0	909.1	102.0	702.0	28.0	128.0	2075.9	1173.6	9.8	8.1	269
ASL	6240.0	903.0	88.0	1172.0	35.0	45.8	2999.5	637.7	20.1	7.7	262
LAH	2969.6	242.8	75.0	691.0	7.0	155.6	1193.9	476.0	2.8	7.6	91
LAHF	10880.0	926.9	407.0	2000.0	53.0	768.6	5120.4	724.5	17.1	7.4	399
RDH	4672.0	907.0	127.0	740.0	7.0	125.1	1749.0	1502.9	4.2	7.3	279
BRK	9472.0	1354.5	392.0	1312.0	34.0	79.3	4887.5	670.6	21.3	7.2	499

Table 3. Summary statistics of groundwater physical and chemical parameters. Ion concentrations and TDS are in mg/l. SD: Standard Deviation; CV: Coefficient of Variation.

	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Br ⁻	TDS	T°C	pH
Max	1550.3	1062.0	3582.0	102.0	1345.4	5378.9	4676.5	30.85	13504.0	29.0	8.3
Min	27.3	28.0	171.9	3.0	45.7	270.7	197.6	0.38	947.2	28.0	7.2
Average	599.1	189.1	1315.1	25.8	283.6	2258.9	1586.9	7.21	5974.8	28.4	7.7
SD	400.1	192.8	788.7	21.8	256.4	1646.8	1086.7	7.46	3332.1	0.49	0.2
CV (%)	66.8	101.9	59.9	84.5	90.4	72.91	68.48	103.4	55.7	1.7	3.6

The spatial variability of the ions contents, expressed using the coefficient of variation (CV), is significantly high (60% < CV < 103%). Chloride concentrations range from 270 mg/l to 5378 mg/l, bromide from 0 to 30 mg/l, sulfate from 197 to 4676 mg/l, bicarbonate from 45 to 1345 mg/l, calcium from 27 to 1550 mg/l, magnesium from 28 to 1062 mg/l, potassium from 3 to 102 mg/l and sodium from 171 to 3582 mg/l. The relative concentrations of the cations occur in the order of Na⁺, Ca²⁺, Mg²⁺, K⁺ and of the anions in the order of Cl⁻, SO₄²⁻,

HCO_3^- . No nitrate was found in the groundwater samples.

Pearson's correlation matrix [12] was used to find relationships between the elements pairwise. The correlation matrix is shown in **Table 4**. TDS is strongly correlated with calcium ($R = 0.77$), magnesium ($R = 0.71$), sodium ($R = 0.89$), chloride ($R = 0.95$), sulfate ($R = 0.58$) and bromide ($R = 0.69$). These relationships clearly identify the main elements contributing to the groundwater salinity and their tendency to follow a similar trend (e.g. due to concentration by evaporation). These elements concentration tend to increase as the salinity of the groundwater increases. The salinization of the groundwater would be expected to result from the ionic concentrations increasing due as well to evaporation of recharge water, to seawater intrusion as to the effects of interactions between the groundwater and the geological formations. The strongest correlations between elements of opposite sign combine Cl^- and Na^+ ($R = 0.73$), Cl^- and Mg^{2+} ($R = 0.69$), and Cl^- and Ca^{2+} ($R = 0.85$). The Na^+ vs. Cl^- relationship suggests dissolution of halite or seawater intrusion. The dissolution of halite in water releases equal concentrations of sodium and chloride into the solution:



The strong relationships Cl^- - Mg^{2+} and Cl^- - Ca^{2+} suggest that cation exchange can also significantly affect groundwater composition. The positive and significant correlations between sulfate and sodium ($R = 0.76$) may indicate the contributions of evaporitic salts. Agricultural activity may also contribute to these elements. Fertilizers based on potassium sulfate, ammonium sulfate and the sulfo-phosphate ammonium [13] may contribute to these elements. Other associations between ions are further interpreted in terms of processes and origin of the mineralization of the groundwater and its evolution.

6. Principal Components Analysis

Multivariate methods have been widely used to study the sources of variation of groundwater chemistry. Principal Components Analysis (PCA) is a multivariate statistical method, which helps to reduce a large data set with underlying linear structures into a set of variables, called Principal Components, without sacrificing much of the original information. PCA proved useful for discovering previously unsuspected relationships in the original data.

In this study a Principal Components Analysis (PCA) was performed on the chemical data for better understanding the groundwater hydrochemistry. Multivariate techniques have been applied to groundwater hydrochemistry by several authors and proved quite efficient to understand a number of geochemical processes [14]-[22].

The extraction method, *i.e.* "Principal Component method" looks for a solution that maximizes the explained variance with orthogonal components, which are independent of each other. The methods to help to choose the number of components are based on relations between the eigenvalues. According to the Kaiser criteria, eigenvalues larger than one [23], explaining more variance than the average component, should be kept. An additional graphical method can also be used, the Scree diagram (or the elbow criterion). In this diagram, the eigenvalues are plotted vs. the number of the components. If the points on the graph tend to level out (show an "elbow"), these eigenvalues are usually close enough to zero that they can be ignored. The data consist of 9 variables

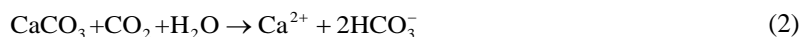
Table 4. Correlation matrix between chemical variables. Significant correlation coefficients are in bold.

	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	Br^-	SO_4^{2-}	HCO_3^-
TDS	1	0.77	0.71	0.89	0.62	0.95	0.69	0.58	-0.07
Ca^{2+}		1	0.49	0.45	0.27	0.85	0.82	0.21	-0.44
Mg^{2+}			1	0.5	0.56	0.69	0.38	0.47	-0.05
Na^+				1	0.65	0.73	0.42	0.76	0.17
K^+					1	0.51	0.28	0.52	0.42
Cl^-						1	0.8	0.32	-0.23
Br^-							1	0.01	-0.26
SO_4^{2-}								1	0.19
HCO_3^-									1

(Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- and TDS and pH) analyzed on all 35 samples collected throughout the study area. Eigen values, percentage of the variance of each principal component (PC) and cumulative percentage of variance of five first PCs are given in **Table 5**. The first two eigenvalues are >1 . The scree plot is shown in **Figure 3**. This figure indicates, according to the elbow and Kaiser criteria, that the first two PCs should be kept for further consideration. They account for 74.7% of the total variance and are assumed to provide an adequate representation of the overall variance of the data set. Hence, in the factor matrix only these two factors are considered.

The 1st PC (Principal Component) accounts for 52.0% of the variance in the data set. PC1 is interpreted as relating mainly to the mineralization of the groundwater as it is associated to Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ and TDS. Loadings for these elements on PC1 are high (**Table 6**). PC1 therefore opposes highly mineralized samples to weakly mineralized samples. PC2 accounts for 22.7% of the data variance. It is mainly associated to HCO_3^- and pH. These elements have the highest loadings on this factor. PC2 is thus related to alkaline waters. The plane associated with PC1 and PC2 accounts for 74.7% of the total variance and is accordingly quite representative of the initial data variability. **Figure 4** and **Figure 5** show the plot of the variables and of the samples on this plane. PC1-PC2 plane discriminates several groups of samples. It discriminates less mineralized waters lying inland in granitic, gneissic and schistic aquifers (Hafafit, Wadi-el-Jimal, Amira, ...), highly mineralized waters located close to the sea (Abu Ghuson, ...), alkaline waters marked in bicarbonates (El Barramia, Beizah, Hafafit, ...), and waters with lower pH marked in calcium and bromide (El Asly, Barika, Ghadir, Abu Ghuson, ...).

The pH of most natural waters is controlled by reactions involving the carbonate system. The relation on PC2 between pH and carbonates suggest that the high pH groundwaters could be the result of calcite dissolution or precipitation. Dissolution of a small amount of calcite from minor cements may overcome the buffering capacity of fresh groundwater allowing its pH to rise. The dissolution of the calcite mineral can take place as:



7. Spatial Distribution of TDS and of the Main Elements

Figure 6 shows the spatial distribution of the main elements in the groundwater. The spatial distribution of concentrations depends on several factors such as lithology, the hydrodynamics of the water, the depth of the water

Table 5. Principal component analysis, eigenvalues and explained variance.

Principal component	Eigen values	% Total variance	Cumulative eigenvalues	Cumulative %
1	5.200054	52.00	5.200054	52.00
2	2.270601	22.70	7.470655	74.70
3	0.830391	8.30	8.301045	83.01
4	0.563402	5.63	8.864447	88.64
5	0.664378	6.64	9.528826	95.28

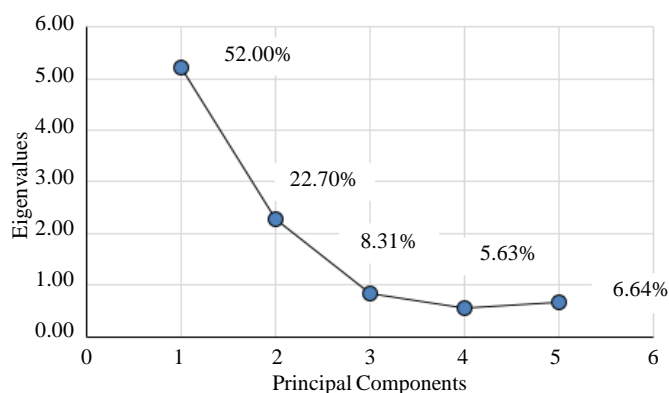


Figure 3. Principal components analysis scree plot.

Table 6. Chemical variables loadings on principal components 1 and 2.

Variables	PC1	PC2
TDS	0.989	0.054
Ca ²⁺	0.813	-0.449
Mg ²⁺	0.755	0.105
Na ⁺	0.832	0.376
K ⁺	0.632	0.630
HCO ₃ ⁻	-0.109	0.774
Cl ⁻	0.956	-0.184
SO ₄ ²⁻	0.561	0.553
Br ⁻	0.739	-0.428
pH	-0.338	0.628

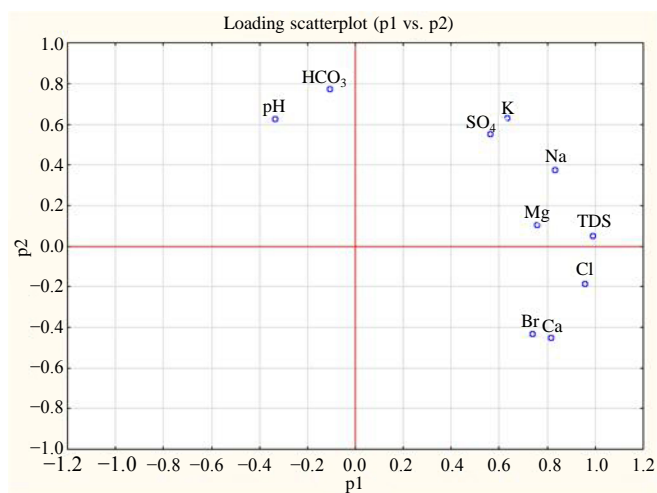


Figure 4. Principal components analysis. Plot of the variables on PC1 vs. PC2.

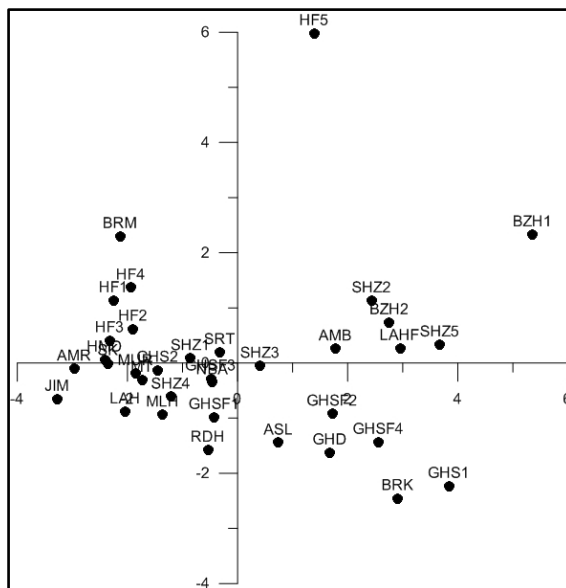


Figure 5. Principal components analysis. Plot of the groundwater samples on PC1 vs. PC2.

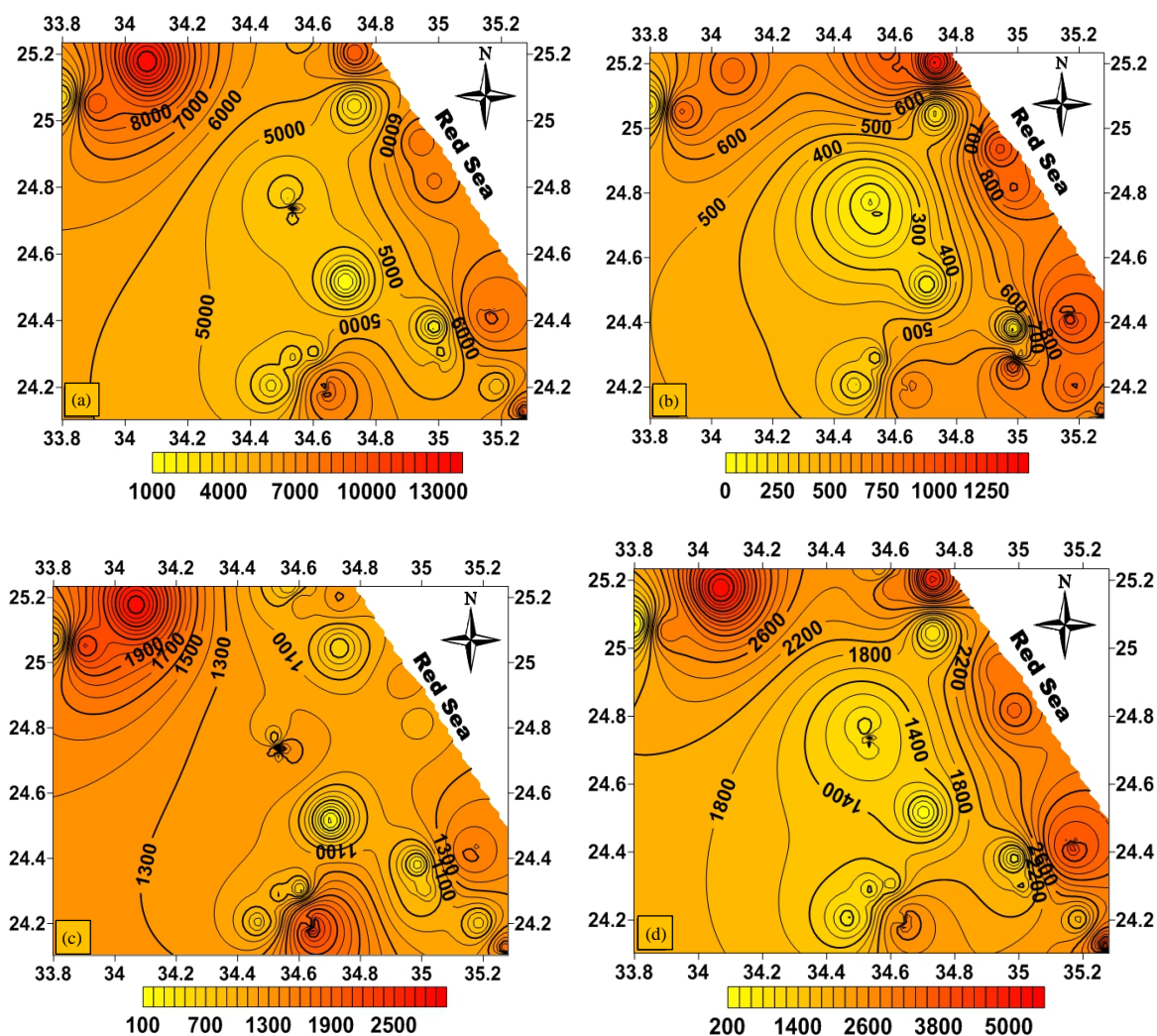


Figure 6. Spatial distribution of TDS and main chemical elements over the study area. (a) TDS; (b) Calcium; (c) Sodium; (d) Chloride.

table, climate conditions and anthropogenic pollution sources. **Figure 6** shows that Cl^- , Ca^{2+} and Na^+ display relatively equivalent spatial pattern. The highest concentrations of these elements are located along the coastline and on the high peaks of the Red Sea mountains. Low contents are located at the center of the study area, where mainly meta-sediments are found.

The spatial distribution of TDS (**Figure 6(a)**) is quite similar to that of chloride, calcium and sodium. This corroborates the hypothesis that the main contributors to the groundwater salinity are chloride, calcium and sodium.

8. Main Hydrochemical Facies

In order to properly identify the hydrochemical facies and to yield an indication of the qualitative aspects of groundwater, the graphical representation of the results of analysis proves an unavoidable tool. In this study, classification and interpretation of the groundwater hydrochemistry were carried out using the Piper diagram [24]. To achieve this goal, the hydrochemical data were processed with the use of the software Diagrammes [25]. **Figure 7** shows the Piper plot of samples. This diagram clearly shows that the groundwater samples have a dominance of chloride and sulfate ions for anions, while sodium is the cation which marks the majority of samples and is followed by the calcium. This reveals the dominance of chloride-sodium facies, and the secondary chloride-calcium and sulfate-sodium facies.

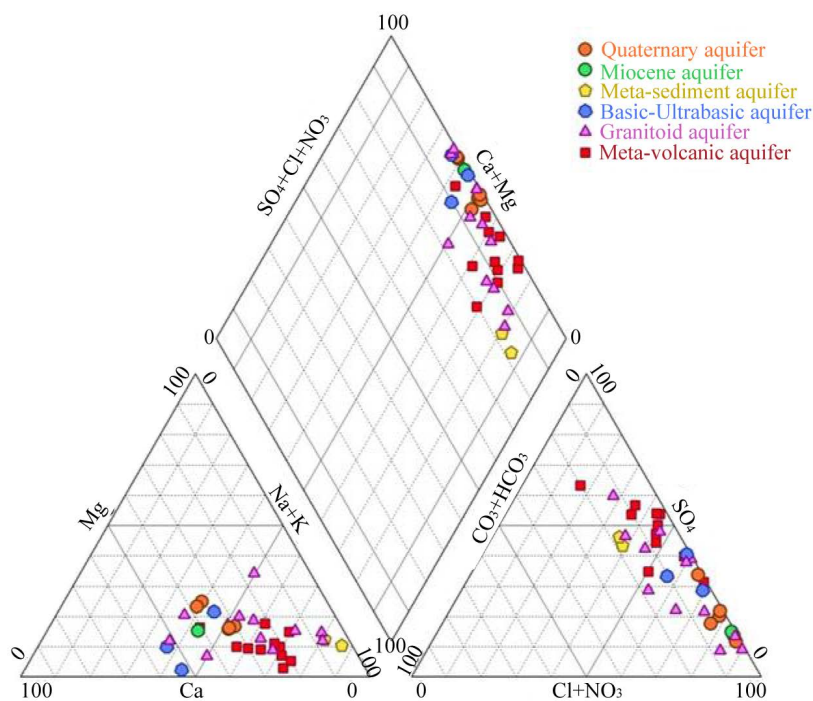


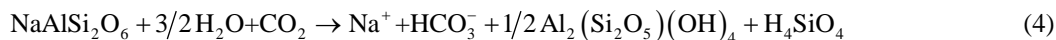
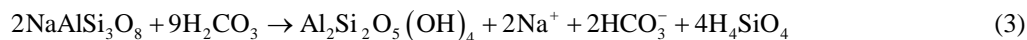
Figure 7. Piper plot of the groundwater samples.

The main hydrochemical facies which characterizes groundwater in each aquifer rock is as following: sulfate-sodium type in meta-volcanic rocks, chloride-sodium and sulfate-sodium types in granitic rocks, chloride-calcium type in basic-ultrabasic rocks. Groundwater in sedimentary rocks displays a chloride-sodium facies (Quaternary rocks) and a chloride-calcium facies (Miocene rocks).

Samples taken in wells close to the Red Sea are of chloride-sodium type, whatever the aquifer, reflecting the effect of marine intrusion.

9. Binary Diagrams and Mineralization Process

Dissolved species and their relationship with each other can reveal the origin of solutes and the processes that generated observed composition of the groundwater [26]-[35]. The relationships between concentrations of major dissolved elements are shown in Figure 8. The Na^+ vs. Cl^- relationship has been often used to identify the mechanism for acquiring salinity. The Na^+ vs. Cl^- plot shows that the samples are not aligned along the 1:1 line, but are quite scattered with a weak correlation ($R = 0.54$) indicating that Na^+ and Cl^- are not for the most part derived from the same source. Figure 8(a) shows however noticeable enrichments or losses in Na^+ contents in the groundwater considering Cl^- as a conservative element. Molar Na/Cl ratios range from as high as 3.91 to 0.41. High values are found for the meta-volcanic rocks (average = 1.63), the granites (average = 1.14) and the meta-sediments (average = 2.20). The lowest values are found in the sedimentary rocks (average = 0.61). The high Na/Cl ratios in crystalline rocks are probably controlled by water-rock interaction, for example, albite (reaction 3) or analcite (reaction 4) weathering according to the following reactions:



Samples with low Na/Cl ratios are probably the result of Na^+ loss or exchange with soils and clays. As discussed below, the Ca^{2+} and Mg^{2+} data support this idea.

In order to understand the origin of the water salinity due partly to chlorides, the bromide and the chloride ions, which are good conservative tracers in aquifers, are considered. This, because they do not participate in oxydo-reductions reactions and do not form insoluble precipitates [36]. The Br/Cl ratio is used in this case to

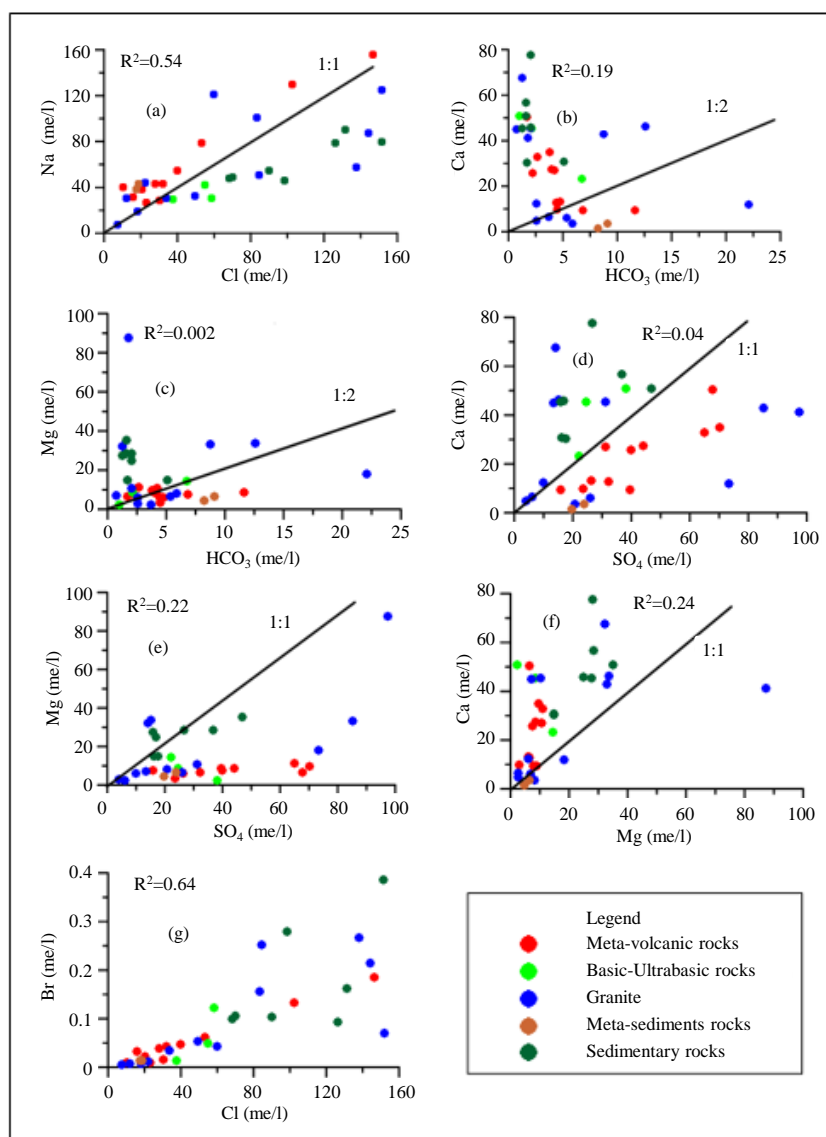


Figure 8. Bi-elements diagrams between the main chemical elements.

determine the origin of salinity. Indeed, it is often the most relevant ratio to explain the salinity of groundwater [37]. The study of the Br/Cl ratio allows discriminating the areas under evaporitic influences

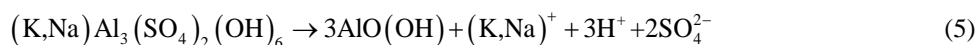
Seawater has molar Cl/Br ratios of 550 - 700 [38]-[40]. Coastal precipitation has similar Cl/Br ratios, however, inland precipitation, especially in arid or semiarid climates, may have lower Cl/Br ratios due to the tendency for Cl to be removed in early rainfall near coastal areas [38] [39] [41]. The average Cl/Br are high in the crystalline rocks (Meta-volcanic rocks: $\text{Cl/Br} = 1046$; Basic-Ultrabasic rocks: $\text{Cl/Br} = 1404$; Granite: $\text{Cl/Br} = 1233$; Metasediments: $\text{Cl/Br} = 1365$). For the sedimentary rocks, the average Cl/Br is 733. This value is close to the seawater Cl/Br ratio. This shows the effect of seawater intrusion in the sedimentary rocks (Quaternary and Miocene), which are located close to the seaside. In all crystalline and sedimentary rocks within the study area, the Cl/Br is much higher compared to the Cl/Br ratio of halite, which is about 105 [42]. Thus, halite dissolution must be relatively minor as a cause of increasing salinity in the area.

The excess of Cl^- can be explained by the combined effect of another source for this ion than the dissolution of halite, together with the Na^+ losses due to the phenomenon of base exchanges, as clays in bedrock can release Ca^{2+} after setting Na^+ . The excess of Cl^- may also have an anthropogenic origin (wastewater, agricultural fertilizers).

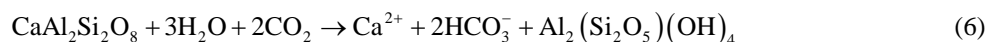
The alkaline earth elements may be derived by dissolution of silicate minerals (e.g., plagioclase feldspar, chlorite, or biotite), carbonates (dolomite or calcite), gypsum, and/or cation exchange of Na^+ for Ca^{2+} and Mg^{2+} on clay minerals. HCO_3^- is poorly correlated with Ca^{2+} ($R^2 = 0.19$; **Figure 8(b)**) and Mg^{2+} ($R^2 = 0.002$). The excess of Ca^{2+} and Mg^{2+} indicates that dissolution of carbonate rocks (calcite, dolomite) is not the main source for these elements, which is also backed by the very poor relation of Ca^{2+} with Mg^{2+} ($R^2 = 0.24$). Carbonate deposits are absent in the study area, but carbonate cements may be present.

Correlation of SO_4^{2-} with Ca^{2+} and Mg^{2+} is also poor (respectively $R^2 = 0.04$ and $R^2 = 0.21$; **Figure 8(d)** and **Figure 8(e)**) and shows that these elements (Ca^{2+} , Mg^{2+} , SO_4^{2-}) are not derived by the dissolution of gypsum or any Mg-sulfate mineral.

In **Figure 8(d)** and **Figure 8(e)**, SO_4^{2-} is in excess compared to Ca^{2+} and Mg^{2+} in water in metavolcanic rocks. The abundance of sulfates could be attributed to the dissolution of minerals as alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ (reaction 5):



Excess of Ca^{2+} compared to SO_4^{2-} in basic-ultrabasic rocks may be caused by means of hydrolysis of plagioclase feldspars, as Anorthite (reaction 6):

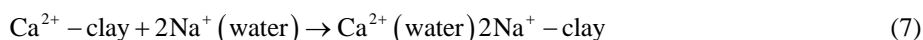


The plot of Mg^{2+} versus Ca^{2+} (**Figure 8(e)**) indicates an excess of Ca^{2+} , which can be explained by the existence of geochemical phenomena such as the $\text{Ca}^{2+} \leftrightarrow \text{Mg}^{2+}$ exchanges during the reactions of precipitation or recrystallization of calcite [43].

Contents of K^+ in waters are very low compared to the contents of other cations (Na^+ , Ca^{2+} , Mg^{2+}). Correlation of K^+ with Ca^{2+} and Mg^{2+} is also rather poor, respectively $R = 0.27$ and $R = 0.56$. The relative amount of K^+ contained within the clay minerals with respect to the concentrations in groundwater is probably much larger than Ca^{2+} or Mg^{2+} . Hence, the reactions amongst the clay minerals are likely to cause larger relative changes in K^+ than in Ca^{2+} or Mg^{2+} . This may explain the poorer correlation of K^+ with Ca^{2+} and Mg^{2+} , respectively $R = 0.27$ and $R = 0.26$.

10. Ions Exchanges Reactions

The plots of Ca^{2+} vs. HCO_3^- (**Figure 8(d)**) and Ca^{2+} vs. Mg^{2+} (**Figure 8(e)**) display a substantial excess of Ca^{2+} , showing that the origin of Ca^{2+} is not the only dissolution of calcite. This is consistent with the hypothesis of a contribution of Ca^{2+} by ion exchange reaction via a basic reaction such as:



Na^+ can exchange Ca^{2+} and Mg^{2+} sorbed on the exchangeable sites of the clay minerals, resulting in the increase of Ca^{2+} and Mg^{2+} and the decrease of Na^+ in groundwater. During this process the host rocks are the primary sources of dissolved solids in the water. Groundwater in which the alkaline earths (Ca^{2+} , Mg^{2+}) have been exchanged for the Na^+ ions is referred to as base-exchange-hardened water [26] (Gupta *et al.*, 2008).

Knowledge of the changes undergone by the chemical composition of the groundwater during its travel in the aquifer is essential. The ion exchange between the groundwater and its host aquifer during travel can be understood analyzing the plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + \text{HCO}_3^-$. In this scatter diagram, the points falling along the equiline ($\text{Ca}^{2+} + \text{Mg}^{2+} = \text{SO}_4^{2-} + \text{HCO}_3^-$) suggest that these ions have resulted from the dissolutions of calcite, dolomite and gypsum [44]-[47]. If reverse ion exchange is the dominant process, it will shift the points to the left due to a large excess of $\text{Ca}^{2+} + \text{Mg}^{2+}$ over $\text{SO}_4^{2-} + \text{HCO}_3^-$. The analysis of the $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + \text{HCO}_3^-$. Plot (**Figure 9**) reveals that all the groundwater samples have undergone the process of ion exchanges. Samples taken in the sedimentary, basic-ultra-basic and some samples in granites fall in the $\text{Ca}^{2+} + \text{Mg}^{2+}$ side (**Figure 9**), suggesting that reverse ion exchange is the major hydrogeochemical process operating in these rocks. All samples taken in the meta-sediments and meta-volcanic rocks and a few samples in granites fall in the $\text{SO}_4^{2-} + \text{HCO}_3^-$ side, suggesting exchanges between earth-alkaline in waters and alkaline in clays. Most samples taken in granitic rocks present excess of Ca^{2+} .

Ion exchange process is further discussed using the chloro-alkaline index (CAI) [48], where all values are expressed in $\text{meq}\cdot\text{l}^{-1}$:

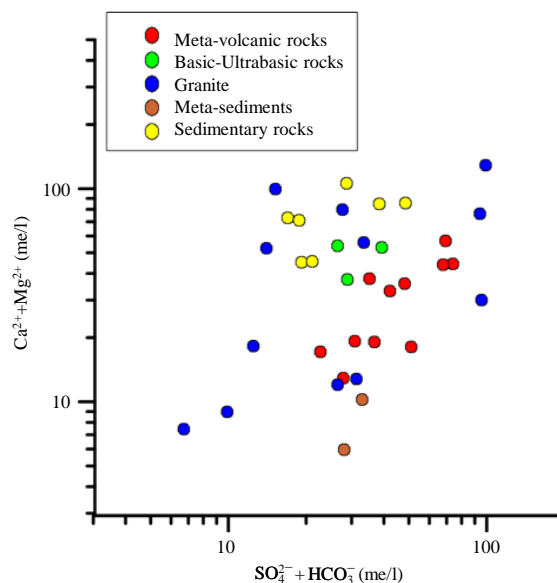


Figure 9. $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. $\text{SO}_4^{2-} + \text{HCO}_3^-$ diagram.

$$\text{CAI} = \left(\text{Cl}^- - (\text{Na}^+ + \text{K}^+) \right) / \text{Cl}^- \quad (8)$$

This ratio is positive when the sodium and potassium contents are low, *i.e.* when groundwater has been in contact with minerals able to release the interchangeable alkaline-earth ions easily. These exchanges of ions contained in the matrix with those present in the groundwater are very variable and depend, among other things, on the nature of the substrate. This ratio is negative when the sodium and potassium contents are high, *i.e.* when groundwater has been strongly in contact with minerals able to release the interchangeable alkaline ions easily. This phenomenon of base exchanges is most generally known with the alumino-silicated clays formed by layers or sheets whose cohesion is ensured by the existence of interlayer ions and water. Indeed, the surface of the layers is negatively charged, thus promoting the possibility of ion exchange with those of the groundwater.

Thus when there is an exchange between adsorbed Na^+ or K^+ with Mg^{2+} or Ca^{2+} in the groundwater, the CAI will be negative and if there is a reverse ion exchange prevalent (exchange between adsorbed Mg^{2+} or Ca^{2+} with Na^+ or K^+ in the groundwater) then this index will be positive. The average CAI (Table 7) is positive for the basic-ultrabasic rocks and sedimentary rocks reflecting the substitution of sodium and potassium in groundwater with calcium and magnesium in the underground environment. In meta-volcanic, granites and meta-sediments rocks, this index is in average negative pointing out gain in Na^+ and K^+ , and losses in Ca^{2+} and Mg^{2+} .

The dominance of positive or negative values of the chloro-alkaline index for each type of rocks corroborates well the relationship previously identified between various elements in solution in the groundwater. Despite the specific hydrogeological conditions of the study area, the chloro-alkaline index (CAI), together with the diagram of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + \text{HCO}_3^-$ allowed to understand that the contact of groundwater with the different aquifer rocks supported the spatial variability of ions by the process of base exchanges.

11. Mineral Saturation Indices

Saturation indices of minerals are very useful for evaluating the extent to which water chemistry is controlled by equilibrium with solid phases (Appelo and Postma, 1993). The saturation indice (SI) was evaluated using the software PHREEQC V2 [49]. PHREEQC can be used via the freeware DIAGRAMMES [25]. The thermodynamic database used to this purpose is Wateq.dat [50]. The saturation indices of minerals that were suspected to be responsible for the chemical composition of the Eastern desert groundwater were computed. PHREEQC uses the specific ionic concentrations in the water and the mass balance approach to calculate all the stoichiometrically available reactions that are responsible for the observed chemical changes between end member waters [51]. The package calculates the saturation indices, SI, of minerals using the concentrations of the major ions in

Table 7. Average Choro-Alcaline Index (CAI) and Saturation Indices (SI) of water samples in aquifer rocks types.

Rocks types	CAI	SI Dolomite	SI Calcite	SI Aragonite	SI Gypsum	SI Anhydrite	SI Halite
Meta-volcanic	-0.64	1.55	0.92	0.78	-0.28	-0.50	-4.57
Basic-ultrabasic	0.29	0.45	0.54	0.40	-0.15	-0.37	-4.58
Granitoids	-0.16	1.66	0.85	0.71	-0.57	-0.78	-4.50
Meta-sediments	-1.24	1.89	0.69	0.54	-1.27	-1.48	-4.91
Sedimentary	0.38	0.88	0.51	0.31	-0.26	-0.48	-4.04

the system. The saturation index of a mineral is obtained from Equation (9) [52] [53]:

$$SI = \log(IAP/KT) \quad (9)$$

where IAP is the ion activity product of the chemical element in solution, KT is the equilibrium constant of the reaction considered at the temperature T(K). When the SI is below 0, the water is undersaturated with respect to the mineral in question. An SI of 0 means water is in equilibrium with the mineral, whereas an SI greater than 0 means a supersaturated solution with respect to the mineral in question.

The saturation indices of the following minerals in all water samples were evaluated: calcite, aragonite, dolomite, anhydrite, gypsum and halite. The average values of the SI for each rock type are given in **Table 7**.

Calculations showed that carbonate minerals have different degrees of saturation. The dolomite SI ranges from -1.18 to +3.90, that of calcite ranges from 0.02 to +1.79. Assuming that equilibrium is in the range of -0.5 to +0.5, the results show that both calcite and dolomite have reached equilibrium in the basic-ultrabasic rocks and are in a state of supersaturation in other rocks.

The evaporitic minerals show degrees of saturation lower than the carbonate minerals. Gypsum SI ranges from -1.49 to 0.13 and anhydrite SI from -1.71 to -0.09. Water is in equilibrium regarding these minerals in all rocks, except in meta-sediments where it is undersaturated. Halite SI ranges from -5.94 to -3.52 indicating that the groundwater is very undersaturated regarding this mineral. This results also indicates that halite is not the main source for Na^+ and Cl^- .

12. Role of Evaporation

The study region experiences dry and semiarid climatic condition, evaporation may also contribute in groundwater chemistry. The sodium versus chloride ratio can be used to identify the evaporation process in groundwater. Evaporation will increase the concentration of total dissolved solids in groundwater and the Na/Cl ratio remains the same. It is a rather efficient indicative factor of evaporation. If evaporation is the dominant process, Na/Cl ratio should remain constant when TDS increases [54]. Accordingly, the plot of Na/Cl versus TDS would give a horizontal line. The TDS versus Na/Cl scatter diagram of the groundwater samples (**Figure 10**) shows that the points fall along a horizontal line which means that the $(\text{Na}^+/\text{Cl}^-)$ remains almost constant despite the increase in TDS. This indicates that evaporation plays a decisive role in controlling the chemistry of groundwater.

13. Groundwater Potability Assessment

The Eastern Desert groundwater potability was assessed according to international standards (WHO 2008) and to the water hardness. The hardness is expressed in French degrees ($^{\circ}\text{F}$). A French degree ($^{\circ}\text{F}$) corresponds to the hardness of a solution containing 10 mg/l of CaCO_3 . 1°F is equivalent to 4 mg of calcium per liter and 2.4 mg of magnesium per liter. 1meq of calcium ion is equivalent to 5°F [55].

The contents of the main elements of samples were compared with WHO standards [56] and are reported in **Table 8**. This table shows that no water sample fully meets the WHO criteria for potability. In each rock type, the contents of several elements exceed WHO standards: metavolcanic rocks (Ca^{2+} , Na^+ , Cl^- , SO_4^{2-} , TDS); basic-ultrabasic rocks (Ca^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , TDS); granites (Na); meta-sediments (Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- , TDS), sedimentary rocks (Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , TDS). The TDS limit value is exceeded in all samples except in 8% of samples in granitic rocks. It appears from this table that only the waters in granitic rocks best meet the WHO criteria for potability. The waters of other rocks are rather far from WHO standards.

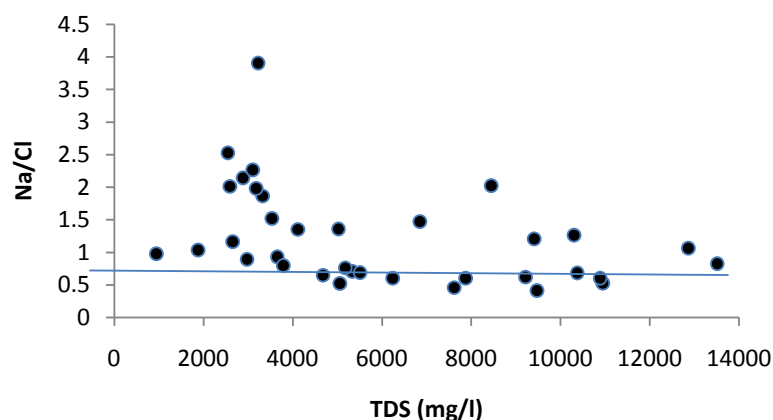


Figure 10. Na^+/Cl^- vs. TDS diagram.

Table 8. Percentage of samples having ion concentrations below the WHO standards.

Elements	WHO standards	Meta-volcanic (%)	Basic-ultrabasic (%)	Granitoids (%)	Meta-sediment (%)	Sedimentary (%)
Ca^{2+} (mg/l)	100	0	0	12	100	0
Mg^{2+} (mg/l)	50	9	33	16	0	0
Na^+ (mg/l)	150	0	0	0	0	0
K^+ (mg/l)	12	63	0	33	0	14
Cl^- (mg/l)	250	0	0	58	0	0
SO_4^{2-} (mg/l)	250	0	0	16	0	0
HCO_3^- (mg/l)	250	45	66	58	0	85
TDS (mg/l)	1500	0	0	8	0	0
pH	6.5 < pH < 9.5	100	100	100	100	100

The hardness ranges from 30°F to 643°F, showing that some samples are soft while other are very hard. The average hardness is as follows for each rock type: Meta-volcanic = 154°F, Basic-ultrabasic = 241°F, granites = 242°F, Meta-sediments = 41°F, sedimentary rocks = 365°F. These figures show that hardness is quite high in all rock types, except in the meta-sediments. The contents of magnesium and calcium that exceed the threshold set by WHO, cause such high hardness in these rock aquifers.

These results show that the groundwater in the study area is of poor to bad quality for drinking purpose.

14. Summary and Conclusions

Understanding groundwater hydrochemistry and quality is vital to preserve this resource so that it can meet the present and future water needs in many countries. In the Eastern Desert in Egypt, groundwater resources play a vital role in supplying water for drinking, industrial and agricultural purposes. However, there is a lack of knowledge of the groundwater mineralization processes and a lack of rational management. This study adds to our understanding of the chemical properties of groundwater in this area in Egypt.

This study allowed first for a hydrogeological synthesis of the aquifer system in this part of the Eastern Desert. This system is composed of several rock types including Pre-Cambrian crystalline fractured rocks and Tertiary/Quaternary sedimentary rocks along the Red Sea border. At the scale of the Eastern Desert, all these formations have a hydraulic continuity and form a single aquifer system. The piezometric map displays an N-S divide line. General groundwater flow takes place on either side of this line, to the East toward Red Sea and to the West towards the Nile River.

The hydrogeochemical study of the groundwater was conducted using several methods (Piper diagram, principal components analysis, ions exchanges, saturation indices of various minerals). This study revealed the presence of different hydrochemical facies in each aquifer rock type: chloride-sodium and sulfate-sodium in granitic rocks, chloride-calcium in basic-ultrabasic rocks, chloride-sodium in quaternary rocks and a chloride-

calcium in Miocene rocks. Close to the Red Sea, groundwater is of chloride-sodium type, reflecting the effect of marine intrusion. The groundwater chemical characteristics are controlled by natural geochemical processes but also by some anthropogenic activities. Evolution of the groundwater chemistry is controlled by multiple processes including natural minerals dissolution as halite or calcite. However silicate weathering and ion exchanges play a prominent role in the ion enrichment of groundwater. Seawater intrusion on the Red Sea coastline and anthropogenic activities affect also the groundwater chemistry. The role of evaporation due to high temperatures in this area was also highlighted.

In the Eastern Desert, the majority of chemical elements analyzed exceed the standards set by WHO. The groundwater is accordingly not perfectly appropriate for human consumption.

The results of this study helped to significantly improve the understanding of the aquifer system of Southern Eastern Desert which is an important resource for the development of this region in Egypt and may contribute as well for a better management of this vital resource.

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