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# HYDROGEOCHEMICAL PROCESSES AND WATER-ROCK INTERACTION OF GROUNDWATER IN AL-DAMMAM AQUIFER AT BAHR AL-NAJAF, CENTRAL IRAQ

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## ABSTRACT

The hydrogeochemistry of groundwater in the Dammam aquifer was studied via 22 wells in Bahr Al-Najaf basin in order to identify the main hydrogeochemical processes and rock-water interaction. Groundwater in the Dammam aquifer is characterized by neutral to slightly alkaline hard water, excessively mineralized, and slightly brackish water type, in which $Na^+$ and $SO_4^{2-}$ are the dominant ions. The average contribution of cations in the aquifer is $Na^+$ (24%), $Ca^{2+}$ (14%), $Mg^{2+}$ (11%) and $K^+$ (1%); whereas the contribution of anions is $SO_4^{2-}$ (23%), $Cl^-$ (20%) and $HCO_3^-$ (7%). Rock-water interaction processes are identified to include dissolution (carbonates, sulfates, halite, and some silicates such as clay minerals), leaching, and cation exchanges, while evaporation has only a very little impact.

# العمليات الهيدروجيوكيميائية وتفاعلات ماء - صخر للمياه الجوفية في خزان الدمام الجوفي في بحر النجف، وسط العراق

**صالح محمد عوض، فراس مظفر عبد الحسين و جودة عيفان الكلابي**

## المستخلص

تمت دراسة هيدروجيوكيمياء المياه الجوفيه في خزان تكوين الدمام من خلال 22 بئر في حوض بحر النجف، لغرض تشخيص العمليات الهيدروجيوكيميائية الرئيسة والتفاعلات الصخرية - المائية. اتصفت المياه الجوفية في خزان الدمام بكونها مياه عسرة، متعادلة تميل نحو القاعدية، شديدة التمعدن من نوع مياه مختلطة قليلا، يسود فيها الصوديوم والكبريتات. معدل مساهمة الأيونات الموجبة في الخزان الجوفي هي: الصوديوم 24% والكالسيوم 14% والمغنيسيزم 11% والبوتاسيوم 1% بينما معدل مساهمة الأيونات السالبة هي: الكبريتات 23% والكلور 20% والبيكربونات 7%. تم تشخيص عمليات التفاعل مابين الصخر والمياه لتشمل عمليات الإذابة (الكربونات والكبريتات والهالايت، وبعض السليكات مثل المعادن الطينية)، والشطف وتبادل الأيونات الموجبة، بينما كانت عملية التبخر ذات تأثير قليل جدا.

## INTRODUCTION

Groundwater is an essential natural water resource that supplies the population for different uses as in domestic, agricultural and industrial purposes, where it provides about half of all the freshwater used worldwide (Shiklomanov, 1996). Chilton *et al*. (1994) stated that groundwater constitutes about two-third of the fresh water reserves of the world. Interaction of groundwater with aquifer mineral species greatly controls the groundwater

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chemistry (Subramani *et al*., 2010). This study was conducted in Bahr Al-Najaf which locates about 40 Km to the west-southwest of Najaf (Fig.1). It covers an area of about 765 $Km^2$ between (44° 04' – 44° 20') East, and (31° 45' – 32° 04') North. The permanent storage of groundwater in Bahr Al-Najaf basin was recommended by Al-Suhail (1996) to be utilized for the agricultural purposes. Some studies were conducted on this basin such as Al-Azawi (2009) and Al-Hasnawi (2009) which focus on groundwater management and hydrogeological setting in Bahr Al-Najaf. The present study describes the water chemistry and identifies the hydrogeochemical processes that result from rock-water interaction and control the groundwater chemistry.

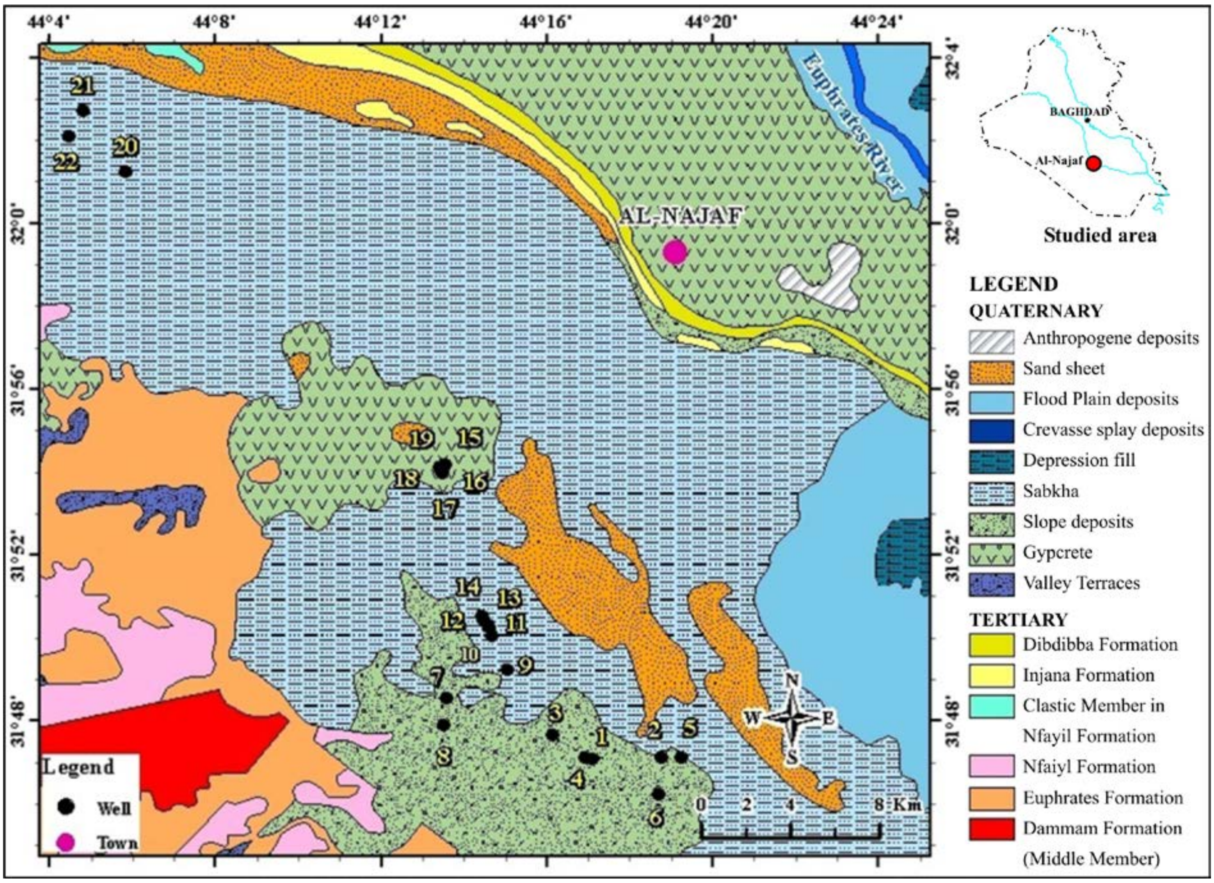

Fig.1: Simplified geological map shows the location of the study area and the groundwater wells (Modified after Barwary, 1996)

## ▪ Materials and Methods

The hydrochemical data used in this paper were formally obtained from the General Commission for Groundwater. It represents a total of 22 groundwater samples that have been collected in April, 2014 from 22 wells drilled in the Dammam aquifer. The measurements were done according to the standard method of APHA (1998). These measurements included hydrogen number (pH), electrical conductivity (EC), TDS and temperature (T) using TDS-EC-pH and T meter, HANNA, type H19811 which was calibrated by specific buffer solution. All samples were analyzed for major cations ($K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$) and also major anions ($CO_3^{2+}$, $HCO_3^-$, $SO_4^{2-}$, and $Cl^-$), as well as the secondary anions ($NO_3^-$). Sodium and potassium were analyzed using flame photometer. Calcium, magnesium, chloride, carbonate and bicarbonate were determined by titrimetric method. Sulfate was determined by spectrophotometer. The analytical accuracy was calculated according to equation (1), and then checked by the equation (2) postulated by Hem (1985):

$$U\% = [(r \sum \text{cations} - r \sum \text{anions}) / (r \sum \text{cations} - r \sum \text{anions})]\ 100 \quad \ldots\ldots.. \quad (1)$$

$$C = 1 - U \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. \quad (2)$$

Where, U is the uncertainty; r is a value in equivalent per mil (epm), and C is the certainty or accuracy. When $U \leq 5$, the result could be accepted, but if $5 < U \leq 10$ the result will be accepted with risk (Al-Hamadani, 2009). Accordingly, accuracy of the results is accepted. The total hardness (TH) was mathematically calculated using the equation (3) (Todd, 1980).

$$TH = 2.497\ Ca^{2+} + 4.115\ Mg^{2+} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots... \quad (3)$$

Hydrochemical formula was computed as average formula based on Kurlolov formula which was referred in Ivanov *et al*., 1968 as follows:

$$TDS\ (\text{g/1})\ \left\{ \frac{\textit{Anions (epm\%) decreasing order}}{\text{Cations } \textit{(epm\%) decreasing order}} \right\}\ pH \quad \ldots\ldots\ldots\ldots.. \quad (4)$$

Stiff and Piper diagrams are used for the data presentation according to Stiff, 1951 and Piper, 1944 respectively.

## GEOLOGICAL SETTING

Four geological formations greatly affect the groundwater chemistry in the study area; Dammam, Euphrates, Nfayil and Rus formations. The groundwater occurs within the Dammam aquifer which underlies the Euphrates and Nfayil formations. The Euphrates Formation overlies the Dammam Formation and has a discontinuous marl and clay layer covering the Dammam Formation. Hence, the Dammam Formation represents a semi-confined aquifer, where marl and clay are present. It is comprised of shallow neritic carbonates (limestone and dolostone) of Middle to Upper Eocene (Al-Sayyab *et al*., 1982). In the Early Miocene, a shallow marine carbonates consisting of well bedded marly limestone overlies the Dammam Formation (Al-Sayyab *et al*., 1982) forming the Euphrates Formation. It may add ions to the Dammam Formation aquifer with the percolated rain water. Green marl of the Nfayil Formation (Middle Miocene) as well as recent deposits (thin sand sheets and gypsiferouse soil) form a discontinuous cover distributed in semi-flat area characterized by small hills forming the general landscape. The study area is located within the Abu-Jir Fault Zone (AJFZ) between the Inner Platform that represents the Western Desert and the Mesopotamia Foredeep that represents the Mesopotamia basin. The AJFZ is an important and major structure in the study area. It is a NW – SE trending deep fault (Barazanji and Al-Yasi, 1987). The surface extension of the AJFZ has been detected to be 467 Km long with an average width of 48 Km (Awadh *et al*., 2013). Most parts of Bahr Al-Najaf basin reflect a hydrotectonic characteristics affected by the AJFZ and is considered as a discharge zone of Al-Shbecha huge basin (Thabit *et al*., 2014).

## RESULTS AND DISCUSSION

### Groundwater Characterization

Hydrochemical results of the investigated groundwater samples are summarized in Table 1. Depth of groundwater wells ranges from 25 – 100 m and according to Biswas (1991) who defined shallow wells as generally less than 15 m deep, while deep well are greater than 50 m in depth. 86% of these wells are considered therefore as deep and the remaining 14% are considered having medium depth. The groundwater in the study area is classified according to Matthess (1982) as a neutral to slightly alkaline, where the pH values range from 7.1 to 7.61. A high variation was found in EC and TDS. The range of EC varied from 2040 to 6900 µs/cm reflecting an excessively mineralized water (Detay, 1997), while the TDS varies from 1537 to 4918 ppm indicating a slightly brackish water (Todd, 2007). The high variation of salinity attributed to different lithology types. Total hardness (TH) showed that all groundwater samples are very hard. The most dominant cation is $Na^+$, where it forms 24% in average, whilst $SO_4^{2-}$ is the most dominant anions and forms 23% in average from the total ions (Fig.2). The detail ionic constituents in groundwater of the Dammam aquifer are clearly displayed by Stiff diagram (Fig.3). The molar value of sodium ranges from 13.6 to 25.6, while sulfate varied between 10.1 and 31.8. The main source of sulfate is the solution of gypsum that originated from gypsiferiouse soil and the Rus Formation, and it doesn't come from oxidizing sulfides which are rarely present in the study area. A high variation in groundwater chemistry was reported and attributed to the partial mixing of water coming from multi-aquifer crosscutting the fault planes of AJFZ. Although groundwater in the Dammam aquifer contains a wide ionic range, but it tends to represent a uniform water quality. Consequently, the Dammam Aquifer in the study area is characterized by the following hydrochemical formula:

$$TDS\ 2.85\ \left(\frac{\mathrm{g}}{l}\right)\ \frac{SO_4\ (45.6)\ Cl\ (39.3)}{Na\ (49.4)\ Ca\ (27.4)\ Mg\ (21.8)}\ pH\ (7.23)$$

There is excess quantity of sodium, which is not come from halite, because it's molar value is higher than that of the chloride. This obviously supports the marine origin of the connate water that had actually been originated from deep source and mixed with meteoric water to become the source of water in the Dammam aquifer. Piper diagram displays that 86% of groundwater samples can be described as an alkali earth waters rich with Ca and Mg with an increase in alkalis and prevailing sulfate and chloride (Field A in Figure 4), but the remaining 14% represents an alkali water rich in Na with prevailing sulfates and chloride (Field B in Figure 4).

Table 1: Results of Hydrochemical parameters of groundwater in the study area

| Well No. | *Depth (m) | Unit | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $Cl^{-}$ | $SO_4^{2-}$ | $HCO_3^{-}$ | $NO_3^{-}$ | pH | EC µs/cm | TDS ppm | TH ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 90 | ppm | 260 | 130 | 411 | 82 | 550 | 1001 | 449 | 7.5 | 7.1 | 3630 | 2200 | 1184 |
| | | epm | 13 | 10.7 | 17.9 | 2.1 | 15.5 | 20.8 | 7.36 | 0.12 | | | | |
| | | epm% | 29.7 | 24.7 | 40.8 | 4.8 | 35.4 | 47.7 | 16.8 | | | | | |
| 2 | 60 | ppm | 139 | 91 | 376 | 3 | 467 | 679 | 352 | 4 | 7.2 | 2920 | 2268 | 722 |
| | | epm | 6.94 | 7.48 | 16.4 | 0.08 | 13.2 | 14.1 | 5.77 | 0.06 | | | | |
| | | epm% | 22.4 | 24.5 | 52.8 | 0.25 | 39.7 | 42.8 | 17.4 | | | | | |
| 3 | 70 | ppm | 215 | 115 | 351 | 4 | 531 | 602 | 453 | 3.1 | 7.17 | 3160 | 2287 | 1010 |
| | | epm | 10.7 | 9.46 | 15.2 | 0.1 | 15 | 12.5 | 7.43 | 0.05 | | | | |
| | | epm% | 30.1 | 26.8 | 42.7 | 0.3 | 42.8 | 35.9 | 21.3 | | | | | |
| 4 | 60 | ppm | 220 | 100 | 340 | 11 | 467 | 864 | 235 | 1.2 | 7.21 | 3470 | 2990 | 961 |
| | | epm | 11 | 8.22 | 14.8 | 0.28 | 13.2 | 18 | 3.85 | 0.02 | | | | |
| | | epm% | 31.9 | 24.2 | 43 | 0.82 | 37.6 | 51.4 | 11 | | | | | |
| 5 | 50 | ppm | 208 | 119 | 530 | 2 | 785 | 775 | 365 | 2 | 7.17 | 4870 | 3554 | 1009 |
| | | epm | 10.4 | 9.79 | 23.0 | 0.05 | 22.1 | 16.3 | 5.98 | 0.03 | | | | |
| | | epm% | 24 | 22.8 | 53 | 0.12 | 50 | 60.5 | 13.5 | | | | | |
| 6 | 90 | ppm | 243 | 130 | 360 | 6.2 | 635 | 806 | 240 | 7 | 7.26 | 4370 | 3076 | 1142 |
| | | epm | 12.1 | 10.7 | 15.7 | 0.16 | 17.9 | 16.8 | 3.9 | 0.11 | | | | |
| | | epm% | 31.3 | 27.9 | 40.3 | 0.41 | 46.3 | 43.5 | 10.2 | | | | | |
| 7 | 86 | ppm | 308 | 145 | 485 | 101 | 639 | 1150 | 459 | 2.8 | 7.27 | 4150 | 3300 | 1366 |
| | | epm | 15.4 | 11.9 | 21.1 | 2.58 | 18.0 | 23.9 | 7.52 | 0.05 | | | | |
| | | epm% | 30.1 | 23.6 | 41.2 | 5.1 | 36.4 | 48.4 | 15.2 | | | | | |
| 8 | 96 | ppm | 168 | 113 | 451 | 25 | 561 | 991 | 150 | 0.1 | 7.11 | 3420 | 2527 | 884 |
| | | epm | 8.4 | 9.29 | 19.6 | 0.64 | 15.8 | 20.6 | 2.46 | 0 | | | | |
| | | epm% | 22.1 | 24.7 | 51.5 | 1.7 | 40.6 | 53.1 | 6.3 | | | | | |
| 9 | 90 | ppm | 224 | 150 | 375 | 3 | 532 | 770 | 310 | 6.5 | 7.15 | 3150 | 2409 | 1177 |
| | | epm | 11.2 | 12.3 | 16.3 | 0.08 | 15 | 16.0 | 5.08 | 0.1 | | | | |
| | | epm% | 27.9 | 31.2 | 40.7 | 0.2 | 41.5 | 44.4 | 14.1 | | | | | |
| 10 | 100 | ppm | 158 | 79 | 320 | 3.8 | 370 | 653 | 243 | 9 | 7.19 | 3110 | 2240 | 720 |
| | | epm | 7.88 | 6.5 | 13.9 | 0.1 | 10.4 | 13.6 | 3.98 | 0.15 | | | | |
| | | epm% | 27.7 | 23.1 | 48.8 | 0.35 | 37.2 | 48.6 | 14.2 | | | | | |
| 11 | 70 | ppm | 115 | 45 | 225 | 3 | 185 | 487 | 166 | 5.4 | 7.2 | 2040 | 1537 | 472 |
| | | epm | 5.74 | 3.7 | 9.78 | 0.08 | 5.22 | 10.1 | 2.72 | 0.09 | | | | |
| | | epm% | 29.7 | 19.4 | 50.5 | 0.4 | 28.8 | 56.1 | 15.1 | | | | | |
| 12 | 75 | ppm | 208 | 88 | 316 | 2.8 | 475 | 648 | 270 | 2.3 | 7.3 | 3010 | 2125 | 881 |
| | | epm | 10.4 | 7.24 | 13.7 | 0.07 | 13.4 | 13.5 | 4.43 | 0.04 | | | | |
| | | epm% | 33 | 23.2 | 43.5 | 0.2 | 42.7 | 43.1 | 14.1 | | | | | |
| 13 | 75 | ppm | 69 | 37 | 428 | 15 | 361 | 511 | 268 | 5 | 7.37 | 3070 | 2367 | 325 |
| | | epm | 3.44 | 3.04 | 18.6 | 0.38 | 10.2 | 10.6 | 4.39 | 0.08 | | | | |
| | | epm% | 13.5 | 12.1 | 72.9 | 1.5 | 40.3 | 42.2 | 17.4 | | | | | |
| 14 | 75 | ppm | 206 | 87 | 314 | 8 | 472 | 645 | 268 | 2.3 | 7.1 | 3000 | 2121 | 872 |
| | | epm | 10.3 | 7.15 | 13.6 | 0.2 | 13.3 | 13.4 | 4.39 | 0.04 | | | | |
| | | epm% | 32.8 | 23.1 | 43.5 | 0.7 | 42.7 | 43.2 | 14.1 | | | | | |
| 15 | 45 | ppm | 350 | 171 | 589 | 100 | 704 | 1525 | 506 | 1.1 | 7.12 | 6900 | 4918 | 1578 |
| | | epm | 17.5 | 14.1 | 25.6 | 2.56 | 19.9 | 31.8 | 8.29 | 0.02 | | | | |
| | | epm% | 29.2 | 23.8 | 42.7 | 4.3 | 33.1 | 53 | 13.9 | | | | | |
| 16 | 25 | ppm | 260 | 130 | 411 | 82 | 550 | 1001 | 449 | 7 | 7.19 | 3620 | 2660 | 1184 |
| | | epm | 13 | 10.7 | 17.9 | 2.1 | 15.5 | 20.8 | 7.36 | 0.11 | | | | |
| | | epm% | 29.7 | 24.7 | 40.8 | 4.8 | 35.4 | 47.7 | 16.8 | | | | | |
| 17 | 32.5 | ppm | 138 | 96 | 365 | 5 | 466 | 681 | 351 | 6 | 7.2 | 3800 | 2880 | 740 |
| | | epm | 6.89 | 7.89 | 15.9 | 0.13 | 13.1 | 14.2 | 5.75 | 0.1 | | | | |
| | | epm% | 22.3 | 25.9 | 51.4 | 0.4 | 39.7 | 42.9 | 17.4 | | | | | |
| 18 | 35 | ppm | 315 | 142 | 492 | 106 | 664 | 1210 | 490 | 7 | 7.61 | 4290 | 3500 | 1371 |
| | | epm | 15.7 | 11.7 | 21.4 | 2.71 | 18.7 | 25.2 | 8.03 | 0.11 | | | | |
| | | epm% | 30.5 | 22.9 | 41.4 | 5.3 | 36 | 48.5 | 15.5 | | | | | |
| 19 | 30 | ppm | 418 | 198 | 721 | 11.1 | 941 | 1557 | 540 | 2.8 | 7.19 | 8160 | 5730 | 1859 |
| | | epm | 20.9 | 16.3 | 31.3 | 0.28 | 26.5 | 32.4 | 8.85 | 0.05 | | | | |
| | | epm% | 30.3 | 23.9 | 45.4 | 0.4 | 39.1 | 47.8 | 13.1 | | | | | |
| 20 | 72 | ppm | 148 | 30 | 489 | 8.1 | 435 | 577 | 367 | 4.5 | 7.17 | 2840 | 2155 | 493 |
| | | epm | 7.39 | 2.47 | 21.3 | 0.21 | 12.3 | 12.0 | 6.02 | 0.07 | | | | |
| | | epm% | 23.6 | 8 | 67.8 | 0.7 | 40.5 | 39.7 | 19.9 | | | | | |
| 21 | 80 | ppm | 146 | 31 | 490 | 7.5 | 431 | 578 | 371 | 3.1 | 7.22 | 2840 | 2160 | 492 |
| | | epm | 7.29 | 2.55 | 21.3 | 0.19 | 12.2 | 12.0 | 6.08 | 0.05 | | | | |
| | | epm% | 23.3 | 8.2 | 67.9 | 0.6 | 40.1 | 39.7 | 20.1 | | | | | |
| 22 | 80 | ppm | 179 | 61 | 281 | 4.1 | 356 | 610 | 213 | 3.5 | 7.33 | 2760 | 2001 | 698 |
| | | epm | 8.93 | 5.02 | 12.2 | 0.1 | 10.0 | 12.7 | 3.49 | 0.06 | | | | |
| | | epm% | 34 | 19.3 | 46.4 | 0.4 | 38.2 | 48.5 | 13.3 | | | | | |

*Depth represents groundwater depth.

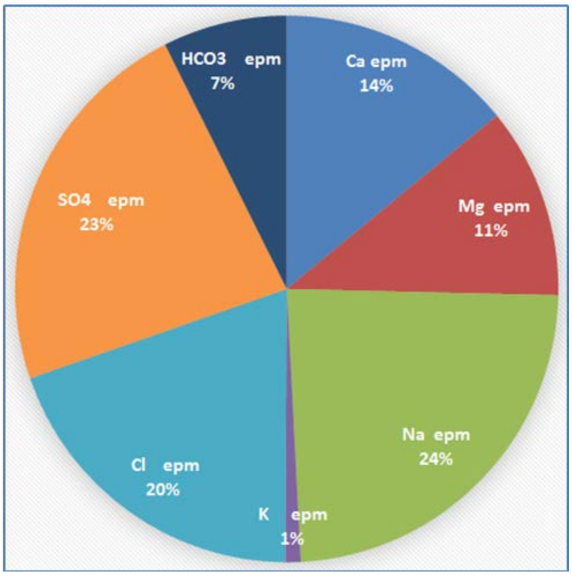

Fig.2: Pie diagram displays the average ionic constituents of groundwater in the Dammam Aquifer

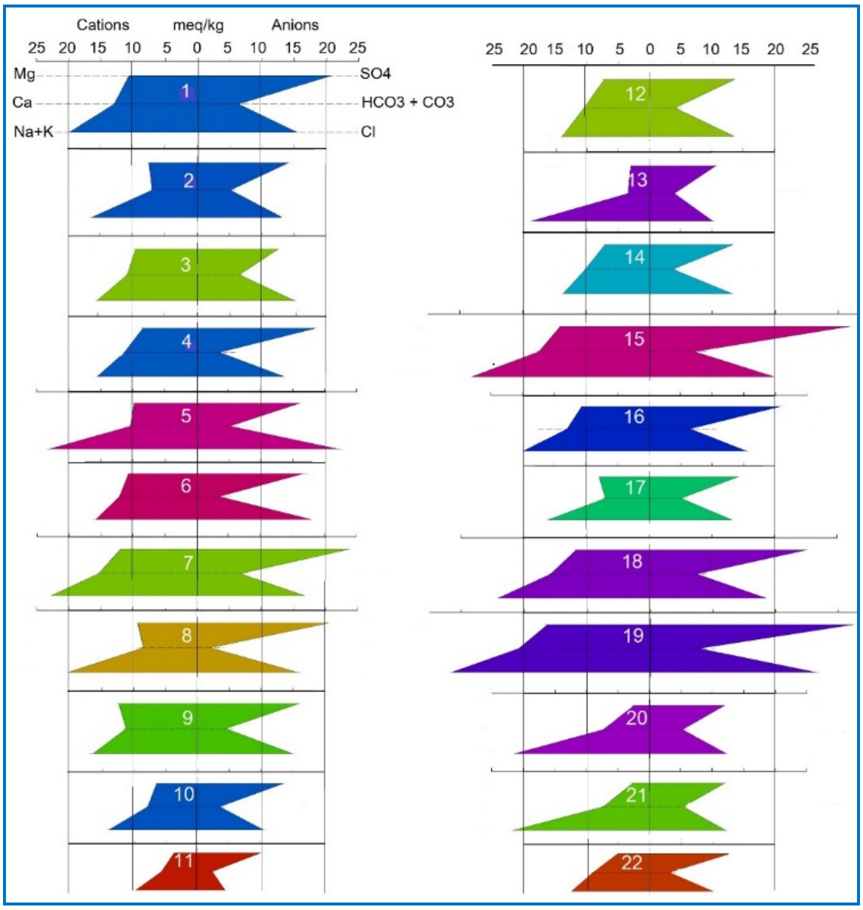

Fig.3: Stiff diagram illustrates the chemistry of groundwater in the Dammam Aquifer

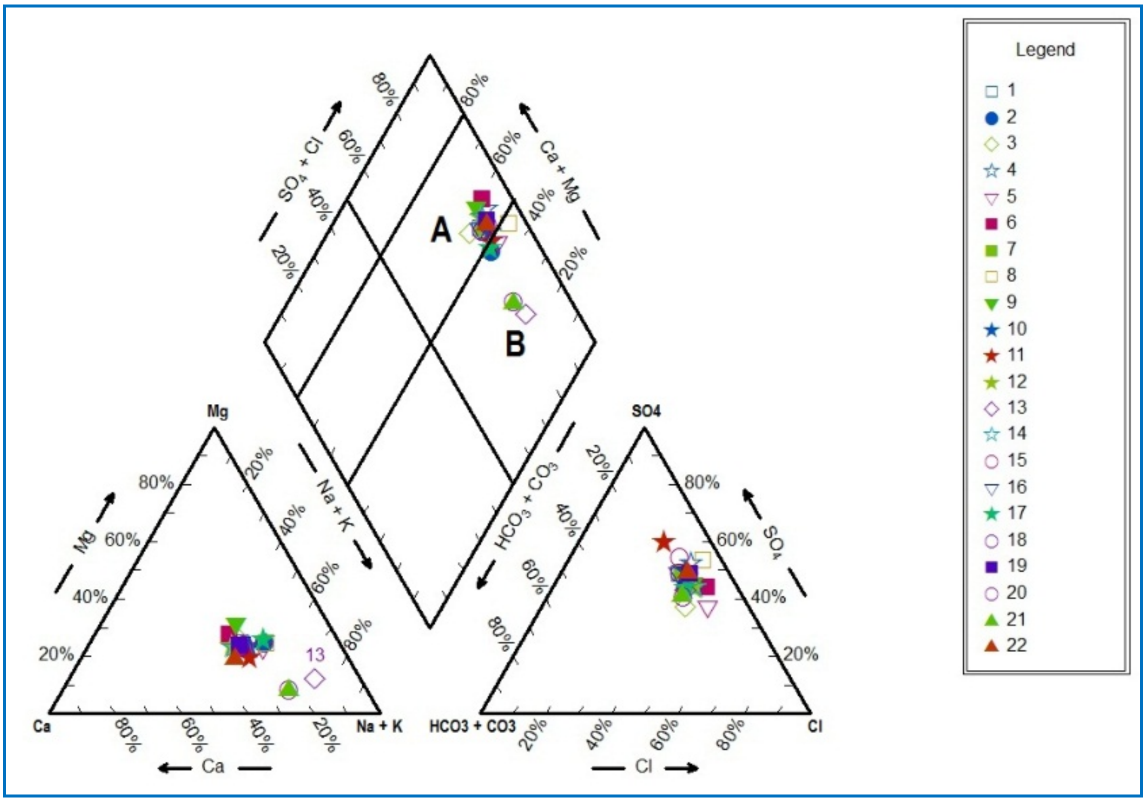

Fig.4: Piper diagram displays groundwater facies in the Dammam aquifer

- **Hydrochemical Functions and Rock-Water Interaction**

The Hydrochemical functions are mathematical ratios of ions which are useful for interpreting the aquifer characterization and help to conclude the rock-water interaction (Subramani *et al.*, 2010). These functions can also be used for detecting changes in groundwater properties due to chemical processes along its flow path. In Table 2, the high Na value relative to the Cl value represented by the average value (1.26) of $rNa^+/rCl^-$ indicates a presence of another source of Na rather than halite (Na-containing fertilizer or released Na during the dissolution of different lithologies) providing an evidence of a dissolution of terrestrial minerals during partial leaching. The ratio of $rCa^{2+}/rMg^{2+}$ of (1.38) occurs between seawater and rainwater, where El-Sayed *et al.* (2012) stated that this ratio in sea water is 0.14, but in rainwater standard it is 7.14. Sea water ratio is 5 times less than that of rainwater and in places it is 10 times greater than that of seawater. The value of this function reflects the interaction between water and aquifer rocks causing dissolution of carbonates (limestone and dolomite) under acidic pH conditions (pH of rainwater). The high average value of $rSO_4^{2-}/ rCl^-$ ratio of (1.19) in groundwater samples reflects the dissolution of the gypsum and anhydrite in the aquifer.

Table 2: Hydrochemical function (in mole) of groundwater in the Dammam aquifer

| **S. No.** | **Ca/Mg** | **$SO_4$/Cl** | **Ca + Mg** | **$SO_4 + HCO_3$** | **Cl** | **Na + K** | **Na/Cl** | **Na** | **Cl/ ($Cl + HCO_3$)** | **Na/ (Na + Ca)** |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.21 | 1.34 | 23.66 | 28.2 | 15.51 | 19.97 | 1.15 | 17.87 | 0.68 | 0.58 |
| 2 | 0.93 | 1.07 | 14.42 | 19.91 | 13.17 | 16.43 | 1.24 | 16.35 | 0.70 | 0.70 |
| 3 | 1.13 | 0.83 | 20.19 | 19.96 | 14.97 | 15.36 | 1.02 | 15.26 | 0.67 | 0.59 |
| 4 | 1.34 | 1.36 | 19.2 | 21.84 | 13.17 | 15.06 | 1.12 | 14.78 | 0.77 | 0.57 |
| 5 | 1.06 | 0.73 | 20.17 | 22.12 | 22.14 | 23.09 | 1.04 | 23.04 | 0.79 | 0.69 |
| 6 | 1.13 | 0.97 | 22.82 | 20.71 | 17.91 | 15.81 | 0.87 | 15.65 | 0.82 | 0.56 |
| 7 | 1.29 | 1.33 | 27.29 | 31.46 | 18.02 | 23.67 | 1.17 | 21.09 | 0.71 | 0.58 |
| 8 | 0.90 | 1.3 | 17.67 | 23.09 | 15.82 | 20.25 | 1.24 | 19.61 | 0.87 | 0.70 |
| 9 | 0.91 | 1.07 | 23.52 | 21.11 | 15 | 16.38 | 1.09 | 16.3 | 0.75 | 0.59 |
| 10 | 1.21 | 1.3 | 14.38 | 17.58 | 10.43 | 14.01 | 1.33 | 13.91 | 0.72 | 0.64 |
| 11 | 1.55 | 1.94 | 9.44 | 12.86 | 5.22 | 9.86 | 1.87 | 9.78 | 0.66 | 0.63 |
| 12 | 1.43 | 1.0 | 17.62 | 17.92 | 13.4 | 13.81 | 1.03 | 13.74 | 0.75 | 0.57 |
| 13 | 1.13 | 1.04 | 6.48 | 15.03 | 10.18 | 18.99 | 1.83 | 18.61 | 0.70 | 0.84 |
| 14 | 1.44 | 1.0 | 17.43 | 17.82 | 13.31 | 13.85 | 1.03 | 13.65 | 0.75 | 0.57 |
| 15 | 1.24 | 1.6 | 31.53 | 40.04 | 19.85 | 28.17 | 1.29 | 25.61 | 0.71 | 0.59 |
| 16 | 1.21 | 1.34 | 23.66 | 28.2 | 15.51 | 19.97 | 1.15 | 17.87 | 0.68 | 0.58 |
| 17 | 0.87 | 1.08 | 14.78 | 19.93 | 13.14 | 16 | 1.21 | 15.87 | 0.70 | 0.70 |
| 18 | 1.35 | 1.34 | 27.4 | 33.22 | 18.73 | 24.1 | 1.14 | 21.39 | 0.70 | 0.58 |
| 19 | 1.28 | 1.22 | 37.14 | 41.27 | 26.54 | 31.63 | 1.18 | 31.35 | 0.75 | 0.60 |
| 20 | 2.99 | 0.98 | 9.86 | 18.03 | 12.27 | 21.47 | 1.73 | 21.26 | 0.67 | 0.74 |
| 21 | 2.86 | 0.99 | 9.84 | 18.11 | 12.15 | 21.49 | 1.75 | 21.3 | 0.67 | 0.75 |
| 22 | 1.78 | 1.26 | 13.95 | 16.19 | 10.04 | 12.32 | 1.22 | 12.22 | 0.74 | 0.58 |
| Av. | 1.38 | 1.19 | 19.45 | 23.26 | 15.07 | 19.02 | 1.26 | 18.30 | 0.72 | 0.64 |

The plot of $Ca^{2+}$ + $Mg^{2+}$ versus $SO_4^{2-}$ + $HCO_3^-$ (Fig.5) is ordinarly (i.e. close to the 1: 1 line) when the dissolutions of calcite, dolomite and gypsum are the dominant reactions in the aquifer. Ion exchange tends to shift points to the right due to an excess of $SO_4^{2-}$ + $HCO_3^-$ (Cerling *et al*., 1989 and Fisher and Mulican, 1997). If reverse ion exchange is the process, the points will be shifted to the left due to a large excess of calcium and magnesium relative to sulfates and bicarbonates. The plot in Figure 5 shows that most of the groundwater samples of the Dammam aquifer are shifted to the right and that does not indicate a cation (Ca and Mg) exchange, but it has results from the common gypsum dissolution and may be attributed partially to the cation exchange with clay minerals. The ratio Ca/Mg of 1.0 indicates a dissolution of dolomite, but a higher ratio reflects a greater calcite contribution (Maya and Loucks, 1995). In the present study, the very high Ca/Mg molar ratio (more than 5.0 to less than 38) indicates that the contribution of Ca and Mg to groundwater is due to the dissolution of calcite, dolomite and gypsum.

Both of calcium and magnesium ions increase proportionally (Fig.6) with increase of salinity indicating that the carbonate weathering in the aquifer is carried out by chloride-bearing water. The major sources of Ca are limestone, dolomite, dolomitic limestone, marl and gypsum, whereas the Mg sources are dolomitic limestone and dolomite. Carbonates of the Euphrates and Dammam formations, and gypsum may have come from the Rus Formation that had been subjected to dissolution, then Ca, Mg, $CO_3$ and $SO_4$ were added to the groundwater system by recharging during rainfall as well as leaching via irrigation. Silicate weathering can be understood by estimating the ratio between ($Na^+$ + $K^+$) and total cations (El-Sayed *et al*., 2012). The distribution pattern of the groundwater samples are plotted along the $Na^+$ + $K^+$ = 0.5 total cations (Fig.7). It doesn't reflect the involvement of silicate weathering in the geochemical processes, but it clearly refers to the halite dissolution because Na contributes 24% from the total ions and K contributes only 1%.

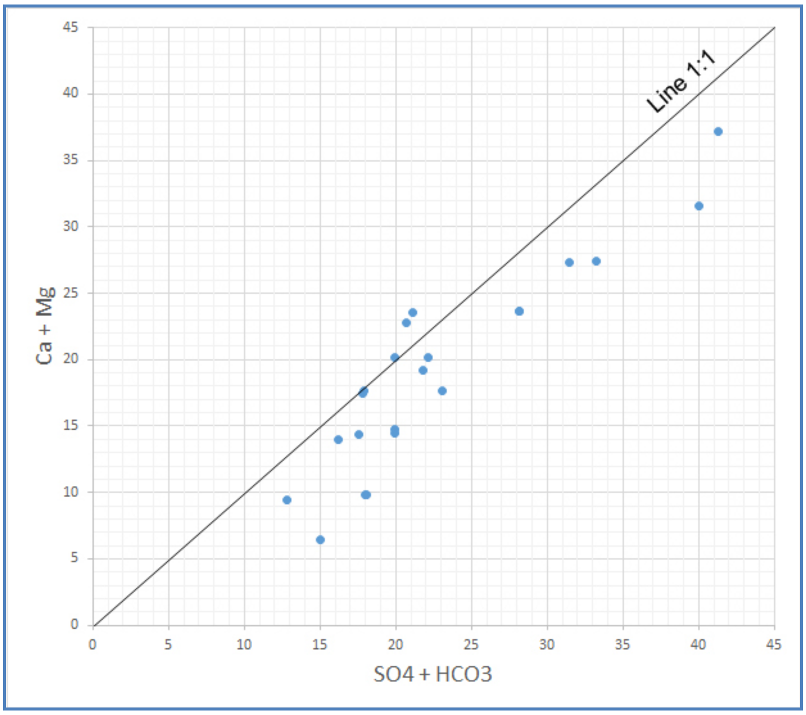

Fig.5: Relation between $Ca^{2+}$ + $Mg^{2+}$ and $SO_4^{2-}$ + $HCO_3^-$ in groundwater of the Dammam aquifer

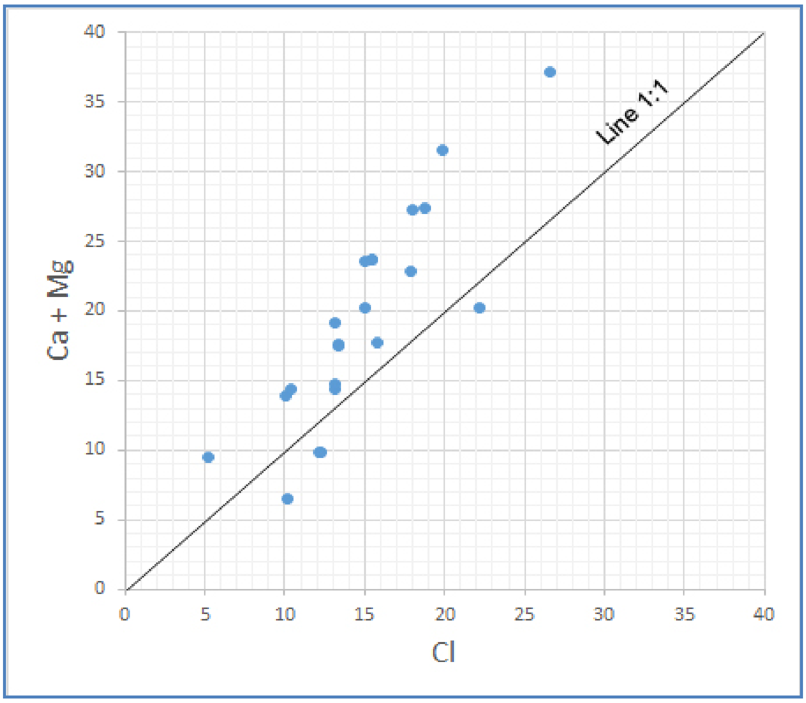

Fig.6: Relationship between (Ca + Mg) and Cl in groundwater of the Dammam aquifer

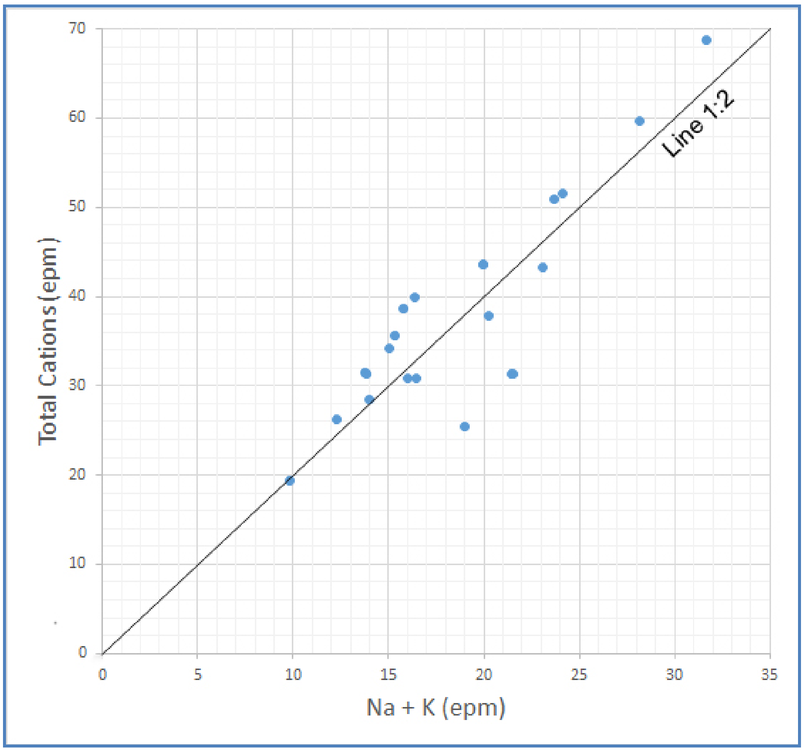

Fig.7: Relationship between (Na + K) and total cations in mole

- **Mechanism Controlling Groundwater Chemistry**

The evaporation is a common phenomenon not only in surface water, but also in groundwater system; Na/Cl molar ratio can be used to identify the evaporation process in groundwater (Subramani *et al*., 2010). Typically, ion concentrations increase due to evaporation. The molar ratio of Na/Cl versus EC plot was used to understand the dominant chemical processes in the Dammam aquifer. A horizontal line resulting from the plot of Na/Cl versus EC means concentration via evaporation (Jankowski and Acworth, 1997). The molar ratio of Na/Cl is still constant and approximately close to 1.0 in case of halite dissolution, but a ratio greater than 1.0 means that the Na released may be from silicate weathering (Mayback, 1987). Based on this ratio, 21 groundwater samples out of 22 samples have ratios greater than 1.0 with an average of 1.26 for the values varied from 0.87 to 1.87 (Table 2 and Figure 8). This means a presence of other processes, beside halite dissolution, that may be silicate (clay minerals) dissolution. The distribution pattern of the molar ratio of Na/Cl versus electrical conductivity displays a random trend meaning lack of evaporation effect on the chemistry of groundwater in the Dammam aquifer. Groundwater has unique chemistry due to several processes such as soil/rock-water interaction during recharge and groundwater flow, prolonged storage in the aquifer and dissolution of mineral species (Hem, 1985).

In Figure 9, all groundwater samples fell above the 1:1 line indicating an additional source of Na rather than halite. It can be clearly seen that Na does not proportionally increase with Cl and the increase of Na may be attributed to the ionic exchange in clay minerals and silicate weathering.

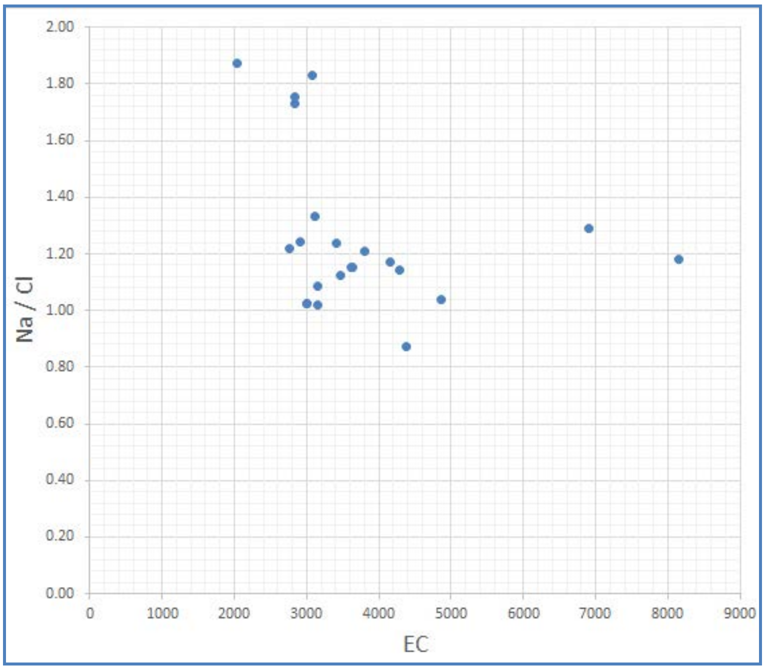

Fig.8: Distribution pattern of (Na/ Cl) against EC in groundwater of the Dammam aquifer

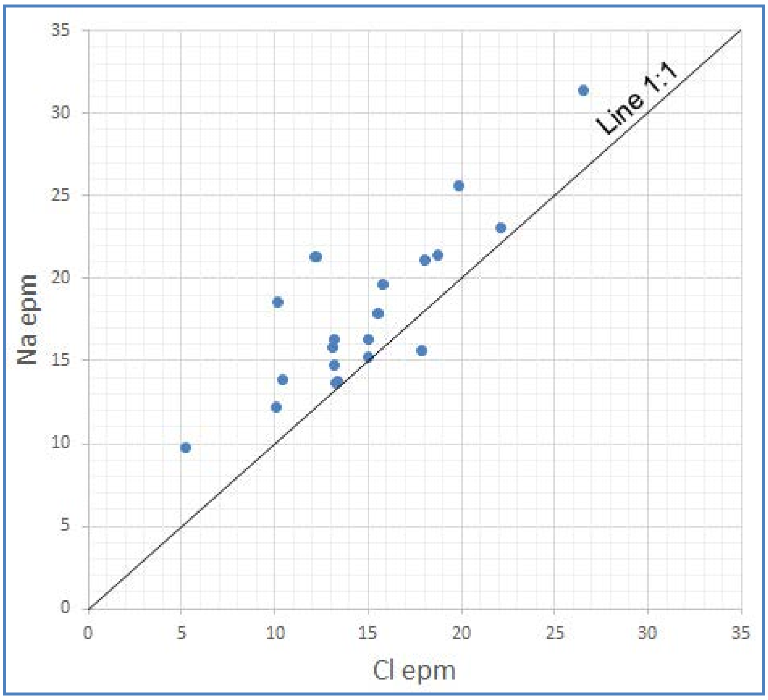

Fig.9: relationship between the molar ratio of Na and Cl

The diagram suggested by Gibbs (1970) is used to discriminate the evaporation, dilution and rock weathering as hydrochemical processes affecting the groundwater of the Dammam aquifer. Gibbs diagram plot (Figure 10A and B) of the chemical data is mainly combining chemical weathering and evaporation. This study suggests evaporation means concentration by dissolution that occurs in case of no dilution, because the concentration process is logically more effective in groundwater. Therefore, it indicates that the groundwater chemistry in the

Dammam aquifer is controlled mainly by weathering reactions. Gibbs Diagram displays that there is no dilution process which reflects lack of annual precipitation in the recharge area that feeds the Dammam aquifer.

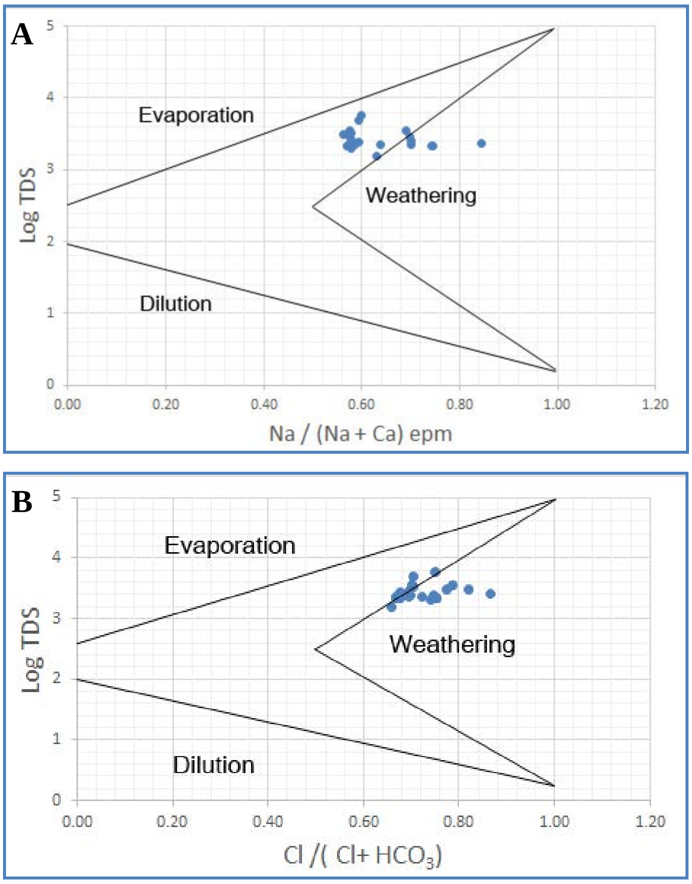

Fig.10: A and B; Gibbs diagrams classification of groundwater samples of the Dammam aquifer

- **Ion Sources**

The water chemistry data derived from the source rocks generally follows many sequential steps (Hounslow, 1995). The interpretation of the probable source rock was done according to the computed results given in Table 3. Basically, ions can be added to the water and the change in water chemistry depends on the type of lithology. To describe source ions and rocks affecting groundwater chemistry, the chemical functions are used as follows:

1. The ratio of Na/(Na + Cl) indicates a contribution of the sea water in the Dammam aquifer, where the values of this ratio in all samples are less than 0.5.
2. The ratio of Mg/(Ca + Mg) greater than 0.5 indicates dolomite dissolution and calcite precipitation, but if it is less than 0.5 it indicates limestone-dolomite weathering. The computed values of this function (less than 0.5) reflect the limestone-dolomite weathering as a dominant process.
3. If the calculated ratio of Ca/(Ca + $SO_4$) is less than 0.5, it means calcium removal by ion exchange or calcite precipitations. But if it is greater than 0.5 it will indicate calcium source rather than gypsum-carbonate or silicates. In the present study, values of this function are less than 0.5 indicating Ca removal by ion exchange or calcite precipitation. The pH values don't support the Ca precipitation in the Dammam aquifer.

4. The ratio of Mg/(Ca + $SO_4$) is less than 0.5 in the Damman aquifer indicating that the contribution of calcite and gypsum is more than the contribution of dolomite.
5. If the computed ratio of (Ca + Mg)/ $SO_4$ falls within 0.8 – 1.2, it will indicate dedolomitization. All computed ratios of this function are outside that range indicating no dedolomitization.
6. If the value of TDS is greater than 500 ppm; it will mostly indicate carbonate weathering or brine or seawater; if it is less than 500 ppm, it will indicate silicate weathering. TDS data refer to the carbonate weathering as the values in the Dammam aquifer are greater than 500 ppm.
7. If the ratio of Cl/∑anions is less than 0.8 it will indicate rock weathering. Accordingly, the rock weathering is the dominant process in the Dammam aquifer, so as the values of these ratios are less than 0.8.
8. If the calculated ratio of $HCO_3$/∑anions is less than 0.8, it will indicate seawater or brine. Consequently all computed data are less than 0.8, thus it indicates a brine water that may have been affected by connate or fossils water feeding along the fault planes of AJFZ.

Table 3: Computed function for the source rock interpretation

| **S. No.** | **Na/ (Na + Cl)** | **Mg/ (Ca + Mg)** | **Ca/ (Ca + $SO_4$)** | **Mg/ (Ca + $SO_4$)** | **(Ca + Mg)/ $SO_4$** | **Cl/ ∑Anions** | **$HCO_3$/ ∑Anions** | **TDS ppm** |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.43 | 0.33 | 0.21 | 0.10 | 0.39 | 0.27 | 0.22 | 2200 |
| 2 | 0.45 | 0.40 | 0.17 | 0.11 | 0.34 | 0.31 | 0.23 | 2268 |
| 3 | 0.40 | 0.35 | 0.26 | 0.14 | 0.55 | 0.33 | 0.29 | 2287 |
| 4 | 0.42 | 0.31 | 0.20 | 0.09 | 0.37 | 0.30 | 0.15 | 2990 |
| 5 | 0.40 | 0.36 | 0.21 | 0.12 | 0.42 | 0.41 | 0.19 | 3554 |
| 6 | 0.36 | 0.35 | 0.23 | 0.12 | 0.46 | 0.38 | 0.14 | 3076 |
| 7 | 0.43 | 0.32 | 0.21 | 0.10 | 0.39 | 0.28 | 0.20 | 3300 |
| 8 | 0.45 | 0.40 | 0.14 | 0.10 | 0.28 | 0.33 | 0.09 | 2527 |
| 9 | 0.41 | 0.40 | 0.23 | 0.15 | 0.49 | 0.33 | 0.19 | 2409 |
| 10 | 0.46 | 0.33 | 0.19 | 0.10 | 0.36 | 0.29 | 0.19 | 2240 |
| 11 | 0.55 | 0.28 | 0.19 | 0.07 | 0.33 | 0.22 | 0.20 | 1537 |
| 12 | 0.40 | 0.30 | 0.24 | 0.10 | 0.46 | 0.34 | 0.19 | 2125 |
| 13 | 0.54 | 0.35 | 0.12 | 0.06 | 0.21 | 0.32 | 0.23 | 2367 |
| 14 | 0.40 | 0.30 | 0.24 | 0.10 | 0.45 | 0.34 | 0.19 | 2121 |
| 15 | 0.46 | 0.33 | 0.19 | 0.09 | 0.34 | 0.26 | 0.18 | 4918 |
| 16 | 0.43 | 0.33 | 0.21 | 0.10 | 0.39 | 0.27 | 0.22 | 2660 |
| 17 | 0.44 | 0.41 | 0.17 | 0.12 | 0.34 | 0.31 | 0.23 | 2880 |
| 18 | 0.43 | 0.31 | 0.21 | 0.09 | 0.38 | 0.28 | 0.21 | 3500 |
| 19 | 0.43 | 0.32 | 0.21 | 0.10 | 0.40 | 0.31 | 0.18 | 5730 |
| 20 | 0.53 | 0.17 | 0.20 | 0.04 | 0.31 | 0.31 | 0.27 | 2155 |
| 21 | 0.53 | 0.18 | 0.20 | 0.04 | 0.31 | 0.31 | 0.27 | 2160 |
| 22 | 0.44 | 0.25 | 0.23 | 0.08 | 0.39 | 0.30 | 0.18 | 2001 |

## CONCLUSIONS

Hydrogeochemical study of the Dammam aquifer in Bahr Al-Najaf area was made to identify the water-rock interaction processes that control the groundwater chemistry. The findings can be drawn as follows:

- A meteoric water origin, neutral to slightly alkaline pH of excessively mineralized and slightly-brackish water characterizes the groundwater of the Dammam aquifer. The common water type is Na – $SO_4$, where groundwater constituents are ordered as:

$$Na > Ca > Mg\ (100\%);\ SO_4 > Cl > HCO_3\ (91\%),\ \text{but}\ Cl > SO_4 > HCO_3\ (9\%)$$

- A total of 86% of groundwater samples can be described as an alkali earth water, rich in $Ca^{2+}$ and $Mg^{2+}$ with increase of alkalis and prevailing sulfate and chloride, but the remaining amount (14%) represents an alkali water rich in $Na^+$ with prevailing sulfates and chloride.
- The groundwater chemistry of the study area is affected by multi-chemical processes; these are dissolution of calcite, dolomite, gypsum, halite as well as silicate weathering represented by ionic exchange between clay minerals and groundwater, leaching by precipitation and irrigation return flow caused by land-use activities. For example, if farmers use fertilizers (ammonium, urea and gypsum), additional ions such as $NO_3^-$, $SO_4^{2-}$ will be added to the groundwater aquifer. Dissolution is the common chemical process and there is no precipitation for any mineral species.
- The contribution of calcite and gypsum in supplying ions is more than the contribution of dolomite as a rock-water interaction in the Dammam aquifer and no dedolomitization occurs.
- Evaporation and oxidation-reduction are not effective processes in the Dammam aquifer, where the main source of sulfate is the dissolution of gypsum; no indication is found for oxidized sulfides in the study area.

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