

# Interaction of Rahaliya–Ekhedhur groundwater with the aquifer rock, West Razzaza Lake, Central Iraq

Moutaz A. Al-Dabbas<sup>1</sup>

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**Abstract** The groundwater of Dammam aquifer in Rahaliya–Ekhedhur area, West Razzaza, Iraq, was studied to identify the main hydrogeochemical processes and the groundwater–rock interaction. The results indicated that  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  are the dominant ions in the groundwater. The average contribution of cations in the aquifer is  $\text{Na}^+ + \text{K}^+$  (24.7 %),  $\text{Ca}^{2+}$  (13.9 %), and  $\text{Mg}^{2+}$  (11.4 %), while anions contribution is  $\text{SO}_4^{2-}$  (23.0 %),  $\text{Cl}^-$  (20.7 %), and  $\text{HCO}_3^-$  (6.3 %). The groundwater characterized by neutral to slightly alkaline hard water, excessively mineralized, and slightly brackish water type. Rock–water interaction processes are identified to include dissolution of carbonates, sulfates, halite, and clay minerals, leaching, and cation exchanges, with little impact of evaporation.

**Keywords** Hydrogeochemistry · Dammam aquifer · West Razzaza · Iraq

## Introduction

It is absolutely necessary taking into account the fact that all the hydrometeorological processes parameters are expected to change accordingly with the effects of the global climate change. The quality of groundwater is of equal importance to quantity when it depends upon its purpose, and thus, the needs for drinking water, industrial water, and irrigation water vary widely (Todd 2007).

The permanent storage of groundwater in Rahaliya–Ekhedhur Area was recommended by Hassan and Al-Kubaisi (2002) and Al-Muqdadi (2012), to be utilized in the agriculture purposes. Some studies that were done on this area are those provided by Al-Bassrawi (1996), Al-Fatlawi (2000), and Hussain et al. (2015), which focus on groundwater management and hydrogeological setting in the Rahaliya –Ekhedhur Area and western desert. Three formations are affected the chemistry of groundwater in the study area; Dammam, Euphrates, and Nfayil Formations. The groundwater in the study area is stored within the Dammam aquifer which underlies the Euphrates and Nfayil Formations. The Euphrates Formation has discontinuous marl and clay layer covered the Dammam Formation. The Dammam Formation is composed of shallow neritic carbonates (limestone and dolomite) of middle to upper Eocene, and overlies by the Euphrates Formation (lower Miocene) of shallow marine carbonates with bedded marly limestone (Awadh et al. 2016). The Nfayil Formation of marl, limestone, and claystone (middle to lower Miocene), and the recent deposits (thin sand sheets and gypsiferous soil) form a discontinuous layer over the old geological formations, and they may add ions to the Al-Dammam aquifer with the percolated rain water through Abu-Jir fault zone and other fault system in the area (Awadh et al. 2013; Thabit et al. 2014). The study area is located in Rahaliya–Ekhedhur Area, Anbar, and Karbala governorates, to the west of the Razzaza Lake in the central part of Iraq. The area is extending from Rahhalia to the Ekhedhur passing through Shithatha city between latitudes ( $32^\circ 25' - 32^\circ 50'$ ) North and longitudes ( $43^\circ 15' - 43^\circ 40'$ ) East (Fig. 1). The aim of this study is to describe groundwater–rock interaction and identify the hydrogeochemical processes.

✉ Moutaz A. Al-Dabbas  
profaldabbas@yahoo.com

<sup>1</sup> College of Science, University of Baghdad, Aljaderia,  
Baghdad University Post Office, P. O. Box: 47138, Baghdad,  
Iraq

## Materials and methods

Sixteen groundwater samples were collected during October 2013 from Rahaliya–Ekhedhur groundwater wells that drilled in the Dammam aquifer (Fig. 1). Depth of groundwater wells ranges from 45 to 140 m, according to Hassan and Al-Kubaisi (2002). The measurements were done using procedure of APHA (1998). All samples were analyzed for major ions  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $CO_3^{2+}$ ,  $HCO_3^-$ ,  $SO_4^{2-}$ , and  $Cl^-$ . Sodium and potassium was analyzed using flame photometer. Calcium, magnesium, chloride, carbonate, and bicarbonate were determined by titrimetric method. Sulfate was determined using of spectrophotometer. The hydrogen number (pH), electrical conductivity (EC), TDS, and temperature ( $T$ ) were measured directly in the field using, HANA (HI 9811). The analytical accuracy was calculated according to Hem (1985) and Al-Hamadani (2009), accordingly, accuracy of results is accepted. Hydrochemical formula was computed as average formula based on Kurlolov formula which was referred in Ivanov et al. (1968).

## Results and discussion

### Groundwater characterization

The results reflect that the groundwater is classified as a neutral to slightly alkaline, where the pH values ranges

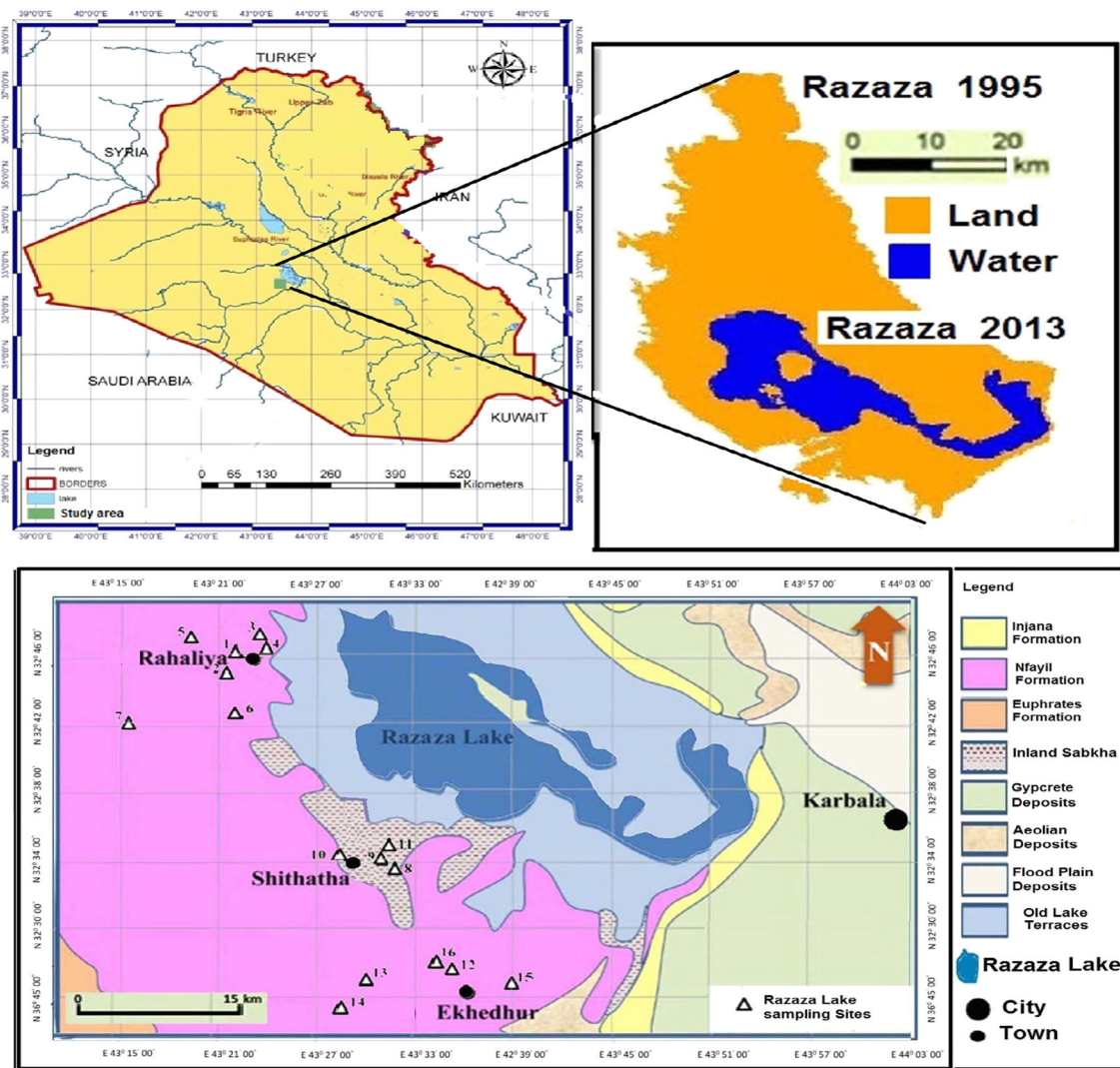
from 7.1 to 7.8 according to Matthes (1982) (Table 1). Wide range of variation was found in EC and TDS. The EC is ranging from 2560 to 3850  $\mu\text{s}/\text{cm}$  reflecting excessively mineralized water (Detay 1997), while the TDS varies from 1740 to 2750 ppm indicating a slightly brackish water (Todd 2007). In addition, according to the results, the groundwater in the studied area is classified as very hard water due to wide exposures of limestone in the recharge area according to Todd 2007. The dominant cation is  $Na^+$  with average of 24 %, while the dominant anion is  $SO_4^{2-}$  with average of 23 % from the total ions (Fig. 2). The ionic constituents of the groundwater in the Dammam aquifer are displayed by Stiff diagram of each studied well within the exposed geological formations (Fig. 3a). The sodium concentration (epm) ranges from 13.6 to 25.6, while sulfate varied between 10.1 and 31.8. The source of sulfate is believed to be from dissolving of secondary gypsum of Nfayil Formation, gypsiferous soil and to the partial mixing of water coming from multi-aquifer through the horizontal and vertical groundwater movement within the fault system in the area (Fig. 3b). The Dammam aquifer in the study area is characterized by Na– $SO_4$  water type represented by the following hydrochemical formula:

$$2176 \frac{SO_4(46.0)Cl(41.4)}{Na(49.4)Ca(27.8)Mg(22.8)} 7.29.$$

The access sodium obviously supports that the marine origin from deep source that has been mixed with meteoric

**Table 1** The hydrochemical parameters of groundwater in the study area

Well no.	$Na^+ + K^+$ epm (%)	$Mg^{2+}$ epm (%)	$Ca^{2+}$ epm (%)	$Cl^-$ epm (%)	$SO_4^{2-}$ epm (%)	$HCO_3^-$ epm (%)	TDS (ppm)	EC ( $\mu\text{s}/\text{cm}$ )	pH	T.H (ppm)
1	56.4	21.6	22.0	55.6	31.3	13.1	2350	3850	7.20	839.4
2	69.4	13.3	17.3	36.6	51.3	12.1	1740	2560	7.21	339.8
3	70.0	14.2	15.4	40.5	42.4	17.1	2204	2900	7.11	389.5
4	69.5	12.5	17.5	36.6	51.2	12.2	2226	2950	7.22	338.4
5	37.1	31.9	31.0	37.4	56.8	5.7	2100	2800	7.21	632.5
6	45.1	23.6	31.4	41.1	44.8	14.0	2305	2800	7.80	978.1
7	45.5	23.3	31.2	40.5	44.5	14.5	2220	2800	7.3	962.4
8	44.4	23.3	32.4	33.4	51.6	11.0	2238	3670	7.36	1032.8
9	71.8	12.7	15.5	40.3	42.5	17.3	2000	3670	7.40	366.4
10	27.3	33.3	39.4	43.5	51.5	5.0	2260	2750	7.20	852.1
11	39.0	31.5	29.5	54.0	37.4	8.7	2228	2700	7.20	979.6
12	36.9	32.0	31.1	35.1	59.1	5.6	2000	2750	7.30	632.4
13	42.0	24.6	33.5	35.7	53.2	11.1	2450	3480	7.22	972.5
14	48.2	22.2	29.5	29.8	46.3	23.1	2750	3260	7.25	813.7
15	44.2	23.1	33.5	40.4	45.2	14.4	2113	2750	7.25	802
16	71.0	13.8	15.2	40.5	42.4	17.1	2476	3260	7.11	389.6
Min.	27.3	12.5	15.2	29.8	31.3	5.0	1740	2560	7.11	338.4
Max.	71.0	33.3	33.5	55.6	59.1	23.1	2750	3850	7.80	1032.8
Mean	49.4	22.8	27.8	41.4	46.0	12.6	2176.2	3042.3	7.29	700.3



**Fig. 1** Simplified geological map shows the location of the study area and the groundwater wells (after Sissakian, et al. 2000)

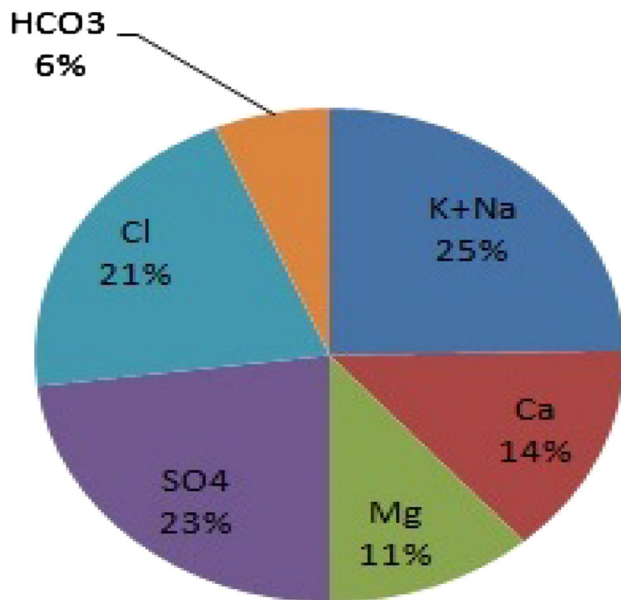
water is the source of the Dammam aquifer. An earth alkali waters rich by  $Ca^{2+}$  and  $Mg^{2+}$  with increase alkalis and prevailing sulfate and chloride can be described by Piper diagram that displays of 86 % groundwater samples (Field A in Fig. 4), but the remnant 14 % represents an alkali water rich by Na with prevailing sulfates and chloride (Field B in Fig. 4).

**Groundwater–rock interaction**

The aquifer characterization may interpret by the hydrochemical functions to conclude the rock–water interaction (Subramani et al. 2010). The results reflect high  $Na^+$  concentration relative to the  $Cl^-$  value that represented by the average value (1.29) of  $rNa^+/rCl^-$ . This finding indicates the presence of another source of Na rather than halite and provides an evidence of

dissolution of terrestrial minerals during partial leaching (Table 2). The ratio of  $rCa^{2+}/rMg^{2+}$  with the average value (1.66) is between of seawater (0.14) and rainwater (7.14) (El-Sayed et al. 2012). Such finding reflects the interaction between water and aquifer rocks causing dissolution of carbonates (limestone and dolomite) under acidic pH conditions (pH of rainwater). The dissolution of the gypsum and anhydrite in the aquifer indicated by  $rSO_4^{2-}/rCl^-$  ratio with the high average value (1.2) in groundwater samples reflects.

The graphic relation of  $Ca^{2+} + Mg^{2+}$  versus  $SO_4^{2-} + HCO_3^-$  shown in Fig. 5 is being close to the 1:1 line which is obvious the normal case if 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; Fisher and Mulican 1997). While the reverse is true, the



**Fig. 2** Pie diagram displays the average ionic constituents of groundwater in the Dammam aquifer

points will be shifted to the left due to a large excess of calcium and magnesium relative to sulfates and bicarbonates. The groundwater samples of the Dammam aquifer are shifted to the right as resulted from the common gypsum dissolution and may be attributed partially to the cation exchange with clay mineral (Fig. 5).

The ratio of Ca/Mg indicates dissolution of dolomite, if it is equal 1.0, but a higher ratio reflects a greater calcite contribution (Maya and Loucks 1995). In this study, the very high  $\text{Ca}^{2+} + \text{Mg}^{2+}$  molar values (more than 5.0 to less than 21) indicate the contribution of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to groundwater due to dissolution of calcite, dolomite, and gypsum (Fig. 6).

The increase in salinity with the relative increase in both calcium and magnesium ions indicating that the carbonate weathering in the aquifer was done by chloride-bearing water (Fig. 7). The major sources of  $\text{Ca}^{2+}$  are limestone, dolomite, dolomitic limestone, marl, and gypsum, whereas the  $\text{Mg}^{2+}$  sources are dolomitic limestone and dolomite. Carbonates of the Euphrates and Dammam Formations, and gypsum of the Nfayil Formation have been subjected to dissolution, then added  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{CO}_3^{2-}$ , and  $\text{SO}_4^{2-}$  to the groundwater system as recharged water during rainfall as well as leaching during irrigation.

Silicate weathering can be understood by estimating the ratio between  $(\text{Na}^+ + \text{K}^+)$  and total cations (El-Sayed et al. 2012). The distribution pattern of the groundwater samples is plotted along the  $\text{Na}^+ + \text{K}^+ = 0.5$  total cations (Fig. 8). It clearly reflects the halite dissolution, because  $\text{Na}^+$  contributes by 24 % from the total ions and  $\text{K}^+$  contributes by only 1 %.

## Groundwater chemistry control

The Na/Cl molar ratio can be used to identify the evaporation process in groundwater (Subramani et al. 2010). The molar ratio of Na/Cl against EC plot was used to understand the dominant chemical processes in the Dammam aquifer. A horizontal line resulted from the plot of Na/Cl against EC means concentration via evaporation (Janowski and Acworth 1997). The molar ratio of Na/Cl is still constant and approximately close to 1.0 in the case of halite dissolution, but the greater than 1.0 means that Na released may be from silicate weathering (Mayback 1987).

Based on this ratio, 14 groundwater samples out of 16 samples are greater than 1.0 having an average of 1.29 for the values varied from 0.6 to 1.9 (Table 2; Fig. 9). This means the presence of other processes beside halite dissolution that might be existed; it would 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 chemistry of groundwater in Dammam aquifer. Groundwater has unique chemistry due to several processes like soil/rock–water interaction during recharge and groundwater flow, prolonged storage in the aquifer, dissolution of mineral species (Hem 1985).

The results reflect about 90 % of groundwater samples fell above the 1:1 line indicating an additional source of  $\text{Na}^+$  rather halite which may be attributed to the ionic exchange in clay minerals and silicate weathering (Fig. 10).

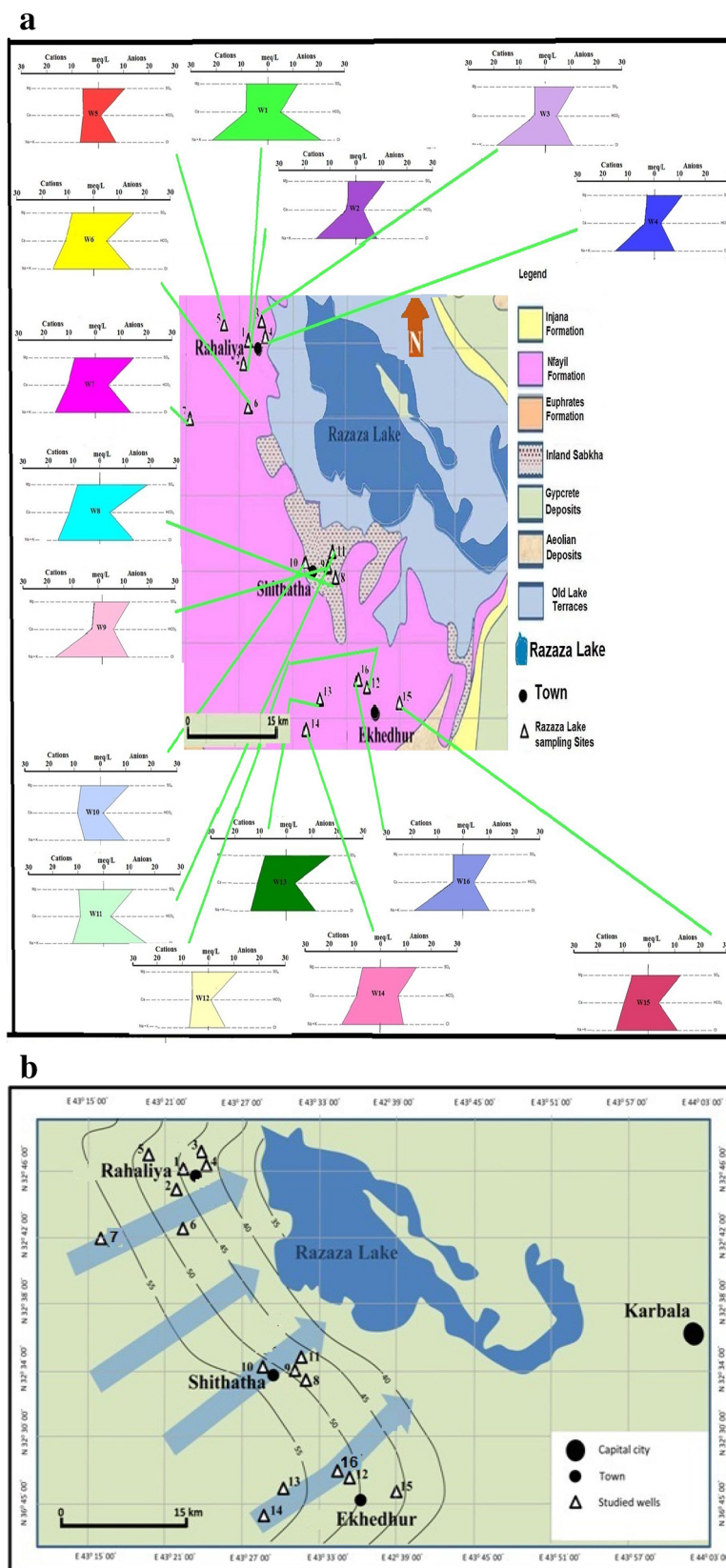
Gibbs (1970) diagram was used to discriminate the evaporation, dilution, and rock weathering as hydrochemical processes affected groundwater of the Dammam aquifer. The Gibbs diagram was mainly shared the chemical weathering and evaporation, and it is indicated that the groundwater chemistry in the Dammam aquifer was mainly controlled by weathering reactions (Fig. 11a, b). Gibbs diagram shows that there is no dilution process which reflects the lack of the amount of annual precipitation in the recharge area that feed the Dammam aquifer.

## Enrichments of ions

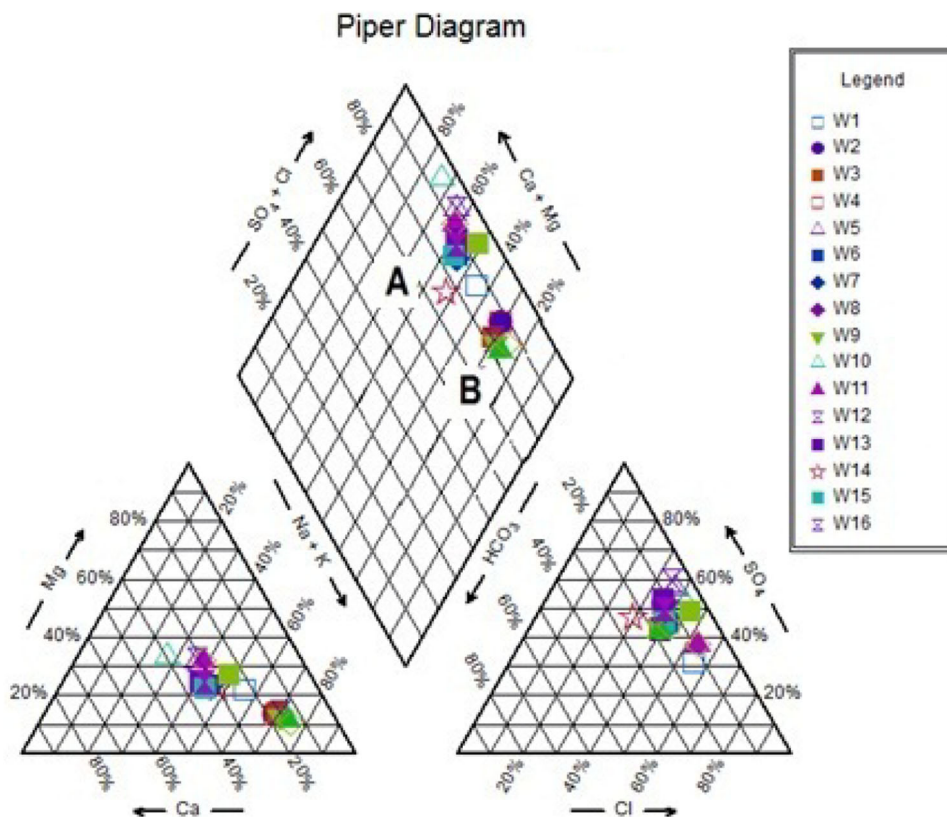
The interpretation of the probable source rock was done following many sequential steps and based on the computed results given in Table 3 (Hounslow 1995). To describe source ions and rocks affected groundwater chemistry, the chemical functions are used as follows:

1. The values of the ratio of  $\text{Na}/(\text{Na} + \text{Cl})$  indicates that there is a possible contribution of the sea water in the Dammam aquifer in 56 % wells, where the values of this ratio are more than 0.5.





**Fig. 3** **a** Stiff diagram shows the chemistry of groundwater in the Damman aquifer with the geological formations outcropped in the study area and studied groundwater wells (Stiff 1951). **b** Groundwater flow of the Damman confined aquifer



**Fig. 4** Piper diagram display groundwater facies in the Dammam aquifer (Piper 1944)

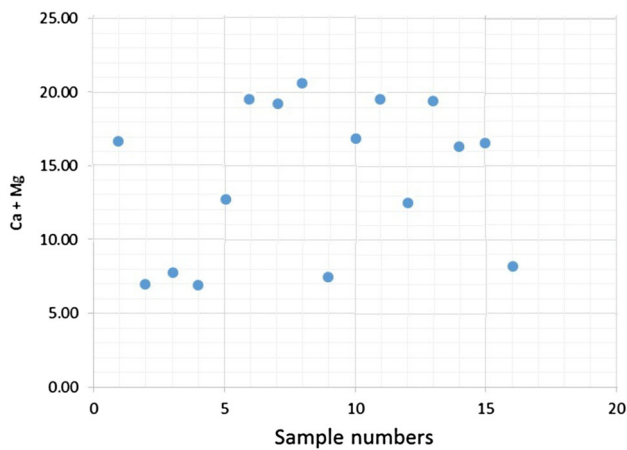
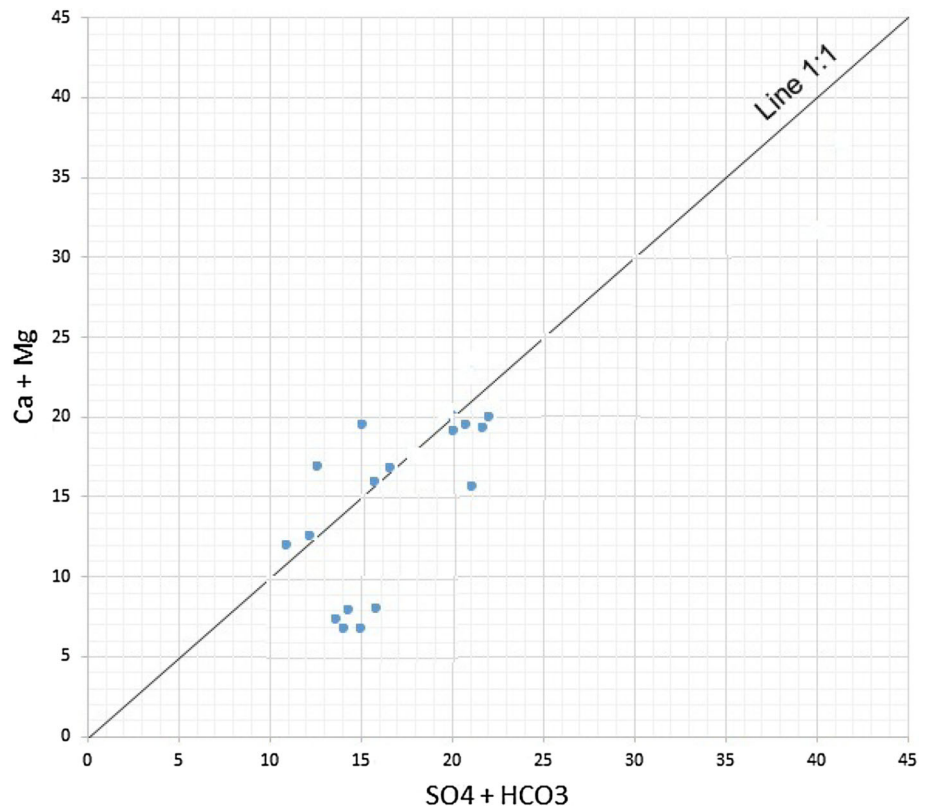
**Table 2** Hydrochemical function (in mole) of groundwater in the Dammam aquifer

S. no.	Ca/Mg	SO <sub>4</sub> /Cl	Ca + Mg	SO <sub>4</sub> + HCO <sub>3</sub>	Cl	Na + K	Na/Cl	Na	Cl/(Cl + HCO <sub>3</sub> )	Na/(Na + Ca)
1	1.02	0.6	16.8	16.73	20.85	21.7	1.02	21.29	0.8	0.7
2	0.3	1.4	6.8	14.06	7.883	15.4	1.9	15.07	0.8	0.8
3	1.08	1.0	7.8	15.77	10.28	18.1	1.7	17.8	0.7	0.8
4	1.35	1.4	6.8	14.08	7.911	15.4	1.9	15.07	0.7	0.8
5	0.9	1.4	12.6	11.08	7.15	7.4	1.0	7.162	0.9	0.5
6	1.3	1.1	19.6	20.7	14.4	16.1	1.08	15.64	0.7	0.6
7	1.3	1.1	19.2	20.45	14.34	16.2	1.09	15.68	0.7	0.6
8	1.4	1.4	20.6	22.86	13.66	16.4	1.2	16.16	0.8	0.6
9	1.2	1.1	7.3	14.7	10.14	18.7	1.8	18.37	0.7	0.8
10	1.2	1.2	17.0	12.37	9.6	6.4	0.6	6.121	0.9	0.5
11	9.5	0.7	19.5	14.97	17.29	12.5	0.7	12.16	0.9	0.6
12	0.97	1.6	12.6	12.32	6.756	7.4	1.04	7.162	0.9	0.5
13	1.36	1.5	19.4	21.69	11.89	14.1	1.2	13.77	0.8	0.6
14	1.3	1.6	16.3	21.47	9.295	15.2	1.6	14.77	0.5	0.6
15	1.3	1.1	16.1	16.93	11.57	12.7	1.1	12.55	0.7	0.6
16	1.08	1.05	7.8	14.77	10.28	19.1	1.8	18.63	0.6	0.8
Av.	1.66	1.2	14.14	16.6	11.5	14.6	1.29	13.2	0.76	0.69

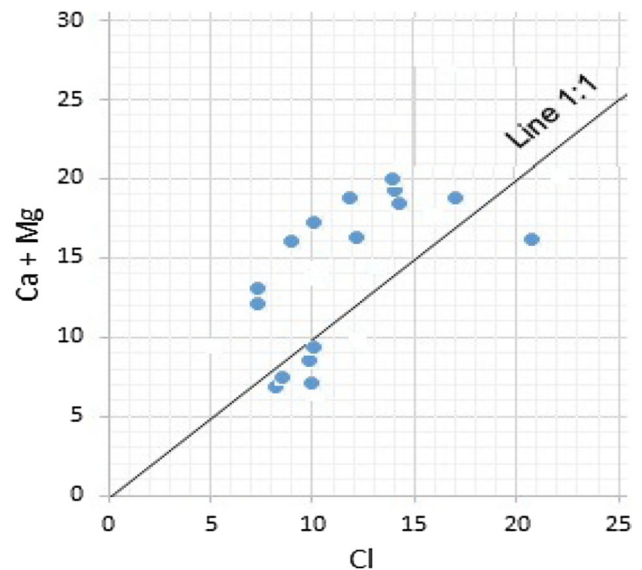
2. The values of the ratio of  $Mg/(Ca + Mg)$  greater than 0.5 indicates dolomite dissolution and calcite precipitation, but if less than 0.5 indicates limestone–

dolomite weathering. The computed values of this function (less than 0.5) reflect the limestone–dolomite weathering as a dominant process.

**Fig. 5** Relation between  $\text{Ca}^{2+} + \text{Mg}^{2+}$  and  $\text{SO}_4^{2-} + \text{HCO}_3^-$  in groundwater of the Dammam aquifer



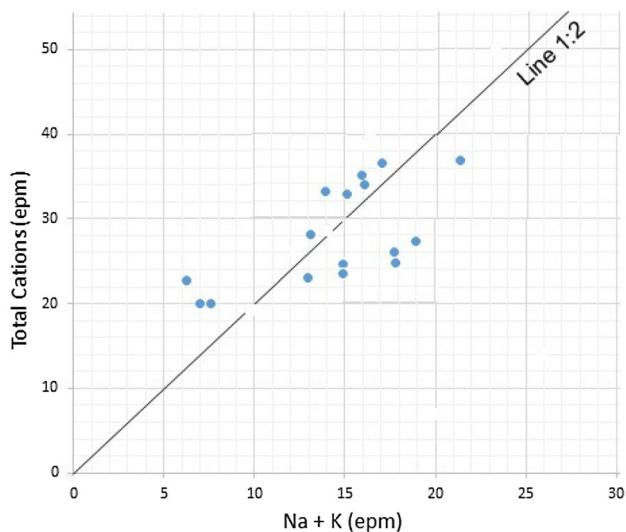
**Fig. 6** The scatter diagram of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  molar values in groundwater samples of the Dammam aquifer



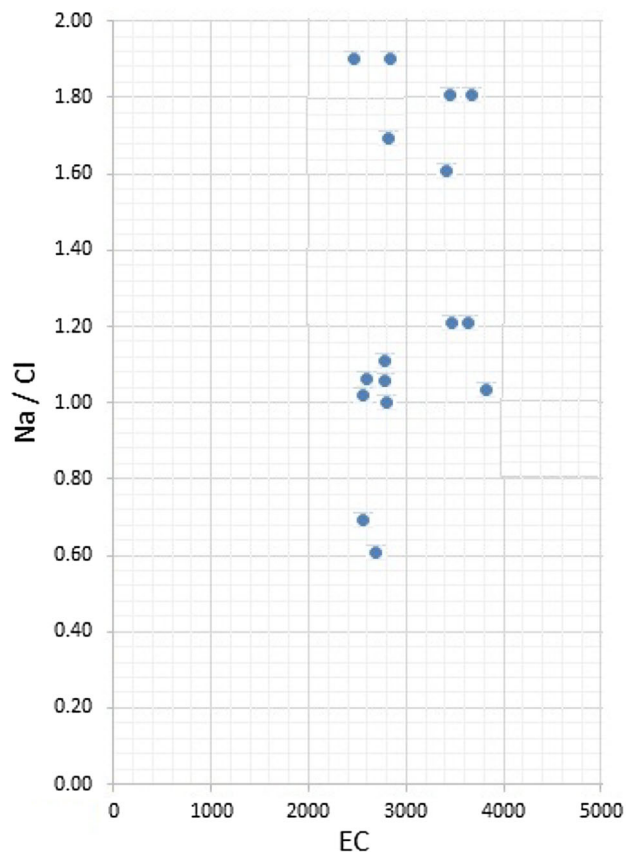
**Fig. 7** Relationship between  $(\text{Ca} + \text{Mg})$  and  $\text{Cl}$  in groundwater of the Dammam aquifer

3. If the calculated values of the ratio of  $\text{Ca}/(\text{Ca} + \text{SO}_4)$  are less 0.5, it means calcium removal by ion exchange or calcite precipitations, but if it is greater than 0.5 indicating calcium source rather than gypsum–carbonate or silicates. In this study, values of this function are less than 0.5 indicating  $\text{Ca}^{2+}$  removal by ion exchange or calcite precipitation. pH values do not support the  $\text{Ca}^{2+}$  precipitation in the Dammam aquifer.
4. The values of the ratio of  $\text{Mg}/(\text{Ca} + \text{SO}_4)$  are less than of 0.5 in the Dammam aquifer indicating contribution

5. If the computed ratio of  $(\text{Ca} + \text{Mg})/\text{SO}_4$  fall within 0.8–1.2 indicating dedolomitization. The result reflects that there is an effective dedolomitization process indicated by about 70 % of the computed ratios of this function for the groundwater samples.

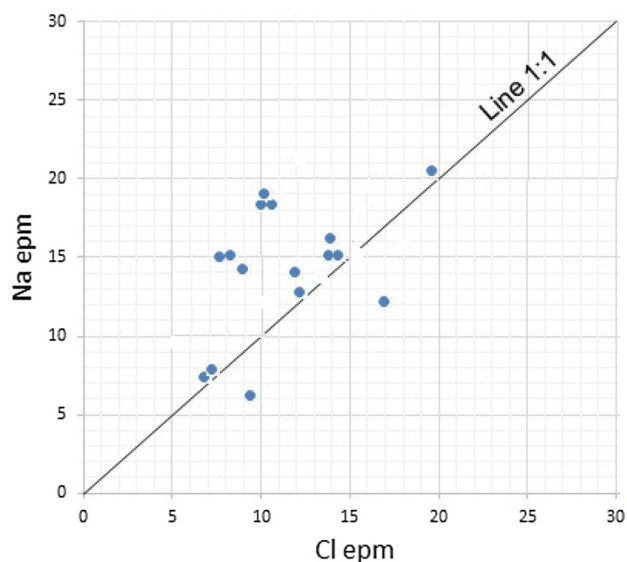


**Fig. 8** Relationship between (Na + K) and total cations in mole



**Fig. 9** Distribution pattern of (Na/Cl) against EC in groundwater of Dammam aquifer

6. If the value of TDS greater than 500 ppm, it mostly indicates carbonate weathering or brine or seawater, and if less than 500 ppm, it indicates silicate weathering. TDS data refer to the carbonate weathering as



**Fig. 10** relationship between the molar ratio of Na and Cl

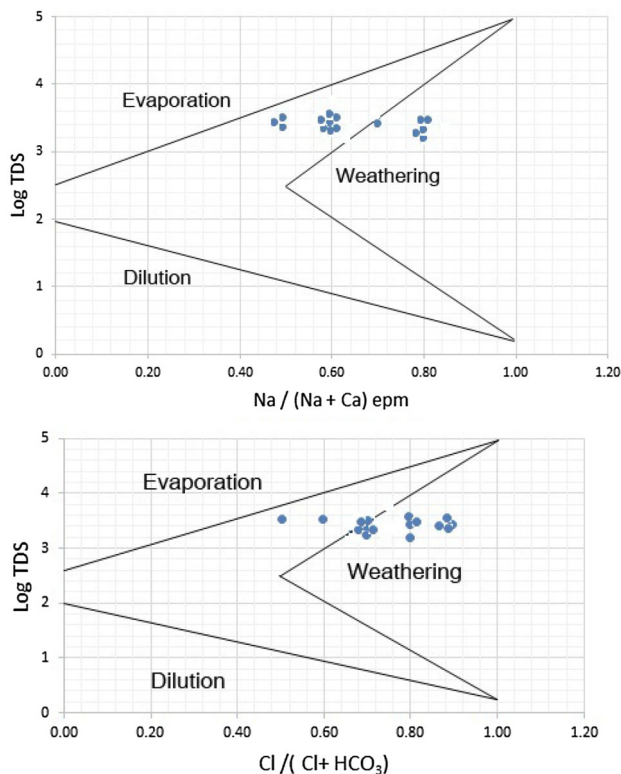
the values in the Dammam aquifer are greater than 500 ppm.

7. If the values of the ratio of  $Cl/\sum$ anions are less than 0.8, it indicates rock weathering. Accordingly, the rock weathering was the dominant process in Dammam aquifer, so as the values of these ratios are less than 0.8.
8. If the calculated value of the ratio of  $HCO_3/\sum$ anions is less than 0.8, it indicates seawater or brine. Consequently, all computed data are less than 0.8, then it indicates a brine water may affected by connate or fossils water that might be feeding along the fault plane of AJFZ.

### Evaluation of groundwater quality

In general, the variation of the groundwater quality can be attributed to the lithological and mineralogical contents of the geological formation as well as to the spatial variation in controlling factors that are responsible for sedimentation and dissolution of different minerals. The existence of several economic projects (industrial and agricultural products), such as the production of washed sand factory and fractionalizing gravels factory, were added more reasons for groundwater contamination. Moreover, some of the studied wells were located in area affected by human activity and domestic sewage effluent to the water sources; therefore, unsatisfactory for drinking may be due to the level of organic matter in the water. Possible sources of contamination include leaking septic systems, runoff from agricultural lots and organically enriched water such as industrial effluents or from decaying plant materials and





**Fig. 11** A and B: Gibbs diagrams classification of groundwater samples of the Dammam aquifer

soils. According to Al-Dabbas et al. (2016), the groundwater chemical analyses indicated that they are unsuitable for human drinking purposes according to the World Health Organization standard (WHO 2008). The microbial

analysis results indicated that about 50 % of groundwater samples are contaminated according to their total microbial count; therefore, all the groundwater samples are unsuitable for drinking purposes (Al-Dabbas et al. 2016).

**Conclusions**

- (a) The groundwater of Dammam aquifer is characterized by a meteoric water origin, neutral to slightly alkaline pH of excessively mineralized and slightly brackish water. The common water type is Na–SO<sub>4</sub>, where groundwater constituent is ordered as: Na > Ca > Mg (100 %); SO<sub>4</sub> > Cl > HCO<sub>3</sub> (91 %), but Cl > SO<sub>4</sub> > HCO<sub>3</sub> (9 %).
- (b) Groundwater samples can be described as an earth alkali water rich by Ca and Mg with increase alkalis and prevailing sulfate and chloride by 86 %, while the rest represents an alkali water rich by Na with prevailing sulfates and chloride.
- (c) Multi-chemical processes were affected the groundwater chemistry in the study area. These are dissolution of carbonate and evaporate rocks, silicate weathering, the ionic exchange between clay minerals and groundwater as well as leaching by precipitation and irrigation returns flow. Fertilizers may provide additional ions to the groundwater aquifer. Dissolution is the common chemical process, and there is no precipitation for any mineral species.
- (d) Groundwater–rock interaction in the Dammam aquifer is represented by the contribution of calcite and

**Table 3** Computed function for the source rock interpretation

S. no	Na/(Na + Cl)	Mg/(Ca + Mg)	Ca/(Ca + SO <sub>4</sub> )	Mg/(Ca + SO <sub>4</sub> )	(Ca + Mg)/SO <sub>4</sub>	Cl/∑anions	HCO <sub>3</sub> /∑anions	TDS ppm
1	0.5	0.5	0.4	0.38	1.4	0.55	0.13	2350
2	0.6	0.44	0.26	0.2	0.63	0.37	0.21	1740
3	0.6	0.47	0.26	0.24	0.7	0.4	0.17	2204
4	0.6	0.4	0.26	0.21	0.46	0.37	0.13	2226
5	0.48	0.5	0.38	0.4	1.2	0.37	0.05	2100
6	0.5	0.4	0.4	0.29	1.24	0.41	0.14	2305
7	0.5	0.4	0.4	0.29	1.2	0.41	0.14	2220
8	0.53	0.4	0.38	0.28	1.1	0.41	0.11	2238
9	0.6	0.45	0.27	0.20	0.63	0.4	0.17	2000
10	0.38	0.46	0.45	0.38	1.5	0.43	0.05	2260
11	0.4	0.51	0.46	0.49	1.1	0.53	0.20	2228
12	0.5	0.5	0.34	0.36	1.1	0.34	0.09	2000
13	0.54	0.4	0.38	0.42	1.1	0.36	0.05	2450
14	0.6	0.43	0.38	0.29	1.1	0.3	0.11	2750
15	0.52	0.4	0.19	0.28	1.2	0.4	0.22	2113
16	0.64	0.5	0.26	0.27	0.7	0.4	0.14	2476

gypsum in supplying ions more than contribution of dolomite.

- (e) The main source of sulfate is dissolving of gypsum. The evaporation and oxidation–reduction are not effective process in the Dammam aquifer, where oxidizing sulfide is not detected in the study area.

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