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The water quality index and hydrochemical characterization of groundwater resources in Hafar Albatin, Saudi Arabia

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Abstract The main objectives of this study were to: evaluate and compare the treated and untreated groundwater quality in Hafar Albatin, Saudi Arabia for drinking purpose using water quality index (WQI), study the suitability of untreated groundwater for irrigation purpose, and investigate hydrochemical processes that control the groundwater chemistry. The WQI calculations required several physiochemical water parameters including EC, pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, and NO_3^-. The results showed that more than 47 % of the untreated wells considered unsuitable (class V), 39 % considered very poor water (class IV), and 14 % considered poor water (class III) for drinking purposes. The treatment of groundwater improved its quality to poor (class III) and even good (class II). Approximately 64 % of all treated waters were of good quality; however, the rest remained poor. Most studied untreated groundwaters were considered unsuitable for irrigation due to salinity hazards; however, no sodicity hazards were anticipated. US salinity laboratory diagram revealed that the groundwater samples were grouped into five categories; 53.6 % of water samples were distributed in category C4–S2 highlighting very high salinity hazards and medium sodium hazards class. Durov and Piper diagrams revealed that the majority of investigated waters were sodium chloride and calcium sulfate–chloride water type. The Gibbs's diagram revealed that the chemical weathering of rock-forming minerals and evaporation are influencing the groundwater quality. The hydrochemical modeling indicated that all water samples were undersaturated for halite and 89 % of water samples were saturated for anhydrite and gypsum.

Keywords Water quality index · Groundwater · PHREEQC model · Hafar Albatin

Introduction

The continuous growth in the world's population means more water is needed for industrial, domestic, environmental, recreational, and agricultural requirements. The increasing demand for water when water resources are limited requires proper water resource management and assessment, especially when the water is to be used for drinking (Niemczynowicz 1999). Poor drinking water quality leads to widespread acute and chronic illness and, in many countries, is a major cause of death (US Environmental Protection Agency (USEPA) 2007). The Kingdom of Saudi Arabia (KSA), like other countries located in arid regions, suffers from water scarcity and limited renewable water resources (Al-Omran et al. 2012). The KSA depends mainly on groundwater and sea water desalination to cover its need for drinking water and irrigation as KSA does not have rivers or fresh water lakes (Saud and Abdullah 2009). A good understanding of the hydrochemical processes that govern groundwater quality is required for the sustainable management of the groundwater resources (El-Sayed et al. 2012). The chemical composition of groundwater is determined by cation exchanges with the surrounding geological layers, dissolution and precipitation of minerals, evaporation

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and oxidation-reduction reactions. Understanding these complicated hydrogeochemical processes will help to get an insight in the contribution of rock–water interactions that influence groundwater quality. Moreover, these geochemical processes are responsible for the spatial and temporal variations of the groundwater's chemistry (Matthess 1982; Kumar et al. 2006). The spatiotemporal monitoring and assessment of groundwater used for drinking and irrigation is essential for sustainable safe use of water. The water quality index (WQI) is one of the most effective tools to assess the quality of water and can be used by policy makers and to reassure concerned citizens (Lateef 2011). The purpose of the WQI is to provide a simple and concise method for assessing the water quality for drinking usage. The WQI expresses the quality of water by integrating the water quality variables into one single number (Stambuck-Giljanovic 1999; Stigter et al. 2006; Saeedi et al. 2010). The traditional approaches for assessing water quality are based on the comparison of experimentally determined parameters with local or international standards. Although these approaches allow a proper identification of contamination sources, and may be essential for checking legal compliance, they do not readily give a global vision of the spatial and temporal trends in the overall water quality (Debels et al. 2005). Numerous studies have proposed the use of a WQI (Horton 1965; Ott 1978; Miller et al. 1986; Bordalo et al. 2001; Cude 2001; Hallock 2002; Saeedi et al. 2010; Lateef 2011), and different methods for the calculation of the WQI have been developed, considering similar physical and chemical parameters but differing in the way the parameter values are statistically integrated and interpreted (Zagatto et al. 1998; Stambuck-Giljanovic 1999; Magesh and Chandrasekar 2013; Magesh et al. 2013). Backman et al. (1998) presented an index for evaluating the degree of groundwater contamination in southwestern Finland and central Slovakia. On the other hand, Soltan (1999) used the WQI to indicate the groundwater quality in Dakhla oasis, Egypt; moreover, Saeedi et al. (2010) used the WQI of groundwater to identify places with the best quality of drinking water in central-west Iran. Ketata-Rokbani et al. (2011) used the WQI and geographical information system to assess groundwater quality in the deep aquifer of El Khairat in Tunisia, and Al-hadithi (2012) applied the WQI to assess suitability of groundwater for drinking water purposes in the Ratmao–Pathri Rao catchment in India.

The main objectives of this study are to: present the use of the WQI as a monitoring tool for groundwater quality used for drinking purposes, evaluate the groundwater resources for irrigation purposes, and classify the hydrochemical characterization of groundwater resources in Hafar Albatin, Saudi Arabia.

Material and methods

Study area

Hafar Albatin is a city in Eastern Province, in the north east of the KSA. The city lies in the dry valley of Wadi Albatin, part of the larger dry valley of Wadi Al-Rummah, which leads inland towards Medina and, at some time in the past would have emptied into the Persian Gulf. The climate of Hafar Albatin is characterized by hot and dry summers with daytime temperatures range between 45 and 55 °C; on the other hand, the winter daytime temperatures range between 20 and 25 °C; in contrast, the winter nights are cold with average temperatures of −3 and 5 °C. The average rainfall during winter is 286 mm; however, no rainfall in summer is recorded (CDSI 2011).

Hydrology

The territory of eastern KSA contains aquifers of good water quality with wide variations in the geological setting (Vincent 2008). The main aquifers can be classified into two broad groups based on their primary and secondary origin. The primary origin aquifers include the quaternary sands of the wadi systems which are quartzose sandstones and conglomerates with primary porosity; and calcarenites, coquinites and oolitic limestone with secondary porosity (Alsharhan et al. 2001; Vincent 2008). Hafar Albatin wadi has a quaternary sand aquifer, where shallow supplies of poor quality water with an electric conductivity (EC) ranging between 2 and 5 dS m^{-1} are used locally for drinking and irrigation (Alsharhan et al. 2001). The very low rainfall in the KSA does not allow substantial recharge of most aquifers. Isotope studies reveal that most aquifers in Hafar Albatin contain fossil groundwater which had been recharged during previous pluvial intervals during the Quaternary age. The fragility of most aquifers in the KSA cannot be ignored; consequently, the rapid exploitation in Hafar Albatin has led to dramatic drops in the groundwater table (Alsharhan et al. 2001; Vincent 2008).

Chemical analysis

In this study, groundwater samples were collected from 28 different locations in the Hafar Albatin region of the KSA, in an attempt to capture the spatial variations in groundwater quality in the study area. Eleven drinking water samples obtained from treated (desalinated) groundwater were also collected for analysis during second quarter of the year 2013 (Table 1; Fig. 1). All samples were stored in the dark at room temperature. The samples were analyzed for EC, pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, and B. The EC was measured by using an EC meter in units of deciSiemens

Table 1 Purpose of use of the studied water resources

Serial	Sample no	Purpose of use
1	W	Irrigation (not for drinking)
2	2W	Irrigation (not for drinking)
3	3W	Irrigation (not for drinking)
4	4W	Swimming Pool
5	5W	Irrigation (not for drinking)
6	6W	Irrigation (not for drinking)
7	7W	Irrigation (not for drinking)
8	8W	Irrigation (not for drinking)
9	9W	Irrigation (not for drinking)
10	10W	Irrigation (not for drinking)
11	11W	Drinking and other domestic use
12	12W	Drinking and other domestic use
13	13W	Drinking and other domestic use
14	14W	Drinking and other domestic use
15	15W	Used for drinking after treatment (6ST)
16	16W	Drinking and other domestic use
17	17W	Drinking and other domestic use
18	18W	Irrigation (not for drinking)
19	19W	Drinking and other domestic use
20	20W	Drinking and other domestic use
21	21W	Used for drinking after treatment (11 ST)
22	22W	Drinking and other domestic use
23	23W	Drinking and other domestic use
24	24W	Drinking and other domestic use
25	25W	Drinking
26	26W	Swimming pool
28	27W	Swimming pool
29	28W	Swimming pool
30	1ST	Irrigation (not for drinking)
31	2ST	Drinking
32	3ST	Drinking
33	4ST	Drinking
34	5ST	Drinking
35	6ST	Drinking
36	7ST	Drinking
37	8ST	Drinking
38	9ST	Drinking
39	10ST	Drinking

W untreated groundwater, *ST* groundwater desalination station

per meter at 25 °C (Test kit Model 1500_20 Cole and Parmer). The water reaction (pH) was determined using a pH meter (pH meter—CG 817). The soluble Ca^{2+} and Mg^{2+} were determined by versenate titration method (EDTA); however, the soluble Na^+ and K^+ concentrations were determined using flame photometer (Corning 400) (Matiti 2004). The HCO_3^- concentration was determined by titration with sulfuric acid (H_2SO_4), whereas the Cl^- concentration was determined by titration with silver nitrate ($AgNO_3$) (Matiti 2004). The sulfate (SO_4^{-2}) concentration was determined by the turbidity method (Tabatabai 1996), and the nitrate (NO_3^-) concentration was determined by the phenoldisulfonic acid method (APHA 1998). The B was determined using azomethine-H method (Bingham 1982).

Ion balance errors

The correctness of the chemical analysis was verified by calculating ion balance errors; furthermore, standard solutions and blanks were commonly run to check for possible errors in the analytical procedures. The level of error in the data was calculated using the following formula (Appelo and Postma 1996):

$$\text{Error of ion balance} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100 \qquad (1)$$

An error of up to ±3 % is tolerable, while every water sample with a calculated error outside this range should be measured again. Approximately 89 % of the measured water samples were within this range. This means that the resultant data quality is sufficient for chemical modeling and/or for drawing simple conclusions about water quality.

WQI computing

The WQI calculations include three successive steps (Horton 1965; Yidana and Yidana 2010; Ketata-Rokbani et al. (2011); Lateef 2011; Al-hadithi 2012).

The first step is "assigning weight": each of the 12 parameters has been assigned a weight (wi) according to its relative importance in the overall quality of drinking water as shown in Table 2. The most significant parameters have a weight of 5 and the least significant have a weight of 1. In this study, the maximum weight of 5 has been assigned to nitrate, due to its major importance in water quality assessment (Ramakrishnalah et al. 2009), the less harmful parameters i.e., calcium, magnesium, and sodium have been given a weight of 2.

The second step is the "relative weight calculation": the relative weight (Wi) is computed from the following equation:

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

Where Wi is the relative weight, wi is the weight of each parameter and *n* is the number of parameters. The calculated relative weight (Wi) values of each parameter are given in Table 2.
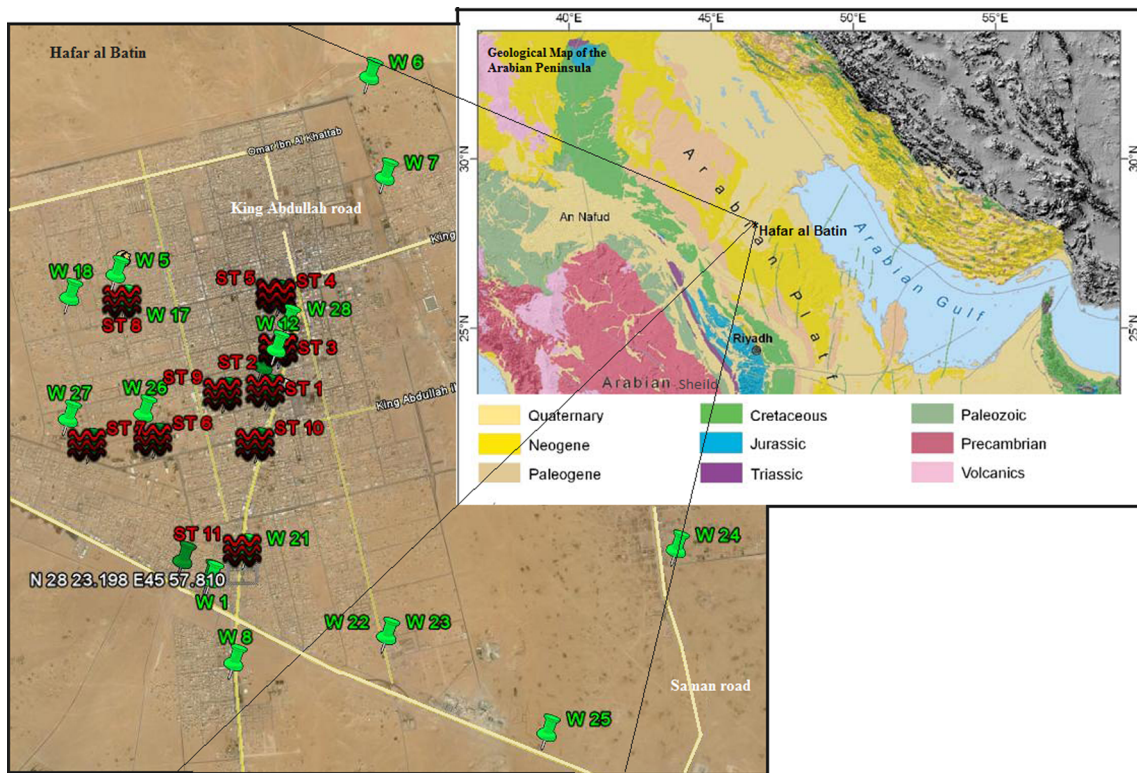
Fig. 1 Location of the study area showing groundwaters sampling sites (*W* untreated groundwater samples, *ST* treated groundwater samples collected from the treatment station)

The third step is "quality rating scale calculation": the quality rating scale (qi) for each parameter is calculated by dividing the parameter concentration in each water sample by its respective standard (WHO 2011) (Table 3) multiplied by 100:

$$qi = \frac{Ci}{Si} \times 100 \tag{3}$$

where qi is the quality rating, Ci is the concentration of each chemical parameter in each water sample in milligrams per liter, except pH, and Si is the WHO (2011) standard for each chemical parameter. Finally, the Wi and qi is used to calculate the SI*i* for each chemical parameter, and then the WQI is calculated from the following equation:

$$SI\textit{i} = Wi \times qi \tag{4}$$

$$WQI = \sum_{i=1}^{n} SI\textit{i} \tag{5}$$

Table 2 Relative weight for parameters (Ramakrishnalah et al. 2009; Lateef 2011)

Chemical parameters	Weights (wi)	Relative weight (Wi)
pH	3	0.091
Hardness (mg L^{-1})	2	0.061
TDS (mg L^{-1})	4	0.121
Calcium (mg L^{-1})	2	0.061
Magnesium (mg L^{-1})	2	0.061
Sodium (mg L^{-1})	2	0.061
Potassium (mg L^{-1})	2	0.061
Bicarbonate (mg L^{-1})	2	0.061
Chloride (mg L^{-1})	3	0.091
Sulfate (mg L^{-1})	3	0.091
Nitrate (mg L^{-1})	5	0.152
Boron (mg L^{-1})	3	0.091
Total	33	1.00

Table 3 The WHO standard for drinking purpose (WHO 2011)

Parameters	WHO standards
pH	6.5–8.5
Hardness (mg L^{-1})	500
TDS (mg L^{-1})	600
Calcium (mg L^{-1})	75[a]
Magnesium (mg L^{-1})	50[a]
Sodium (mg L^{-1})	200
Potassium (mg L^{-1})	12
Bicarbonate (mg L^{-1})	120
Chloride (mg L^{-1})	250
Sulfate (mg L^{-1})	250
Nitrate (mg L^{-1})	10
Boron (mg L^{-1})	0.5

[a] WHO 2004

Table 4 Water quality classification based on WQI value (Ramakrishnalah et al. 2009; Ketata-Rokbani et al. (2011))

Classification of drinking water quality

WQI Range	Class	Type of water
<50	I	Excellent water
50–100.1	II	Good water
100–200.1	III	Poor water
200–300.1	IV	Very poor water
>300	V	Water unsuitable for drinking

where SI_i is the sub index of each parameter; q_i is the rating based on concentration of each parameter and n is the number of parameters. The computed WQI values are classified into five categories, as shown in Table 4.

Hydrochemical characteristics

The hydrochemical characterization of the untreated groundwater samples were evaluated by means of major ions, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, and SO_4^2. The chemical analysis data of the water samples were plotted on the Piper, Schoeller, and Durov diagrams using Geochemistry Software Aq.QA, version AQC10664 (Rockware AqQA Software 2011) for the identification of water types. The Gibbs (Gibbs 1970) and US salinity laboratory (Richards 1954) diagrams were also presented in this study. In addition, salinity hazard, sodium adsorption ratio (SAR), total hardness (as $CaCO_3$), and Kelly's ratio (KR) were calculated to investigate the groundwater suitability for irrigation.

Geochemical modeling

Interactions between water and the surrounding rocks and soil are considered to be the main processes controlling the observed chemical characteristics of the water. The deviation of water from equilibrium with respect to dissolved minerals is

quantitatively described by the saturation index (SI). The SI of a mineral is obtained from the following formula:

$$SI = \log IAP/k_t \qquad (6)$$

where IAP is the Ion Activity Product of the dissociated chemical species in solution and k_t is the equilibrium solubility product of the chemical involved (Alexakis 2011).

The hydrogeochemical equilibrium model, PHREEQC model (Parkhurst and Appelo 1999), was used to calculate the SI of the untreated groundwater with respect to the main mineral phases.

Statistical analysis

Statistical analysis was carried out using the statistical package for social sciences (IBM SPSS Statistics 21 Core System, IBM Corporation 2012). The statistical tests applied were basic statistics (maximum, minimum, mean, standard deviation, variance, standard error, median, skewness) and Spearman's correlation matrix (assuming $p < 0.01$).

Results and discussion

Water quality assessment for drinking purpose

The statistical analysis of the groundwater was done to identify the chemical parameters that are deviating from WHO drinking water standard (Tables 5 and 6). It was noted that the mean, median, and maximum for most parameters in the untreated groundwater exceeded the acceptable limits of the standard used; however, with exception of nitrate, the minima of the parameters were within the acceptable limits (Table 5). The statistical analysis of the treated groundwater; however, showed that all parameters were within the acceptable limits, except for nitrate as the nitrate concentrations exceeded the permissible limits of the WHO standard (Table 6).

Table 5 Descriptive statistics of Hafar Albatin untreated groundwater chemical composition ($n=28$)

	PH	TDS mg L^{-1}	Ca^{2+} mg L^{-1}	Mg^{2+}	Na$^+$	K$^+$	HCO$_3^-$	Cl$^-$	SO$_4^{-2}$	NO$_3^-$ mg L^{-1}	B	Total Har.	SAR	KR
Max.	7.6	6641.5	780.0	144.0	1796.3	23.4	414.8	2272.0	1771.2	110.80	1.10	2250.0	17.5	1.95
Mini.	6.8	537.6	50.0	15.6	119.6	3.9	109.8	85.2	163.2	29.20	0.16	200.0	3.0	0.45
Mean	7.2	2943.4	370.0	66.3	562.8	13.1	203.3	822.3	822.7	69.57	0.55	1200.8	6.8	1.02
Stdev	0.2	1438.2	165.1	36.4	393.1	6.7	79.9	507.4	386.6	19.45	0.20	524.9	3.4	0.41
Vari.	0.5	37.9	12.9	6.0	19.8	2.6	8.9	22.5	19.7	4.41	0.45	22.9	1.8	0.64
St. error	0.1	1.3	0.8	0.5	1.0	0.4	0.7	1.0	1.0	0.46	0.15	1.0	0.3	0.17
Med.	7.2	2575.8	346.0	61.2	473.8	11.7	192.2	656.8	801.6	71.20	0.53	1075.0	5.9	0.87
Skew	−0.2	0.9	0.4	0.5	1.7	0.5	1.1	1.1	0.6	0.23	0.43	0.3	1.6	0.90

Table 6 Descriptive statistics of Hafar Albatin treated groundwater chemical composition ($n=11$)

	PH	TDS mg L^{-1}	Ca^{2+} mg L^{-1}	Mg^{2+}	Na$^+$	K$^+$	HCO$_3^-$	Cl$^-$	SO$_4^{-2}$	NO$_3^-$ mg L^{-1}	B	Total Hardness
Max.	7.4	272.8	15.00	3.60	56.12	1.95	91.50	99.40	280.80	57.7	0.56	52.5
Mini.	6.2	101.3	3.00	0.36	19.78	1.17	15.25	21.30	10.08	45.1	0.13	8.8
Mean	6.8	172.2	8.09	1.84	38.37	1.52	31.05	54.86	42.28	51.0	0.33	27.9
Stdev	0.4	54.9	4.09	1.24	11.11	0.27	21.77	25.62	79.26	3.9	0.12	14.8
Vari.	0.7	7.4	2.02	1.11	3.33	0.52	4.67	5.06	8.90	2.0	0.35	3.8
St. error	0.2	0.6	0.31	0.23	0.40	0.16	0.47	0.49	0.65	0.3	0.13	0.4
Med.	7.0	155.9	8.00	1.80	41.17	1.56	27.45	56.80	21.60	51.1	0.36	30.0
Skew	−0.2	0.9	0.55	0.21	−0.23	0.12	2.47	0.21	3.29	0.3	−0.05	0.3

The degree of a linear association between the water quality parameters and WQI has been measured by the simple correlation coefficient (r) (Tables 7 and 8). Correlation analysis measures the closeness of the relationship between chosen variables; if the correlation coefficient is nearer to +1 or −1, the linear relationship between the two variables is perfected (Al-hadithi 2012). It was observed, for the untreated groundwater, that the total dissolved solid (TDS) variations are mainly controlled by calcium ($r=0.93$), magnesium ($r=0.89$), sodium ($r=0.96$), sulfate ($r=0.95$), and chloride ($r=0.98$) concentrations. The relationship between magnesium and chloride was highly significant indicated that the hardness of the water was permanent in nature; moreover, the calculated WQI showed also highly significant interrelation between its values and pH ($r=0.92$), TDS ($r=0.88$), Mg ($r=0.87$), HCO$_3^-$ ($r=0.88$), Cl$^-$ ($r=0.90$), NO$_3^-$ ($r=0.80$), B ($r=0.88$), and total hardness ($r=0.88$) (Table 7). The treated groundwater TDS are mainly controlled by only sodium ($r=0.87$), and chloride ($r=0.88$) concentration and the WQI showed highly significant interrelation between its values and only TDS ($r=0.88$)

and NO$_3^-$ (0.93) (Table 8) (Al-Omran et al. 2012; Aly et al. 2013).

Water quality index

The computed WQI values for the 28 untreated well waters in Hafar Albatin ranged from 102.6 to 597.5 (Fig. 2), with 14 % of the waters being class (III) "poor water", 39 % were class (IV) "very poor water", and 47 % were class (V) or "water unsuitable for drinking". The reasons for the high WQI values obtained for this study area were high values of pH, TDS, Mg$^2-$, HCO$_3^-$, Cl$^-$, NO$_3^-$, B, and total hardness. Very high correlation coefficients between these values were also reported by Deshpande and Aher (2012), WHO (1993), Mitra et al. (2007), and Gupta et al. (2004). As shown in Table 1 and Fig. 2, the wells 11, 12, 13, 14, 16, 17, 19, 20, 22, 23, 24, and 25 were used for drinking water; however, only water of well 11 was considered good for drinking. The other wells waters were considered poor, very poor, or unsuitable for drinking.

Table 7 Correlation coefficient matrix of water quality parameters and WQI of untreated groundwater ($n=28$)

Parameters	pH	TDS	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	HCO$_3^-$	Cl$^-$	SO$_4^{-2}$	NO$_3^-$	B	Total Hardness	WQI
pH	1	0.34	0.30	0.37	0.27	0.13	0.19	0.31	0.31	0.20	0.04	0.33	0.92
TDS		1	0.93	0.89	0.96	0.73	0.44	0.98	0.95	0.63	0.81	0.95	0.88
Ca^{2+}			1	0.83	0.83	0.80	0.61	0.88	0.93	0.60	0.79	0.99	0.78
Mg^{2+}				1	0.84	0.62	0.33	0.86	0.85	0.54	0.68	0.90	0.87
Na$^+$					1	0.65	0.30	0.94	0.89	0.60	0.81	0.86	0.75
K$^+$						1	0.72	0.61	0.80	0.49	0.79	0.78	0.53
HCO$_3^-$							1	0.32	0.49	0.31	0.37	0.56	0.88
Cl$^-$								1	0.86	0.59	0.74	0.90	0.90
SO$_4^{-2}$									1	0.62	0.85	0.94	0.65
NO$_3^-$										1	0.59	0.60	0.80
B											1	0.79	0.88
Total hardness												1	0.88
WQI													1

Table 8 Correlation coefficient matrix of water quality parameters and WQI of treated groundwater ($n=11$)

	pH	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{-2}	NO_3^-	B	Total Hardness	WQI
pH	1	−0.16	0.06	0.03	0.04	0.05	0.10	0.11	−0.41	−0.25	−0.35	0.05	−0.32
TDS		1	0.62	0.34	0.87	0.43	−0.47	0.88	0.63	0.76	0.36	0.55	0.88
Ca^{2+}			1	0.81	0.42	0.21	−0.59	0.78	0.57	0.39	0.17	0.98	0.53
Mg^{2+}				1	0.09	0.27	−0.44	0.47	0.49	0.05	−0.09	0.91	0.22
Na^+					1	0.05	−0.14	0.80	0.39	0.65	0.27	0.32	0.73
K^+						1	−0.30	0.19	0.55	0.38	0.48	0.24	0.54
HCO_3^-							1	−0.64	−0.26	−0.66	−0.49	−0.57	−0.56
Cl^-								1	0.40	0.74	0.42	0.71	0.79
SO_4^{-2}									1	0.38	0.16	0.56	0.65
NO_3^-										1	0.73	0.29	0.93
B											1	0.09	0.69
Total hardness												1	0.45
WQI													1

The computed WQI values for the 11 treated (desalinated) well waters ranged between 88.8 and 122.0, as shown in Fig. 2; with 63.6 % falling in the class (II) "good water" category and 36.4 % in class (III) or "poor water" category. The reason of the high WQI value of these treated groundwater is mainly due to the high NO_3^- content, as the correlation coefficient between WQI and NO_3^- was very high (Table 8). The main reason of high nitrate concentrations in all waters is the over-application of fertilizer on surrounding agricultural land (Al-hadithi 2012). The result emphasis that the groundwater treatment used in the study area is not efficient in nitrate removal. A suitable and approved technology for the nitrate removal (e.g., ion exchange or electrodialysis) is required (Hell and Lahnsteiner 2002; Lahnsteiner and Hell 1993; Mizutani 1990).

Water quality evaluation for irrigation purpose

The major ions chemistry of untreated groundwater samples of Hafar Albatin statistically analyzed and the results summarized by minimum, maximum, mean (Table 5).

Suitability of the groundwater for irrigation purpose was discussed based on the following basic criteria: (i) the cations; the concentrations of Ca^{++}, Mg^{++}, Na^+, and K^+ ions ranged between 5 and 780, 15.6 and 144, 119.6 and 1,796.3, and 3.9 and 23.4 ppm with a mean value of 370, 66.3, 562.8, and 13.1 ppm, respectively (Table 5). The maximum permissible limit of these ions in irrigation water is 80, 35, 200, and 30 ppm, respectively (Duncan et al. 2000; Sharifi and Safari Sinegani 2012; Nagaraju et al. 2014). On the basis of these permissible limits: 92.9, 78.6, and 96.4 % of the water samples are unsuitable for irrigation usage with respect to Ca^{++}, Mg^{++},

Fig. 2 Values of WQI of studied samples
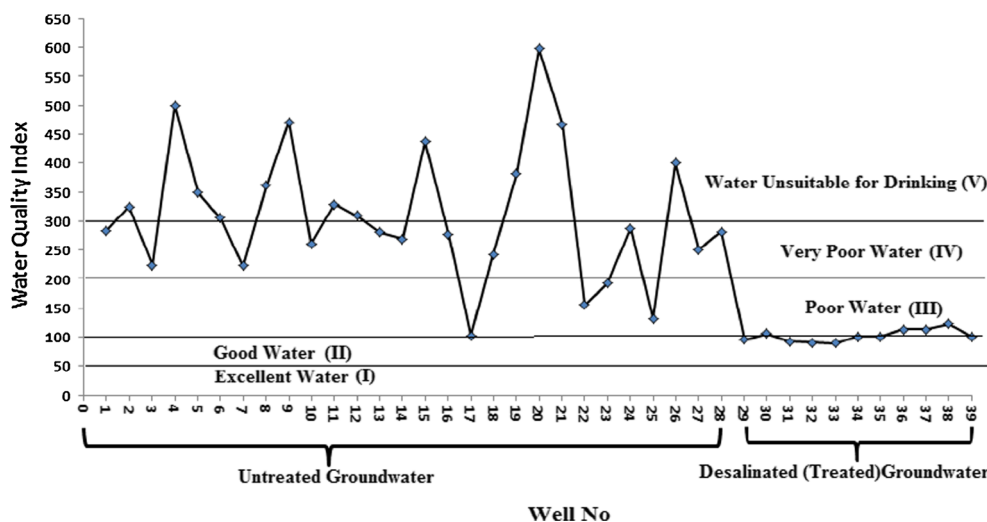
Na⁺, respectively. (ii) the anions; the concentrations of HCO₃⁻, Cl-, SO₄⁻, and NO₃⁻ ions lie in between: 109.8 and 414.8; 85.2 and 2,272.0; 163.2 and 1,771.2; and 29.2 and 110.8 ppm, respectively with a mean value of 203.3, 822.2, 822.7, and 69.6 ppm, respectively (Table 5). The maximum permissible limit of HCO₃⁻, Cl⁻, SO₄⁻, and NO₃⁻ in irrigation water is 250, 250, 180, and 30 ppm, respectively (McKee and Wolf 1963; Ayers and Westcot 1985; Duncan et al. 2000; Sharifi and Safari Sinegani 2012). According to the grading standards 25, 92.9, 96.4, and 96.4 % of the water samples are unsuitable for irrigation usage with respect to HCO₃⁻, Cl⁻, SO₄⁻, and NO₃⁻, respectively. The order of ionic concentrations in milligrams per liter for the cations is Na⁺+K⁺>Ca²⁺> Mg²⁺ and the anions order is Cl⁻>SO₄²⁻>HCO₃⁻ (Fig. 3). (iii) pH; the pH is a term used universally to express the intensity of the acid or alkaline condition of a water. Table 5 concluded that the pH values of the water samples ranged between 6.8 and 7.6 with a mean value of 7.2. These mean that all studied water samples were within safe limit with respect to pH (Ayers and Westcot 1985). (iv) Salinity hazard; determination of salinity hazard is very important in irrigation water, as high salt content renders the soil saline. This also affects the salt intake capacity of the plants through the roots. EC is a measure of water capacity to convey electric current. It represents the amount of TDS. Thus, in the present study, the salinity hazard was evaluated by TDS, their amounts varied from 537.6 to 6,641.1 mg L⁻¹ with an average value of 2,943.4 mg L⁻¹, respectively. Based on the classification of

TDS suggested by Ayers and Westcot (1985), most of the water samples (71.4 %) are classified as severe saline water. (v) Sodium hazard; the excessive sodium content in water sample reduces the permeability, and hence, the available water for the plant is reduced. Sodium replacing adsorbed calcium and magnesium is a hazard, as it causes damage to the soil structure resulting in compact and impervious soil (Arveti et al. 2011). Excess absorption of sodium can cause sodium toxicity in sensitive plants, causing marginal leaf burn on older foliage and possibly defoliation. The water containing excessive amount of sodium may immobilize other nutrient ions particularly calcium, magnesium, and potassium, which can result in deficiencies of these elements in plants (Sharifi and Safari Sinegani 2012). One of the most important criteria in determining sodium hazard is SAR (Todd and Mays 2005). The sodium adsorption ratio is computed as:

$$SAR = \frac{Na}{\sqrt{\dfrac{Ca + Mg}{2}}} \tag{7}$$

where the ionic concentration is in milliequivalents per liter.

The SAR values of the untreated groundwater samples varied between 3.0 and 17.5 with an average value of 6.8 (Table 5). About 85 % of the SAR values of the water samples were less than 10 and are classified as excellent for irrigation (Richards 1954). Kelly (1940) was also determined the hazardous effect of

Fig. 3 Schoeller diagram indicating ionic concentrations of groundwater in the study area
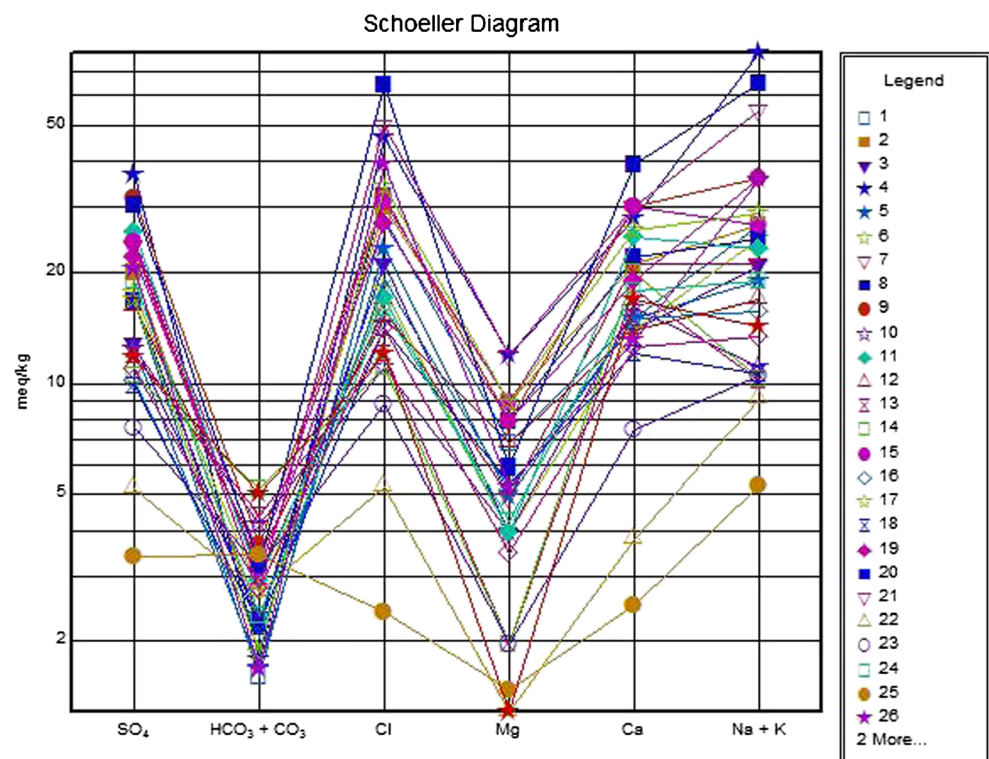
sodium on water quality for irrigation usage in terms of Kelly's ratio (KR). The Kelly's ratio is computed as:

$$KR = \frac{Na}{Ca + Mg} \qquad (8)$$

where the ionic concentrations are in milliequivalents per liter.

A Kelly's ratio of more than one indicates excessive sodium in water. Therefore, water with a Kelly's ratio less than one is considered suitable for irrigation; on the other hand, the ratio more than one is unsuitable. The Kelly's ratios in the studied water ranged between 0.45 and 1.95, with an average value of 1.02 (Table 5). About 60 % of the studied waters are considered suitable for irrigation with Kelly's ratio less than one. (vi) Boron toxicity; the boron concentrations were within permissible limits in 85.7 % of studied water samples and the remaining samples were considered slight to moderate boron toxicity (Ayers and Westcot 1985).

Salinity and alkalinity hazard class

According to the US Salinity Laboratory's diagram (Richards 1954) in Fig. 4, salinity and alkalinity hazard class of water samples were C4–S2 (53.6 %), C4–S3 (21.4 %), C4–S4 (14.3 %), C3–S2 (7.1 %), and C3–S1 (3.6 %). The result shows that a majority of the groundwaters possess very high salinity

hazards with medium sodium hazards (C4–S2). Lauchli and Epstein (1990) have pointed out that salinity can have effect on growth and development of plants in different ways, such as osmotic effects, specific ion toxicity and/or nutritional disorders. Thus, the excessive amount of salts can be one of the major problems with water used for irrigation in this area and the water cannot be used for irrigation for most crops without special circumstances for salinity control such as leaching requirement or cropping of salt-tolerant plants. In this study about 21.4 % of the water samples fall in very high salinity and high alkalinity hazard class (C4–S3) and about 14.3 % fall in very high salinity and very high alkalinity hazard (C4–S4) with continuous use of such water samples in the long term will increase both salinity and alkalinity hazard in the soil. However, only 7.1 % of samples fall in high salinity and medium alkalinity hazard (C3–S2) and 3.6 % considered high salinity and law alkalinity hazard class (C3–S1).

Hydrochemical aspects

The chemical data of the untreated groundwater samples were plotted on a Piper trilinear (Piper 1944) and Schoeller (1955) diagrams (Figs. 5 and 3). The Piper diagrams provide a convenient method to classify water types collected from different groundwater resources, based on the ionic composition of different water samples (Al-Omran et al. 2012; Semerjian

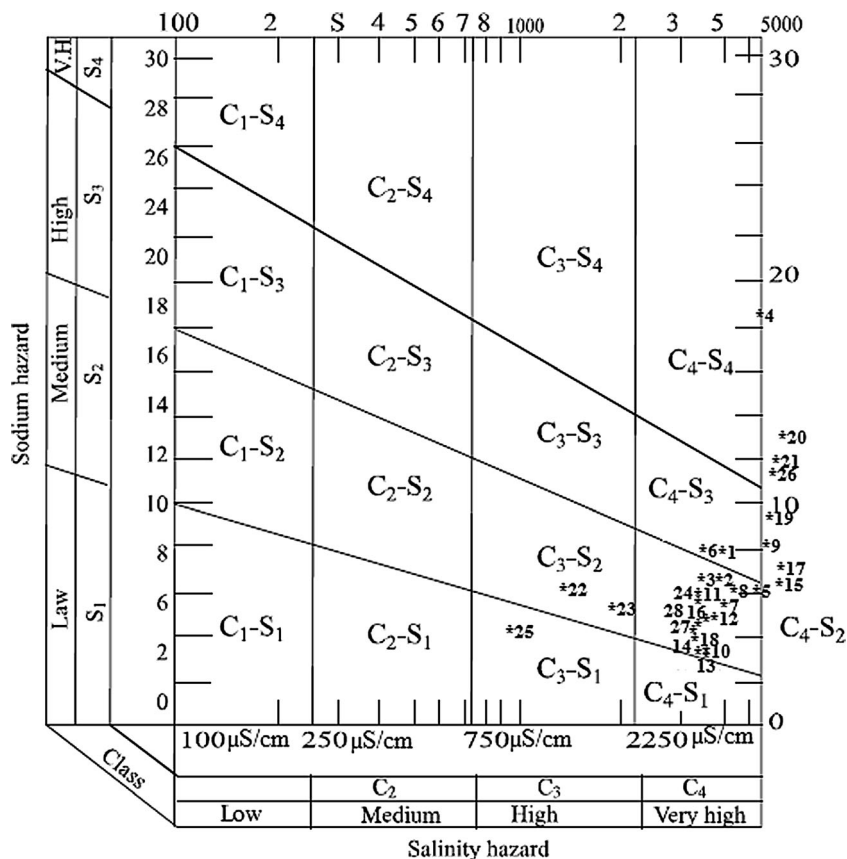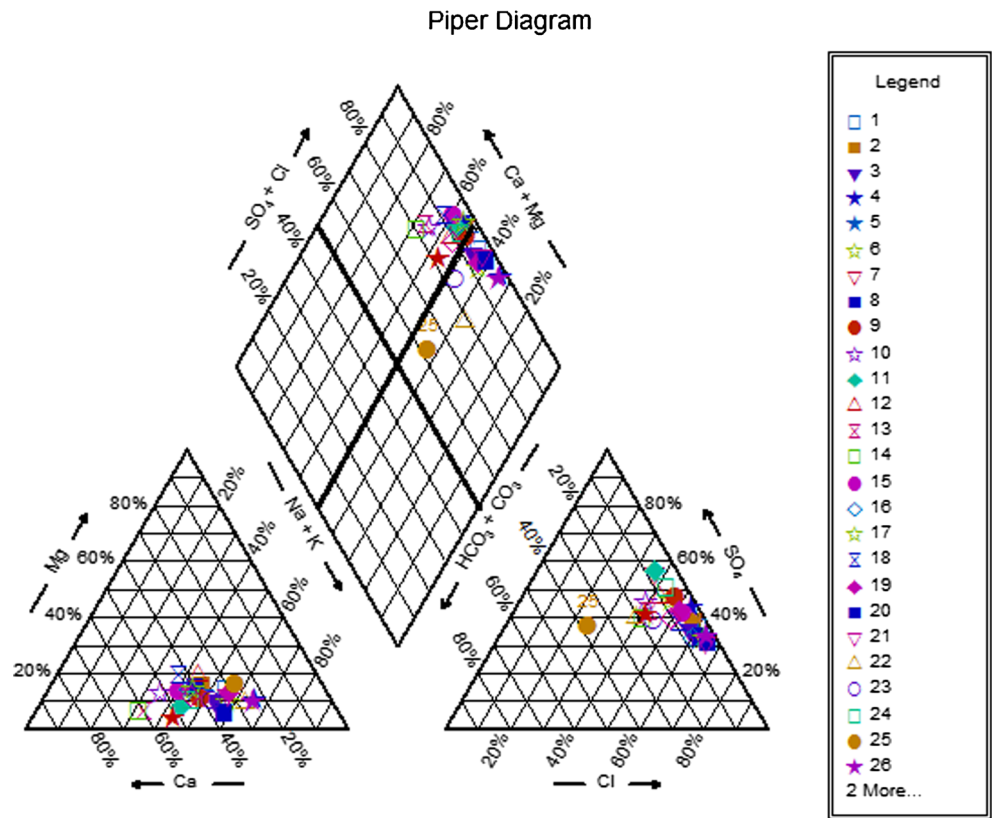**Fig. 4** Salinity classification of groundwater used irrigation

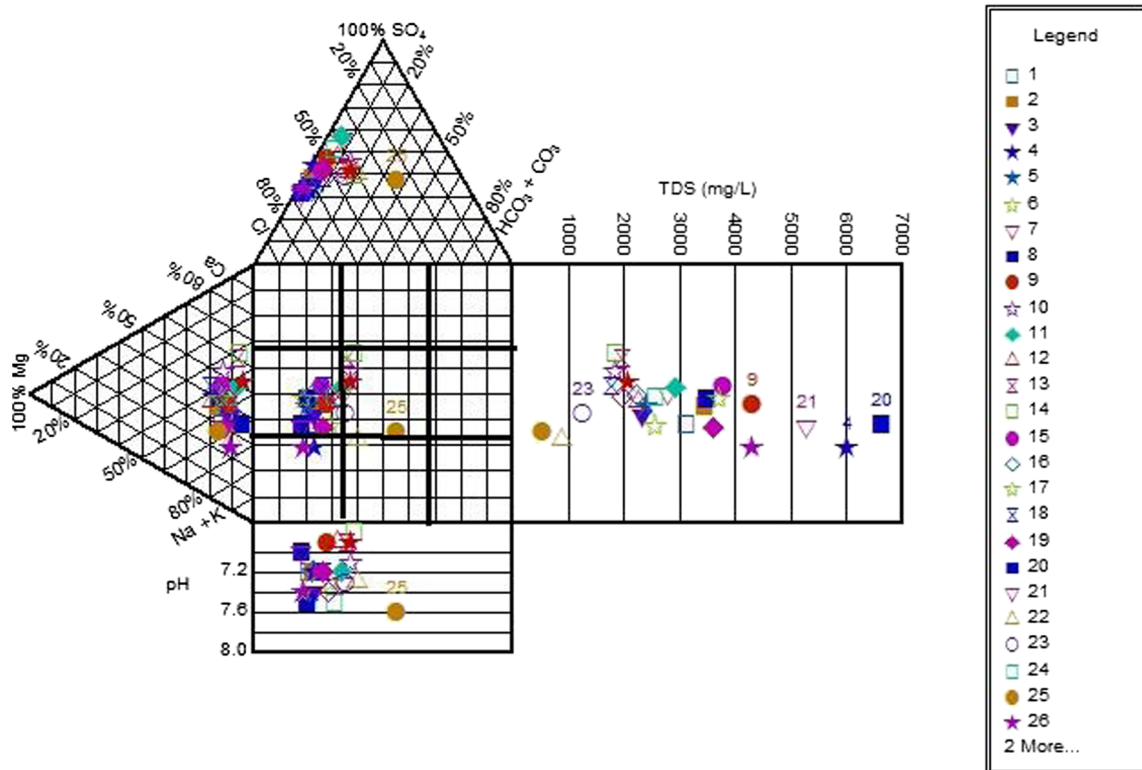**Fig. 5** Piper trilinear diagram

Fig. 6 Durov's diagram for Hafar Albatin groundwater samples

2011; Baba et al. 2008). The main water types have been identified on the basis of the major ion concentrations as in Aly and Benaabidate (2010), and Aly et al. (2013). The Piper diagram reveals that there are two different types of groundwater in Hafar Albatin., the first type is rich in sodium chloride–sulfate water, and the second is rich in calcium sulfate–chloride. The water type indicated that the geology in the study area mainly consist of halite, gypsum, and anhydrite.

In the Schoeller diagram (Fig. 3), it may be seen that there is a predominance of sodium and calcium which influences the tendencies towards the chloride/sulfate–sodium/calcium facies.

The major cation and anion concentrations of the samples collected from groundwaters in the region were plotted on Durov's diagram (Fig. 6). Durov's diagram helps the interpretation of the evolutionary trends and the hydrochemical processes occurring in the groundwater system and can indicate mixing of different water types, ion exchange and reverse ion exchange processes. The result shows that the majority (75 %) of the samples fall in field 4, the zone of high water salinity. The samples belonging to field 4 suggest the presence of SO_4^{-2} and Ca^{2+} as dominant type of water, indicating gypsum-bearing sedimentary aquifer and the groundwater affected by oxidation of pyrite and other sulfide minerals. However, around 17.9 % of water samples located in field 5 of Durov's diagram indicating mixing processes of two or more different facies might be

occurring, and 7.1 % located in field 7 suggest presence of Cl^- and Ca^{2+} as dominant type of water and indicating the invasion of fresh water by saline water.

In high salinity water environment, the process of reverse ion exchange may create $CaCl_2$ waters due to removal of Na^+ from solution by exchanging Ca^{2+} from clay fraction in aquifer. Alternatively, $CaCl_2$ type waters could also be a result of mixing process between fresh water with more saline older water (Adams et al. 2001). Gibbs's diagrams, representing the ratios of $Na^+ + K^+$: ($Na^+ + Ca^{2+} + Mg^{2+}$) and Cl^-: ($Cl^- + HCO_3^-$) as a function of TDS, are widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance and evaporation-dominance (Gibbs 1970). The chemical data of groundwater sample points of the studied area were plotted in Gibbs's diagrams (Fig. 7). The distribution of sample points suggests that the chemical weathering of rock-forming minerals and evaporation are influencing the groundwater quality. Evaporation increases salinity by increasing Na^+ and Cl^- with relation to increase of TDS. The rock domain suggests that rock–water interaction is the major source of dissolved ions over the control of groundwater chemistry. The rock–water interaction process includes the chemical weathering of rocks, dissolution–precipitation of secondary carbonates and ion exchange between water and clay minerals. The evaporation
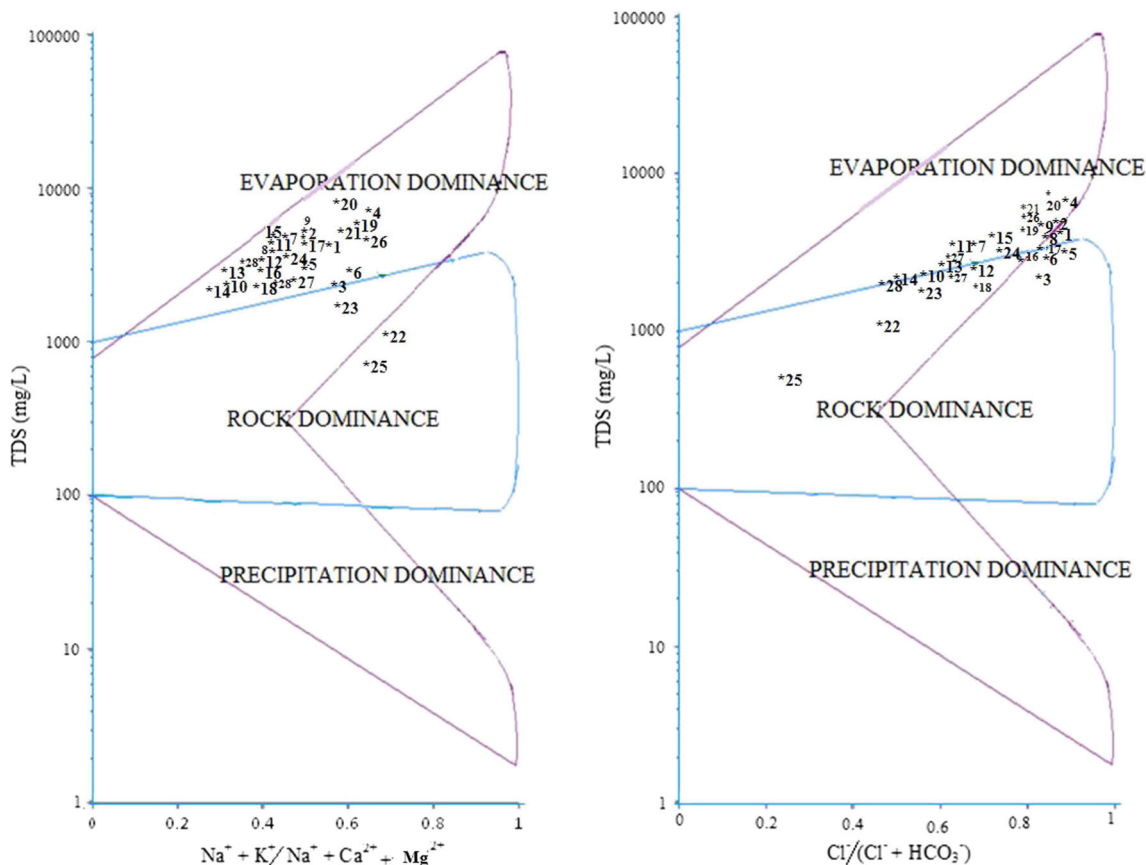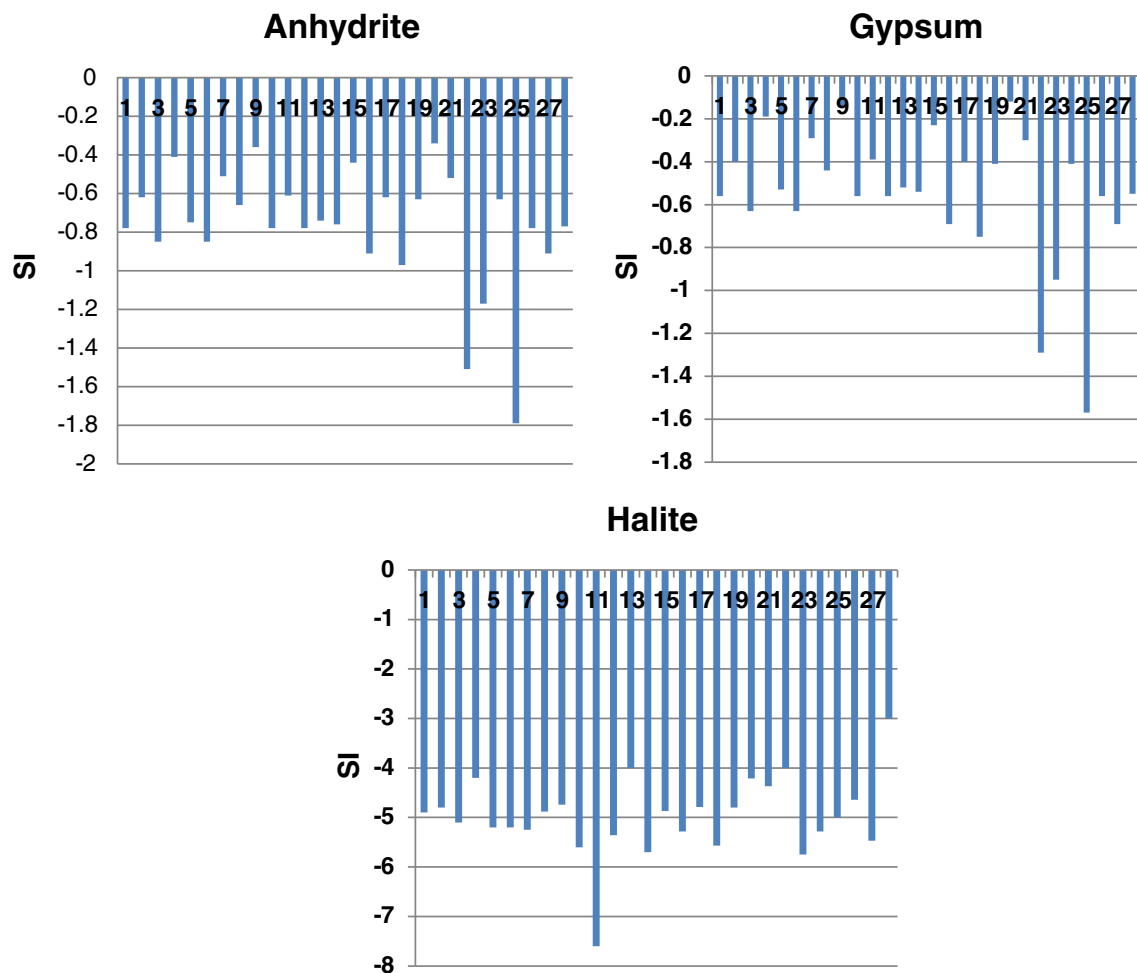

Fig. 7 Diagram depicting the mechanism controlling groundwater quality

Anhydrite

Gypsum

Halite

Fig. 8 The mineral saturation indices (SI) of studied water samples

greatly increases the concentrations of ions formed by chemical weathering, leading to higher salinity. The moving of groundwater sampling points in the Gibbs field towards the evaporation domain from the rock domain suggests an increase of Na^+ and Cl^- ions and consequent higher TDS due to water contamination, caused by the influences of poor sanitary conditions, agricultural fertilizers, and irrigation-return flows (Subba Rao 2006; Kumar et al. 2014).

Geochemical modelling

The SI is the parameter most commonly used for groundwater. Water is in equilibrium with a mineral when the SI of this mineral is equal to zero. It is undersaturated if this index is below zero and it is oversaturated when the SI is above zero. However, in order to allow for measurement inaccuracies and changes in the water composition as it makes its way towards the surface, it is recommended to consider a wider area for SI, such as $-1 < SI < +1$ (Daoud 1995).

Figure 8 shows the mineral SIs of water calculated by PHREEQC model (Alexakis 2011). The minerals considered in

the model were; anhydrite ($CaSO_4$), gypsum ($CaSO_4:2H_2O$), and halite (NaCl). The use of the SI showed that almost all studied waters are undersaturated with respect to halite and saturated with respect to anhydrite and gypsum, with exception of samples 22, 23, and 25 which were undersaturated for anhydrite and gypsum. Consequently, the halite minerals tend to dissolve (Alexakis 2011; Aly et al. 2011). Therefore, there is a possibility for further Na^+ and Cl^- concentration increase in all studied water samples due to the dissolution of halite and possibility for further Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-} and Cl^- concentration increase in samples 22, 23, and 25 due to the dissolution of anhydrite and gypsum. Consequently, continuous treatment and desalination of groundwater used for drinking in the study area is recommended; especially, with the expectation of groundwater salinity increases.

Conclusions

In the present study, WQI has been computed to assess the suitability of untreated and treated groundwater for drinking

water purposes in Hafar Albatin, Kingdom of Saudi Arabia. The result shows that approximately half of the untreated groundwater samples fall in class V "water unsuitable for drinking", the remaining waters fall in class (III) "poor water" or class (IV) "very poor water".

The high value of the WQI at this study area is mainly due to the high values of pH, TDS, Mg^{2-}, HCO_3^-, Cl^-, NO_3^-, B, and total hardness in the groundwater. Almost, two thirds of the treaded groundwater samples fall in class (II) "good water" with the remaining falling in class (III) "poor water". The reason of the high value of WQI of the treated groundwater is due to high values of NO_3^- concentration. Most studied untreated groundwaters were considered unsuitable for irrigation due to salinity hazards; however, no sodicity hazards anticipated. Gibbs's diagram suggests an increase of Na^+ and Cl^- ions and consequent higher TDS due to water contamination, caused by the influences of poor sanitary conditions, agricultural fertilizers, and irrigation-return. The hydrochemical analysis shows that the studied water samples corresponded mainly to sodium chloride–sulfate and calcium sulfate–chloride water types which are mainly due to the geology of the study area comprising halite, gypsum, and anhydrite. The geochemical modeling shows that almost all water samples were undersaturated with respect to halite and saturated with respect to anhydrite and gypsum; however, only three samples were undersaturated for anhydrite and gypsum. Consequently, the halite minerals tend to dissolve; therefore, there is a possibility for further groundwater salinity increase. The study recommends adoption of continuous and more efficient treatment and desalination of groundwater used for drinking in the study area; especially, with expectation of groundwater salinity increases and high groundwater nitrate contamination.

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