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Reverse ion exchange as a major process controlling the groundwater chemistry in an arid environment: a case study from northwestern Saudi Arabia

Faisal K. Zaidi · Yousef Nazzal · Muhammad Kamran Jafri · Muhammad Naeem · Izrar Ahmed

Abstract Assessment of groundwater quality is of utmost significance in arid regions like Saudi Arabia where the lack of present-day recharge and high evaporation rates coupled with increasing groundwater withdrawal may restrict its usage for domestic or agricultural purposes. In the present study, groundwater samples collected from agricultural farms in Hail (15 samples), Al Jawf (15 samples), and Tabuk (30 samples) regions were analyzed for their major ion concentration. The objective of the study was to determine the groundwater facies, the main hydrochemical process governing the groundwater chemistry, the saturation index with respect to the principal mineral phases, and the suitability of the groundwater for irrigational use. The groundwater samples fall within the Ca–Cl type, mixed Ca–Mg–Cl type, and Na–Cl type. Evaporation and reverse ion exchange appear to be the major processes controlling the groundwater chemistry though reverse ion exchange process is the more dominating factor. The various ionic relationships confirmed the reverse ion exchange process where the Ca and Mg in the aquifer matrix have been replaced by Na at favorable exchange sites. This phenomenon has accounted for the dominance of Ca and Mg ions over Na ion at all the sites. The process of reverse ion exchange was further substantiated by the use of modified Piper diagram (Chadha's classification) and the chloro-alkaline indices. Evaporation as a result of extreme aridity has resulted in the groundwater being oversaturated with aragonite/calcite and dolomite as revealed by the saturation indices. The groundwater samples were classified as safe (less than 10) in terms of sodium adsorption ratio (SAR) values, good (less than 1.25) in terms of residual sodium carbonate (RSC) values, and safe to moderate (between 0 and 3) in terms of Mg hazard for irrigation purposes. Though the high salinity groundwater in the three regions coupled with low SAR values are good for the soil structure, it can have a negative impact on the crop production by adversely affecting the crop physiology. Cultivation of high-salinity-resistant varieties of crops is recommended for maximum agricultural productivity.

Keywords Arid regions · Northwestern Saudi Arabia · Evaporation · Reverse ion exchange · Salinity

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Introduction

Despite the extremely arid conditions, Saudi Arabia has considerable groundwater reserves stored in its deep-

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seated sedimentary aquifers, thanks to its geological history. The Arabian platform comprising sedimentary formations ranging from the Cambrian to Neogene period, having an estimated thickness of 5500 m, hosts the major principal and secondary aquifers of the country (Powers et al. 1966). With an estimated water use of 21 billion cubic meters in 2012 and only 3 million cubic meters of annual rainfall recharge, the groundwater stored in these aquifers essentially can be regarded as non-renewable (MOWE 2014). Irrigation water supplies take the maximum share of the available groundwater reserves to an extent that the agricultural water consumption in the country is about ten times the available renewable water resources (FAO 2009). The ratio of the total water demand to the total area of the aquifer which is a means for assessing the water stress in a given region is believed to be the highest for Saudi Arabia (Gleeson et al. 2012a). Decline in groundwater levels due to over-exploitation and deterioration of groundwater quality due to unscientific practices restrict the amount of groundwater available for use, thereby further increasing the water stress.

Rock–water interaction, evaporation/crystallization and dilution due to precipitation are the major natural processes which control the groundwater chemistry of an area (Corteel et al. 2005; Zaidi et al. 2015; Loni et al. 2014). In arid regions, low rainfall and high evaporation rates result in negligible recharge (Qin et al. 2011) often leading to groundwater salinization (Umar and Absar 2003). In recent times, groundwater chemistry has been significantly altered by anthropogenic influences such as application of fertilizers on agricultural lands (Lockhart et al. 2013), changes in land use/land cover (Lavoie et al. 2015), waste water disposal (McArthur et al. 2012), and excessive pumping (Askri 2015).

Evaluation of the processes governing the groundwater quality has been studied extensively all across the globe (Jiang et al. 2009; Mondal et al. 2010; Selle et al. 2013; Yu et al. 2013; Zaidi et al. 2015) and plays a significant role in sustainable groundwater management practices (Rao and Mamatha 2004; Gleeson et al. 2012b).

The present study focuses on the hydrochemical analyses to ascertain the major processes governing the overall groundwater chemistry in three regions falling within the extent of the Saq aquifer, namely Hail, Al Jawf, and Tabuk and its suitability for agricultural purposes. These are important agricultural regions of the country known mainly for the production of cereals (wheat), vegetables (tomatoes, potatoes and onions), fodder (Alfalfa), and fruits (Alzahrani et al. 2012).

The Cambrian-Ordovician Saq aquifer comprising mainly of medium- to coarse-grained sandstone is the major aquifer present in northwestern Saudi Arabia and has been exploited extensively for agricultural water demands and is home to four major agricultural companies of the kingdom, namely the Tabuk Agricultural Development Company (TADCO), Al Jawf Agricultural Development Company, Hail Agricultural Development Company (HADCO), and Qassim Agricultural Development Company (GACO) (Eljelly 2004). Saq aquifer has been the subject of many scientific studies both from the quantitative and qualitative aspects (Sharaf and Hussein 1996; Al-Aswad and Al-Bassam 1997; MoWE 2008; Al-Ahmadi 2009; Al-Salamah et al. 2011; Nazzal et al. 2014; Ahmed et al. 2015).

Study area description

Physiography and climate

The present study encompasses parts of the provincial boundaries of Hail, Al Jawf, and Tabuk regions (Fig. 1). The Hail region lies between approximately 40° E to 42° 30″ E and 26° 50″ N to 28° 33″ N. This is a predominately flat region having no drainage network with general slope towards the South-East. The northern part of the Hail region is covered by great Nafud Sand, while the southern part is characterized by rugged rocks of variable origin. The Al Jawf region lies to the north of the Tabuk and Hail regions, lying between approximately 38° E to 42° E and 28° 20″ N to 31° 50″ N. The region is characterized by a low relief with a mean average elevation of 700 m above mean sea level (amsl). The Tabuk region lies approximately between 36° E to 40°E and 26° 50″ N to 28° 58″ N. Physiographically, this region has significant drainage network draining to the South East. The maximum elevation is approximately 1500 m amsl along its northwestern periphery.

The Hail region experiences a continental desert type of climate with hot summers and cool winters with temperature ranging from a high of 45 to 27 °C and a low of 23 to 3 °C (Almazroui 2011). The average annual rainfall values have been calculated for the period between 1985 and 2010 from the rainfall data available from the Ministry of Water and Electricity, Saudi
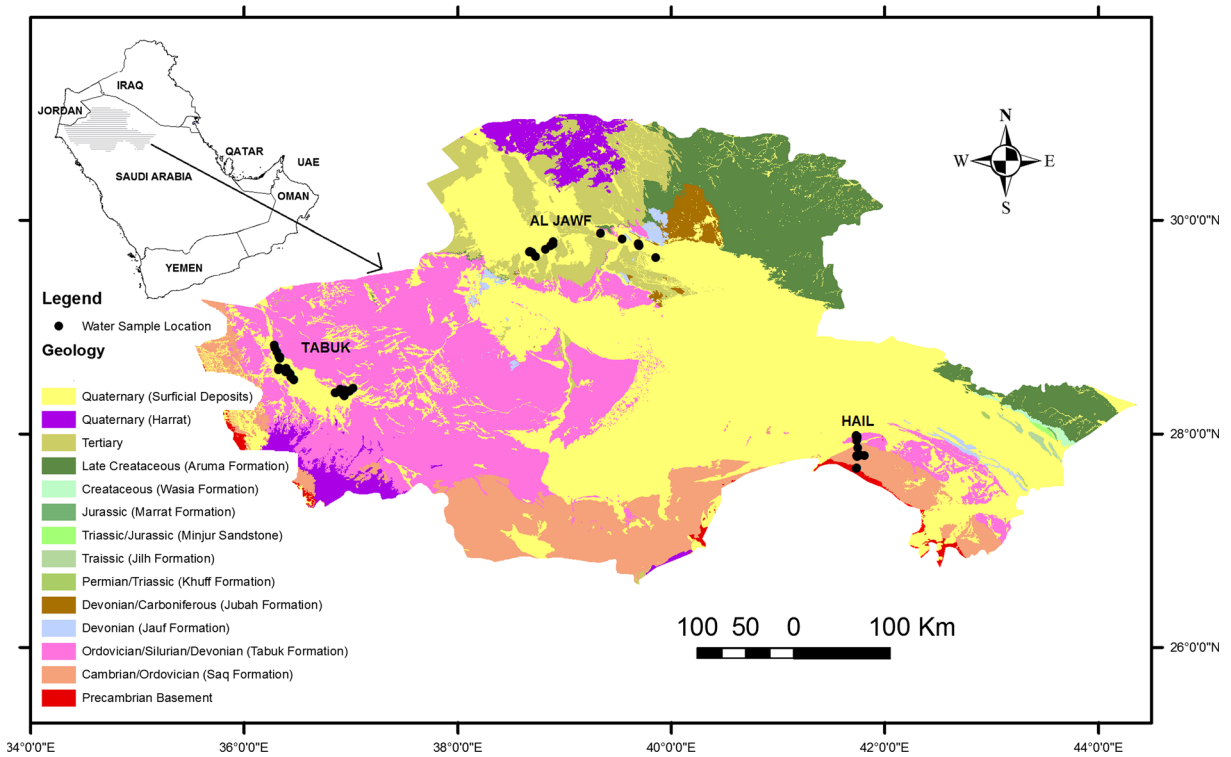
Fig. 1 Location and geological map of the study area (*black dots* represent the locations of the collected groundwater samples)

Arabia. The average annual rainfall in the Hail region ranges from 100 to 120 mm with negligible or no rainfall in the month of June, July, August, and September. Annual evaporation rates at the central part of Saudi Arabia, including Hail, approach 3480 mm (Edgell 2006). Al Jawf province falls in dry, arid to extremely arid region. The mean annual temperature is about 23 °C, with summer temperatures reaching more than 40 °C and winter temperature falling up to 9 °C during January and February. The annual mean precipitation is about 60 to 70 mm. The climate in the Tabuk area is of the continental type but is influenced occasionally by its proximity to the Mediterranean Sea (Şen 1983). The maximum and minimum temperatures are about 47 °C in summer and −2 °C in winter (Alsharhan et al. 2001). The average annual rainfall ranges between 50 to 100 mm.

Geology and hydrogeology

The Arabian Peninsula can be divided into two main geologic units, a western part comprising Precambrian basement rocks known as the Arabian shield and an eastern part consisting of gradually thickening Phanerozoic sedimentary sequence from west to east known as the Arabian Platform (Şeber and Mitchell 1992; Rodgers et al. 1999). The western boundary of the area (Fig. 1) is marked by the contact between the Precambrian basement and the overlying sedimentary rocks of the Arabian Shelf. The Precambrian basement rock comprises felsic and intermediate igneous and metamorphic rocks. The sedimentary sequence comprises mainly of sandstone and limestone that are exposed in a great curved belt along the eastern margin of the shield.

The Cambrian-Ordovician Saq Sandstone is found at the base of the sedimentary sequence. Moving away from the contact with the basement towards the east, the overlying formations appear one after the other in chronological order (Powers et al. 1966). Table 1 shows the generalized geological succession of the study area.

The study area is represented by a typical multilayered aquifer system with the Saq formation being the most prolific source of large-scale water supply, though it is not the only aquifer which is exploited in the region. Depending upon the thickness, hydraulic characteristics, water quality, and aquifer type (confined or unconfined), other aquifer units exposed in the area are also exploited.

Table 1 Stratigraphic succession of the study area (after Laboun 2013; Al-Dabbagh 2013)

Age	Formation	Generalized geology	Average thickness (m)
Cenozoic			
Quaternary	Quaternary Eolian deposits	Calcareous, silty sandstone, sandy limestone; local chert	100–150
Quaternary	Harrats	Basaltic lava flows	<560
Tertiary	Tertiary deposits	Marl, shale, and limestones	
Mesozoic			
Upper Cretaceous	Aruma	Limestone; subordinate dolomite and shale	150–165
Upper Cretaceous	Wasia	Sandstone; subordinate shale	42–125
Lower Jurassic	Marrat	Shale and aphanitic limestone; subordinate sandstone	111
Upper Triassic	Minjur	Sandstone, aphanitic limestone, and shale; subordinate gypsum	315
Middle/Upper Triassic	Jilh	Sandstone, aphanitic limestone, and shale; subordinate gypsum	307
Lower Triassic	Sudair	Red and green shale	116
Palaeozoic			
Upper Permian	Khuff	Limestone and shale	170
Upper Devonian	Jubah	Sandstone	300–410
Devonian	Jauf	Limestone, shale, and sandstone	270–280
Ordovician/Silurian/Devonian	Tabuk	Sandstone and shale	140–160
Cambrian/Ordovician	Saq	Sandstone	400–930
Precambrian	Basement	Felsic and intermediate igneous and metamorphic rocks	

Individual farmers are able to satisfy their water demands for small-scale agricultural activities by drilling wells ranging from 100 to 150 m in depth tapping geological formations which act as local aquifers. Most of the aquifers are exploited in parts where they occur in the unconfined conditions. The main hydrogeological units in the present study as inferred from the geological mapping, well lithologs, and aquifer tests can be classified into five aquifers or aquifer groups and one aquitard (MoWE 2008). From bottom to top they include:

• Saq sandstone
• Sarah sandstones (Tabuk formation)
• Jubah sandstone
• Khuff limestone
• Secondary (Mesozoic)-Tertiary-Quaternary (STQ) sandstone and limestone

The Jauf limestone and sandstone which lies between the Tabuk and Jubah formations act regionally as an aquitard but contain units that are locally exploited as aquifer. The Cambro-Ordovician Saq formation comprising mainly of medium to coarse sandstones and ranging in thickness from 400 to 928 m forms the major aquifer system in Northern Saudi Arabia (Alsharhan et al. 2001) and covers the entire study area.

Figure 2 shows the piezometric contours for the region. The water levels were obtained from bore wells (mostly unconfined condition) used for irrigation purposes. The piezometric levels range from 950 to 200 m above mean sea level with a general groundwater flow direction from the south-west to north-east.

Methodology

A total of 60 groundwater samples from bore wells (15 each from Hail and Al Jawf and 30 from Tabuk) were collected from agricultural farms in the study area (Fig. 1). Unstable parameters such as hydrogen ion concentration (pH), total dissolved solids (TDS), and electrical conductivity (EC) were determined at the sampling sites with the help of a pH meter, a portable
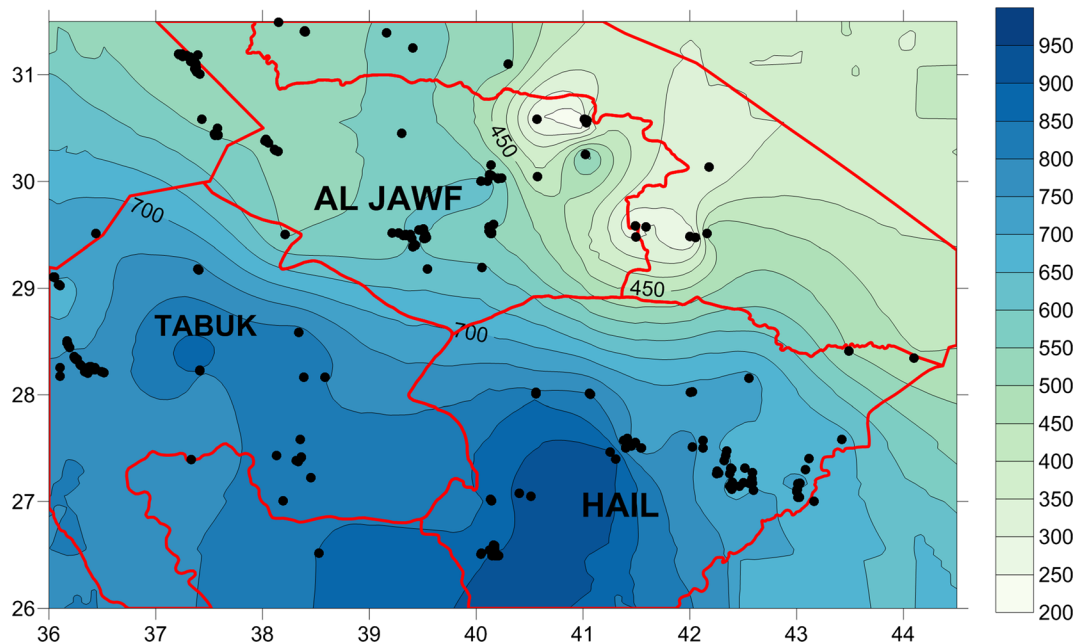
Fig. 2 Piezometric map of the area. *Black dots* represent the piezometers. Values are in meters above mean sea level

EC meter, and a TDS meter (Hanna Instruments, Michigan, USA). The samples were collected in poly-ethylene bottles of 1-l capacity by pumping the bore wells. Care was taken to pump the bore wells for suffi-cient time to get rid of the water in the well bore storage, before collecting the samples. Prior to their filling with sampled water, these bottles were rinsed to minimize the chance of any contamination. The sampling bottles were acidified with reagent-grade nitric acid to prevent the precipitation of carbonates till they were transferred to the laboratory. In the laboratory, the samples were fil-tered through 0.45 μm pore diameter fiber glass filters to remove the suspended particles. The sampling, preser-vation, and analytical techniques were in accordance with the standard methods from American Public Health Association (APHA 2005). The sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) ions were determined by atomic absorption spectropho-tometer (AAS). Bicarbonate (HCO_3^-) and chloride (Cl^-) were analyzed by volumetric methods. Sulfate (SO_4^{2-}) was estimated by the colorimetric method. Nitrate (NO_3^-) was measured by ionic chromatography. Fluoride was determined potentiometrically using an ion-selective electrode. The accuracy of the chemical analyses was verified using the charge balance error. All the analyzed samples in the present case had a charge balance error of less than 5 %; therefore, no samples were discarded for the hydrochemical interpretation.

Groundwater facies classification and major process-es governing the overall groundwater chemistry of the region was discussed using bivariate plots, Piper's plot, and modified Piper's plot. Chloro-alkaline indices were also calculated to understand the base ion exchange reactions. For the speciation analyses, the saturation indices of the principal mineral phases were calculated using the speciation code PHREEQC 2.8. The impact of the groundwater on the soil structure and plant growth was assessed using the sodium adsorption ratio (SAR) versus EC plots. Other factors like residual sodium car-bonate and magnesium hazard were also assessed to check the suitability of the groundwater for irrigation purpose. Surfer 9.0, Aquachem 4.0, ArcGIS 10.1, and Microsoft Excel 2010 were the main software used for preparing the various maps and plots in the present work.

Results and discussion

General chemistry

The minimum, maximum, mean, and standard deviation for the measured physiochemical parameters for the Hail, Al Jawf, and Tabuk regions are shown in Table 2. The waters are very mildly alkaline with mean values of 7.5, 7.6, and 7.3 for Hail, Al Jawf, and Tabuk, respectively. EC values are very high (mean, 3351.3 μS/

Table 2 Summary statistics of groundwater quality parameters

Parameters	Minimum			Maximum			Mean			Standard Deviation		
Area	Hail	Al Jawf	Tabuk	Hail	Al Jawf	Tabuk	Hail	Al Jawf	Tabuk	Hail	Al Jawf	Tabuk
pH	7.6	7.8	7.7	7.3	7.3	7.0	7.5	7.6	7.3	0.1	0.1	0.2
EC (µS/cm)	10330.0	4350.0	6870.0	773.0	349.0	434.0	3351.3	1161.7	1752.9	3110.5	1100.0	1571.6
TDS (mg/l)	3970.4	1371.0	3678.0	1074.2	373.1	523.0	1767.7	852.7	1205.0	1041.7	320.1	702.6
Ca (mg/l)	874.0	211.0	680.0	156.0	26.0	32.0	327.9	94.3	147.0	258.3	68.1	147.7
Na (mg/l)	310.0	143.0	255.0	106.0	66.0	82.0	154.0	107.6	142.0	71.2	26.3	37.2
K (mg/l)	20.0	16.0	19.0	9.0	7.0	7.0	13.4	11.1	11.0	3.3	2.3	2.9
Mg (mg/l)	102.0	68.0	196.0	44.0	12.0	24.0	63.5	45.4	65.7	16.8	14.1	41.8
HCO3 (mg/l)	305.0	244.0	268.0	61.0	49.0	52.0	176.7	108.8	124.6	77.8	71.5	71.2
Cl (mg/l)	1442.0	450.0	1282.0	305.0	95.0	122.0	572.0	223.1	384.5	413.6	114.1	280.3
SO4 (mg/l)	922.0	336.0	960.0	240.0	98.0	144.0	434.8	243.7	307.8	225.9	69.7	168.8
NO3(mg/l)	34.0	28.0	34.0	16.0	5.0	9.0	23.8	17.2	20.7	4.4	6.9	5.5
F (mg/l)	2.1	2.0	2.1	1.1	1.1	1.0	1.6	1.7	1.7	0.3	0.3	0.3

cm) for Hail followed by Tabuk (mean, 1752.9 µS/cm), and Al Jawf (mean, 1161.7 µS/cm). The large variation in EC is probably due to the geochemical evolution of water in an evaporation-dominant environment. The TDS values were calculated after adding up all the major ions. Samples from Hail show the highest mean TDS values (1767.7 mg/l) followed by Tabuk (1205 mg/l) and Al Jawf (852.7 mg/l).

Groundwater samples from Hail and Tabuk show similar distribution of major ions ($Ca^{2+} > Na^+ > Mg^{2+} > K^+$ and $Cl^- > SO_4^{2-} > HCO_3^- > NO_3^-$); whereas, ionic abundance for Al Jawf is as follows: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $SO_4^{2-} > Cl^- > HCO_3^- > NO_3^-$.

Nitrate (NO_3^-) values fall within the maximum permissible limit of 50 mg/l in all the samples with average values of 23.8, 17.2, and 20.7 mg/l for Hail, Al Jawf, and Tabuk, respectively. Elevated concentration of nitrate in groundwater can be a consequence of agricultural activity (excess application of inorganic nitrogenous fertilizers and manures), wastewater disposal, and waste products in human and animal excreta, including septic tanks (Böhlke 2002; WHO 2011). Since all the groundwater samples in the present study were collected from agricultural farms, their presence in groundwater can be attributed mainly to the agriculture activities. Fluoride (F^-) is a minor constituent in groundwater and is essential for the teeth and bones. Average F concentrations for Hail, Al Jawf, and Tabuk are 1.6, 1.7, and 1.7 mg/l, which are higher than the maximum permissible limit of 1.5 mg/l (WHO 2011). Concentrations in excess of

1.5 mg/l can have adverse impact on human health, including dental and skeletal fluorosis and renal disorders (Ayoob and Gupta 2006). Arid regions with high evaporation rates often have high concentrations of fluoride (Gao et al. 2007; Deng et al. 2009; Naseem et al. 2010). Rock-water interaction with fluoride-bearing mineral is believed to be the main source of F concentration in groundwater (Weinstein and Davison 2004; Salifu et al. 2012; He et al. 2013). Agricultural activities such as application of phosphatic fertilizers also lead to elevated concentration of F in groundwater (Saxena and Ahmed 2003). In the present study, the origin of fluoride in groundwater can be mainly attributed to geogenic sources rather than anthropogenic sources as no correlation between nitrate and fluoride values for the collected samples were observed. However, to ascertain the exact origin of fluoride, more detailed studies related to rock-water interaction and changes in fluoride concentrations with depths are required.

Hydrochemical classification

The groundwater facies classification was carried out using the Piper diagram (Fig. 3a). The samples from Hail fall on the Ca-dominant type and no-dominant type on the cationic triangle; whereas, samples from Al Jawf and Tabuk fall within the Ca-dominant, no-dominant, and Na+K-dominant types. On the anionic triangle, the samples from Hail fall within the no-dominant and Cl-dominant classes; whereas, samples from Al Jawf and Tabuk fall within the SO4-dominant, no-dominant, and
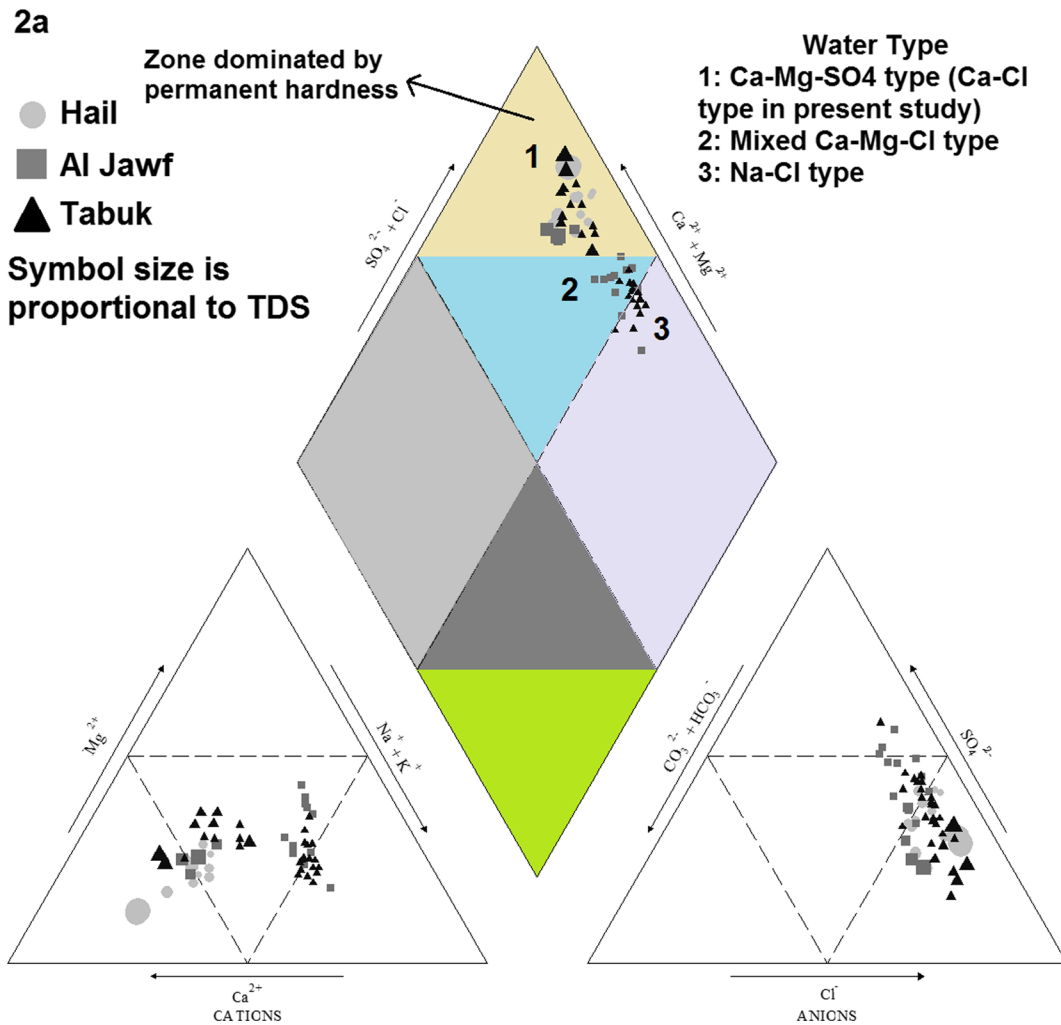
Fig. 3 Piper plot for groundwater facies classification

Cl-dominant classes. The samples can be grouped into three major groundwater facies based on their position on the diamond-shaped field of Piper's plot. All the samples from Hail, five samples from Al Jawf, and thirteen samples from Tabuk fall in the zone dominated by permanent hardness and belong to the Ca–Cl groundwater type (type 1). Such water types can be formed due to reverse ion exchange reactions. Typically, these waters are also characterized by very high TDS owing to the high concentration of Ca and Cl. The second group consisting of mixed Ca–Mg–Cl type (type 2) consists of nine water samples from Al Jawf and seven samples from the Tabuk region. They represent the evolved water type. Their meteoric signature has been lost due rock-water interaction and ion exchange reactions. The type 3 groundwater facies represented by one sample

from Al Jawf and ten samples from the Tabuk region belong to the Na–Cl type and are indicative of evaporation processes controlling the groundwater chemistry. The various factors which govern the overall water chemistry of the three areas have been explored further by studying the ionic relationships between the collected groundwater samples and have been described in the following paragraphs.

The plot of Na/Cl versus EC shows the influence of evaporation on the overall groundwater chemistry of the area (Fisher and Mullican 1997). The Na/Cl ratio represented by a horizontal line on the Na/Cl versus EC plot indicates a constant Na/Cl ratio with the increasing salinity. In the present study, all the samples from Hail, Al Jawf, and Tabuk (Fig. 4a) shows a decreasing Na/Cl ratio with the increasing salinity. There are two possible
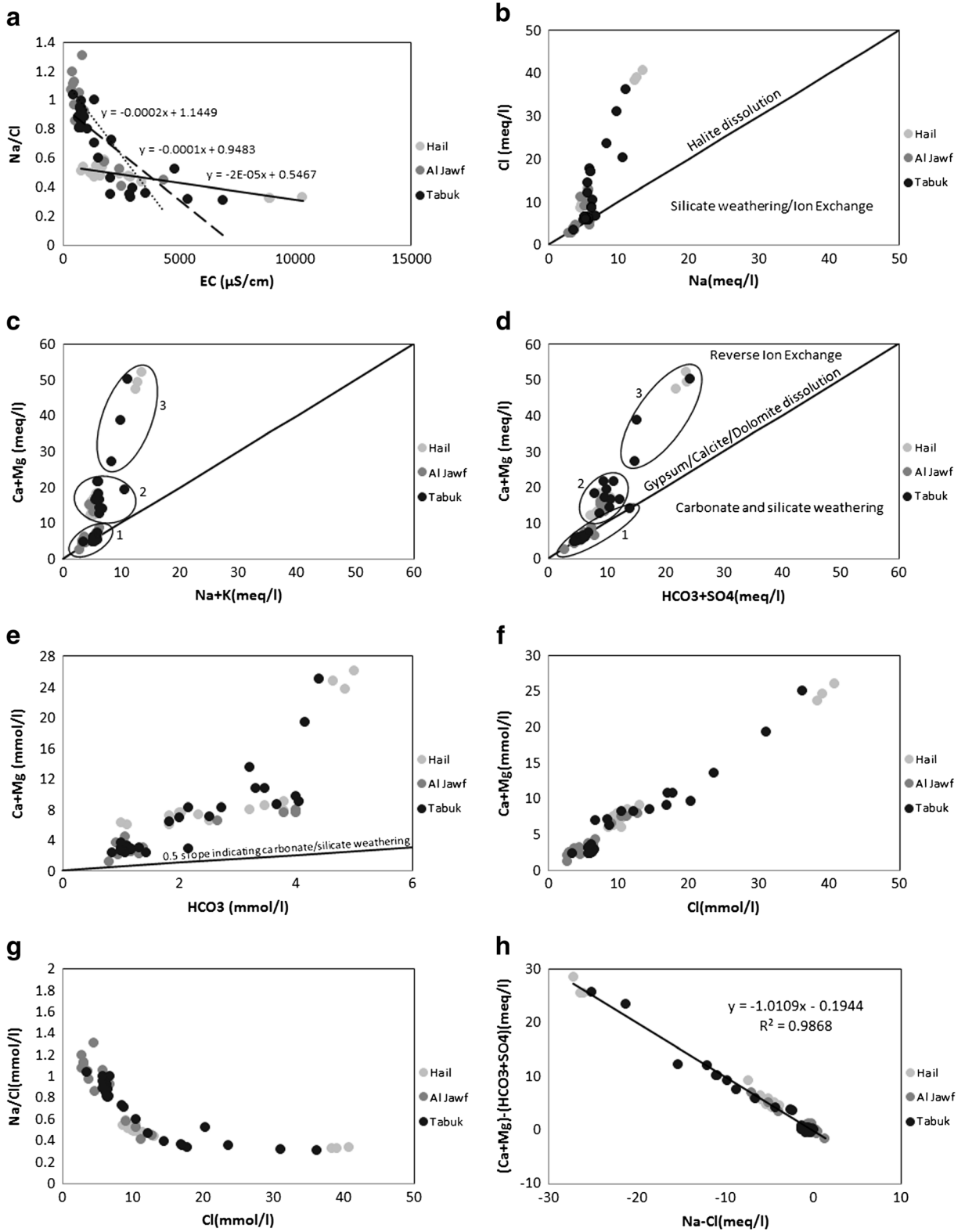
◀ **Fig. 4** Ionic relationships: **a** Na/Cl versus EC; **b** Cl versus Na; **c** Ca+Mg versus Na+K; **d** Ca+Mg versus HCO₃+SO₄; **e** Ca+Mg versus HCO₃; **f** Ca+Mg versus Cl; **g** Na/Cl versus Cl; **h** (Ca+Mg)–(HCO₃−SO₄) versus Na–Cl. Units for the ionic concentrations have been mentioned in each figure

explanations for the decreasing Na/Cl ratio in this study. The Cl enrichment can be attributed to atmospheric deposition or possible mixing of connate sea water (Biswas et al. 2012). Atmospheric deposition of Cl will be balanced by a corresponding increase in Na; however, Fig. 4b shows the dominance of Cl over Na and rules out this possibility. The water samples have been collected from relatively shallow depths (100–150 m); therefore, the possibility of Cl enrichment from connate sea water can also be ruled out. It can either be due to Cl enrichment or due to the removal of Na from groundwater. The Cl enrichment can be attributed to anthropogenic sources such as irrigation return flows or domestic waste disposal (Jacks et al. 1999; Srinivasamoorthy et al. 2008). Isotopic studies may provide an idea about the enrichment of Cl from anthropogenic sources. However, in the present study, it appears that the decreasing Na/Cl ratio with increasing salinity is mainly a result of Na depletion due to reverse ion exchange. The phenomenon of reverse ion exchange in the study area is also evident from the various ionic plots, modified piper diagram, and the chloro-alkaline indices.

The Cl versus Na plot (Fig. 4b) shows that there is an overall dominance of Cl as compared with Na. If halite dissolution is the only source of Na and Cl, the samples should fall along the 1:1 equiline. This phenomenon is exhibited by a few samples from Al Jawf and Tabuk, indicating halite dissolution as the main source of Na and Cl. Na/Cl ratio greater than 1 is an indication of silicate weathering (Mayback 1987), but in the present study, there is an overall dominance of Cl. The depletion of Na ions can be attributed to reverse ion exchange.

Ca+Mg versus Na+K plot reveals that overall alkaline earth elements dominate over alkali; however, three groups can be identified (Fig. 4c). The first group consisting of groundwater samples from Al Jawf and Tabuk area shows equal amounts of Ca+Mg and Na+ K. The second group is characterized by the slight abundance of alkaline earth elements over alkalis and is represented by water samples from Hail, Al Jawf, and Tabuk. The third group is characterized by the excess of alkaline earth elements and is represented by samples from the Hail and Tabuk regions. The high

concentrations of Ca and Mg as compared with Na and K can be attributed to base ion exchanges where the Na present in groundwater is replaced by Ca and Mg at favorable exchange sights (Jankowski and Acworth 1997).

The Ca+Mg versus HCO₃+SO₄ plot (Fig. 4d) can also be divided into three groups. Samples from Al Jawf and Tabuk fall along the 1:1 equiline showing the dissolution of gypsum, calcite, and dolomite (Fisher and Mullican 1997). The second group is represented by samples from all the three regions showing slight dominance of Ca+Mg over HCO₃+SO₄, and the third group is represented by samples from Hail and a few samples from Tabuk showing a marked increase in the concentration of Ca+Mg. The high concentration of Ca+Mg relative to SO₄+HCO₃ can be a result of reverse ion exchange (Rajmohan and Elango 2004). The source of Ca and Mg in groundwater can also be determined from m(Ca+Mg)/HCO₃ ratio. If the only source of Ca and Mg in groundwater is carbonate weathering or the weathering of silicate minerals such as pyroxenes and amphiboles, the ratio of m(Ca+Mg)/HCO₃ should be close to 0.5 (Sami 1992). A ratio of less than 0.5 could be a result of depletion of Ca and Mg relative to HCO₃ due to ion exchange or enrichment of HCO₃. In the present study, however, all the samples fall well above the 0.5 slope (Fig. 4e). The high ratios cannot be attributed to the depletion of HCO₃ as carbonic acid is not formed under alkaline conditions (Spears 1986). Therefore, the only explanation for the high ratio is the reverse ion exchange process. A lower than 1 ratio of Ca+Mg/HCO₃ is also suggestive of fresh recharge or the meteoric nature of groundwater (Nazzal et al. 2014). In the present study, all samples have a very high Ca+Mg/ HCO₃ ratio (ranging from 2.66 to 12.39) thus showing the absence of fresh groundwater recharge in the investigated area.

Assuming that all Cl in the groundwater system has been derived from halite dissolution, the increase in Cl concentration will correspond to an increase in salinity. The relationship between Ca+Mg versus salinity (Cl) and Na versus salinity can provide information about the interaction between Ca, Mg, and Na in the groundwater system (Sami 1992). The plot of m(Ca+Mg) versus m(Cl) indicates that the Ca+Mg increases with the increasing salinity (Fig. 4f) whereas m(Na/Cl) ratio decreases with the increase in salinity (Fig. 4g). This can be explained by the fact that dissolved Na in the groundwater (derived from halite dissolution) is exchanged by

the bound Ca+Mg in the clays within the aquifer matrix (Rajmohan and Elango 2004).

The plot of (Ca+Mg−SO₄−HCO₃) versus (Na−Cl) shows the cation exchange reactions between Ca, Mg, and Na (Fisher and Mullican 1997). In case of Na, Ca, and Mg participation in the ion exchange process, the relationship between (Ca+Mg−SO₄−HCO₃) versus (Na−Cl) should be a straight line with a slope of −1.0. The plot (Fig. 4h) shows that the samples fall on a straight line with a slope of −1.010, thereby confirming the fact that Na, Ca, and Mg participate in the ion exchange reactions.

The hydro-geochemical diagram (modified Piper diagram) proposed by Chadha (1999) which helps in understanding the major geochemical processes controlling the groundwater chemistry was applied to this study as well. Majority of the samples fall within the field dominated by reverse ion exchange (Fig. 5) and reconfirms the fact that reverse ion exchange is the most dominant process which has resulted in the depletion of Na ions with respect to Ca and Mg ions in the study area. Few samples from Al Jawf and Tabuk fall within the sea water zone and can be attributed to the evaporation processes.

Base ion exchange

The chloro-alkaline indices provide valuable information about the ion exchange reactions between the groundwater and the aquifer material. It was proposed by Schoeller (1977) and has been subsequently used by many workers to identify the base ion exchange processes controlling the groundwater chemistry (Zhu et al. 2007; Aghazadeh and Mogaddam 2011; Toumi et al. 2015) The chloro-alkaline indices (CAI) are calculated using the following formula:

$$CAI\ 1 = [Cl-(Na + K)]/Cl$$

and

$$CAI\ 2 = [Cl-(Na + K)]/(Cl + HCO3 + SO4 + NO3)$$

An exchange between Na and K in the groundwater with Ca and Mg in the aquifer material will result in a positive index indicating reverse ion exchange. On the other hand, an exchange between the Na and K in the aquifer with Ca and Mg in groundwater will result in a negative index indication ion exchange. The average value of CAI 1 and CAI 2 is 0.25 and 0.36, respectively, with 48 samples showing positive and 12 samples showing negative values for both the indices in the analyzed samples. The results of the chloro-alkaline indices also support the fact that reverse ion exchange is the main hydrochemical process controlling the groundwater chemistry in the region. The reverse ion exchange process is more dominant in the Hail and Tabuk regions as compared with Al Jawf (Fig. 6a, b).

Saturation index

The natural groundwater quality is influenced by the presence of different solutes which can be derived from the atmosphere or by the weathering and erosion of rocks and soils (Saleh et al. 1999). Dissolution of mineral species occurs as a result of rock-water interaction. The groundwater is said to be saturated with a given mineral species under equilibrium conditions; however, it may continue to dissolve more minerals which may finally precipitate and the water becomes over saturated with respect to that mineral (Deutsch 1997). Chemical equilibrium for a particular mineral species can be examined by calculating the Saturation Index. It is expressed as

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

where IAP stands for ion activity product and KT stands for solubility constant. If the water is in thermodynamic equilibrium $\log(IAP/KT) = 0$, over saturated $\log(IAP/KT) > 0$ or under saturated $\log(IAP/KT) < 0$ with respect to the solid phases (Truesdell and Jones 1974).

Saturation Indices for the groundwater samples collected from the three regions were carried out using the PHREEQC 2.8 speciation code. Figure 7 shows the saturation indices for the groundwater samples with respect to the different mineral phases. The aquifer is found to be over saturated with respect to aragonite, calcite and dolomite and under saturated with respect to anhydrite, gypsum and fluorite. Evaporation dominant environment often results in precipitation of calcite/aragonite and dolomite (Rajmohan and Elango 2004). The extreme aridity in the region is responsible for the groundwater being oversaturated with aragonite/calcite and dolomite. A closer look at the saturation indices for aragonite, calcite and dolomite in Fig. 7a–c shows that the groundwater in Hail area shows the maximum saturation followed by Tabuk and Al Jawf. One sample each

Fig. 5 Main geochemical processes controlling the groundwater chemistry (modified Piper diagram, after Chadha 1999)
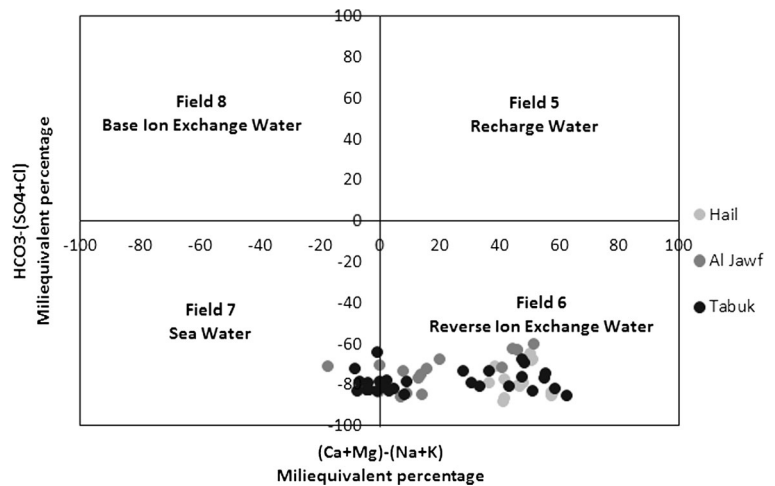

from Hail and Tabuk is slightly oversaturated with respect to Fluorite (Fig. 7f). An alkaline pH is favorable for F dissolution (Saxena and Ahmed 2003).In the present study the pH values ranges between 7.0 and 7.79 and is slightly alkaline however the fluoride concentrations are not high enough to allow saturation.

Suitability for irrigation use

Since the groundwater is mainly used for irrigating the agricultural farms it was necessary to determine the suitability of water for irrigation. The central pivot system is mainly used for irrigating the fields in the region

Fig. 6 Chloro-Alkaline Indices (*CAI*) for the analyzed groundwater samples: **a** CAI 1 and **b** CAI 2
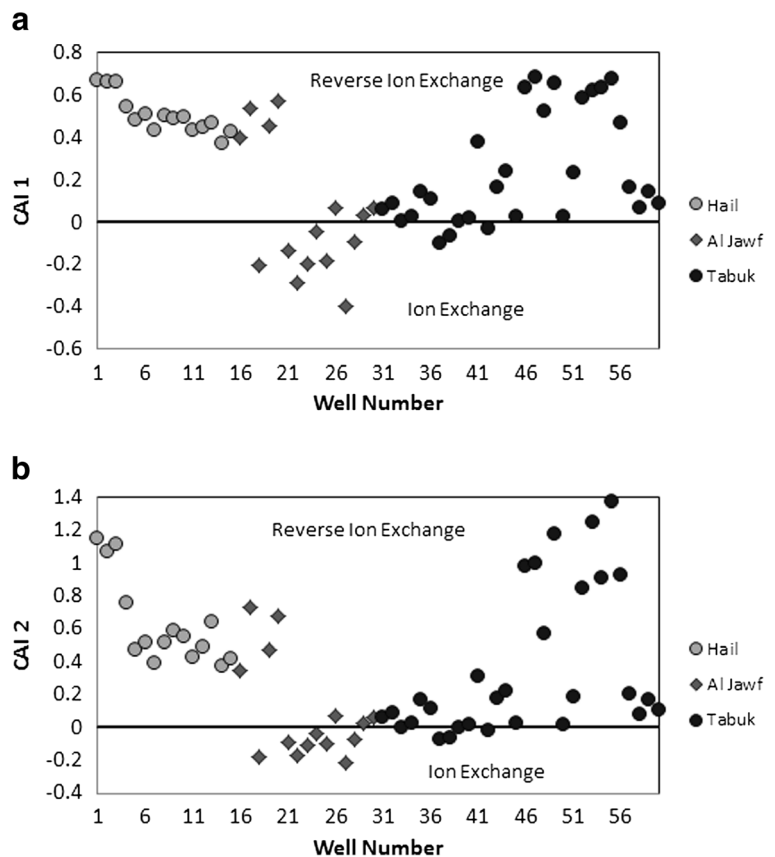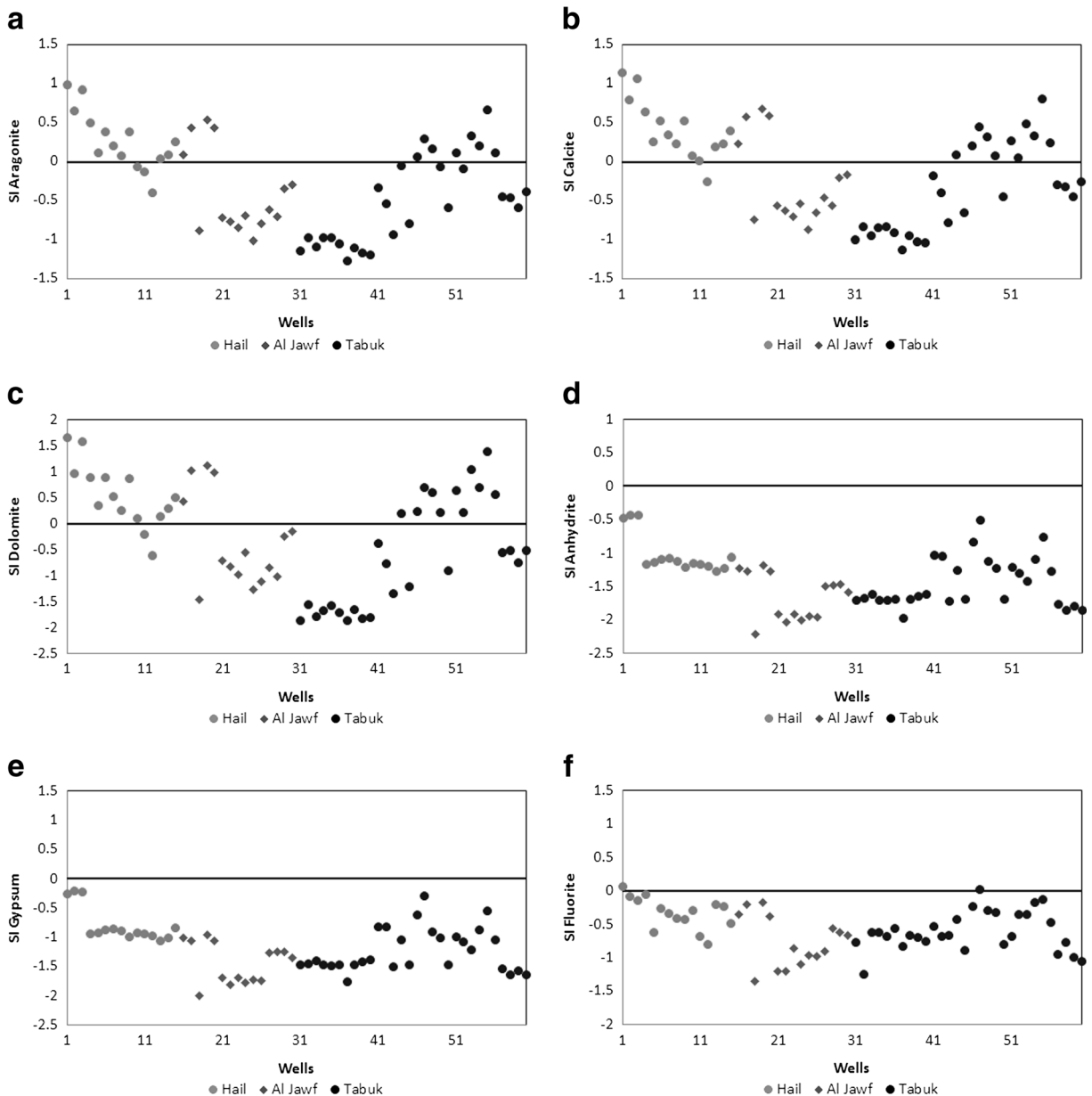
Fig. 7 Saturation indices for the different mineral phases: **a** aragonite, **b** calcite, **c** dolomite, **d** anhydrite, **e** gypsum, and **f** fluorite

(Al-Ghobari 2014). Irrigation water can have adverse impact on plants and crops growth due to physical changes (modification of osmotic process) or chemical changes (changes in metabolic reactions). These changes can be brought about by the presence of high concentrations of a particular salt or due to the presence of toxic constituents in groundwater (Alam 2014). Na is perhaps the most important constituent of groundwater, the abundance of which can impair the groundwater quality for irrigation purposes.

Na exchange in the soil is enhanced by irrigation water high in Na concentration, thereby affecting the soil permeability and texture (Sujatha and Reddy 2003). If the Na percentage exceeds more than 50 % percent of the total cations present in groundwater, it triggers reverse ion exchange reactions, where the Ca and Mg present in the soil is replaced by Na present in the water thereby causing deflocculation and reducing the fertility and permeability of the soils (Karanth 1987). Thus the excess concentration of a particular salt in irrigation

water not only has an adverse impact on plant physiology but also alters the soil properties such as permeability and aeration which in turn restricts the growth of plants (Mohan et al. 2000; Umar et al. 2001).

The criteria generally used for assessing the groundwater quality for irrigation purposes involves the measurement of EC and calculation of parameters such as SAR, residual sodium carbonate (RSC) and magnesium hazard. All these parameters related to irrigation water suitability were assessed in the present study. The outcome of the study can be used as guidelines by the farmers for selecting appropriate management practices for minimizing the risks associated with substandard irrigation water quality.

Sodium adsorption ratio

SAR of irrigation water represents the tendency of the Na ions to be adsorbed at ion exchange sites within the soil matrix at the expense of Ca and Mg and causes the dispersion of soil particles thereby reducing the soil infiltration capacity (Hanson et al. 1999; Wang et al.

Fig. 8 a SAR versus EC plot showing the impact of the sampled groundwater on the soil infiltration rates (after Hanson et al. 1999). b Classification of irrigation waters by USSL (after Richards 1954)
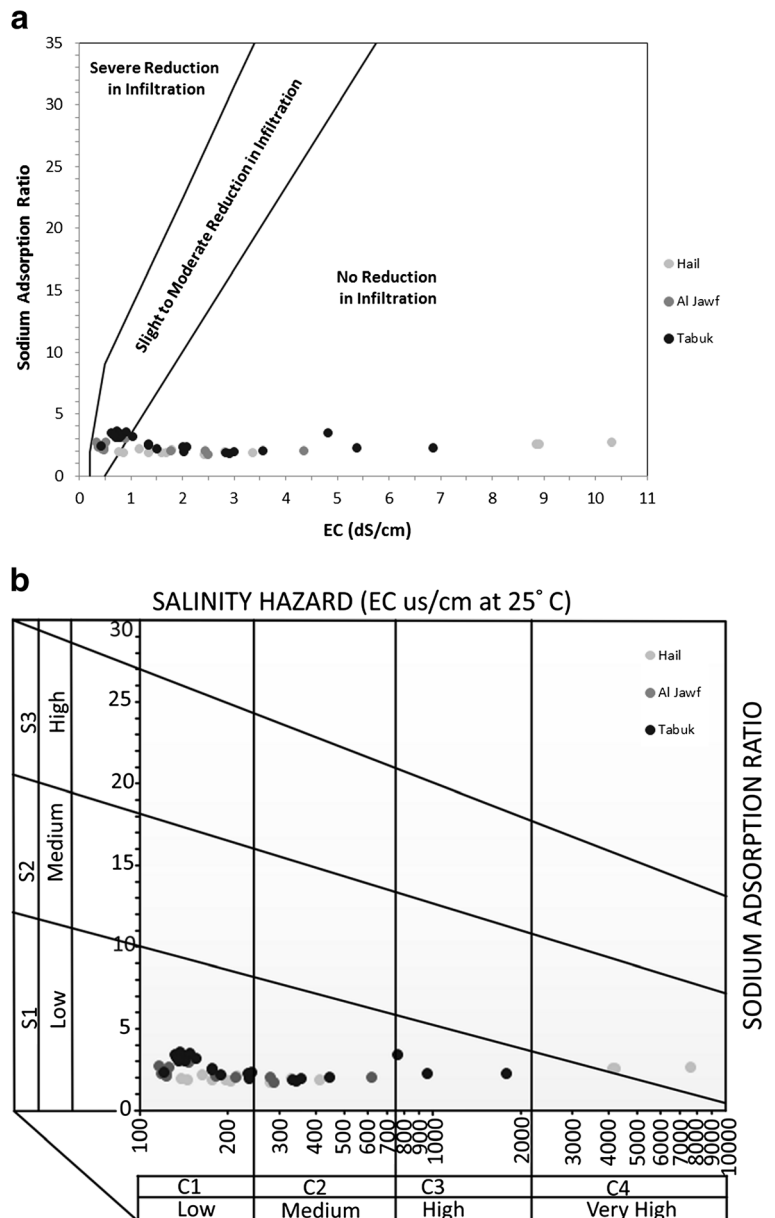
2012). SAR represents the ratio of Na to the ratio of Ca and Mg and is expressed as

$$\frac{Na^+}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}}$$

where all the values are in milliequivalents per liter. However, the reduction in soil permeability brought about by the high SAR values of irrigation water can be counterbalanced by the high salinity values (EC of groundwater).

With similar SAR values, samples with higher salinity are better suited for the soil structure (Hanson et al. 1999). The map of SAR versus EC (Fig. 8a) shows the impact of irrigation water on the soil properties (infiltration rate in the present case). The low SAR values (average of 2.51) and high salinity values (average of 2.004 dS/m) results in the water samples falling in two categories, i.e., slight to moderate reduction in infiltration and no reduction in infiltration in the three regions. Water samples from the Hail region in terms of its impact on the soil structure appears to be the best as only one sample falls within the zone represented by slight to moderate reduction in infiltration capacity.

High salinity on one hand can improve the structure of the soil (increasing infiltration rates but on the other hand can result in water stress condition for crops and plants. The high salt concentration in irrigation water requires plants to exert more energy to extract water from the soil thereby leading to stress conditions. The USSL map (Richards 1954) of SAR versus EC (Fig. 8b) shows the suitability of irrigation water in terms of its effect on plant growth. The groundwater in the present study are classified as low sodium water (S1 class) with SAR values of less than 10 (maximum value is 3.61). In terms of salinity hazard, the water samples fall within the medium salinity class (C2), high salinity class (C3), and very high salinity class (C4). All the samples from Hail fall within the C3-S1 and C4-S1 class except one which falls within the C2-S1 class. Samples from Al Jawf and Tabuk fall within these three classes.

To conclude, the groundwater in the three regions does not have any effect on the soil infiltration properties and does not require any extra effort (such as addition of calcium) to improve the soil property, but the high salinity values can have adverse impact on plant growth. The best option under such conditions would be to grow plants and crops which are high salinity resistant.

Residual sodium carbonate

RSC is expressed

$$(CO_3 + HCO_3) - (Ca + Mg)$$

where all the values are expressed in milliequivalents per liter. RSC indicates the potential of Ca and Mg

Table 3 Classification of groundwater for irrigation use

Parameters	Range	Water class	Samples
Alkalinity hazard (SAR)			
	<10	Excellent	60
	10–18	Good	0
	18–26	Doubtful	0
	>26	Unsuitable	0
Salinity hazard (EC)	<250	Excellent	0
	250–750	Good	16 (8 Al Jawf, 8 Tabuk)
	750–2000	Permissible	24 (8 Hail, 4 Al Jawf, 12 Tabuk)
	2000–3000	Doubtful	10 (3 Hail, 2 Al Jawf, 5 Tabuk)
	>3000	Unsuitable	10 (4 Hail, 1 Al Jawf, 5 Tabuk)
RSC	<1.25	Good	60
	1.25–2.5	Doubtful	–
	>2.5	Unsuitable	–
Residual Mg/Ca ratio	<1.5	Safe	54 (15 Hail,10 Al Jawf, 29 Tabuk)
	1.5–3.0	Moderate	6 (5 Al Jawf, 1 Tabuk)
	>3.0	Unsafe	–

precipitation at the soil surface and its removal from soil solution. Generally, groundwater used for irrigation purposes in arid and semi-arid regions is characterized by high RSC which leads to salinization and sodification of agricultural soils (Prasad et al. 2001). Irrigation water with RSC values of less than 1.25 are considered good for irrigation whereas those having RSC values above 2.5 are not suitable for irrigation purposes. Groundwater rich in carbonates can still be used for irrigation if they have high Ca and Mg concentrations. As shown earlier in the section on hydrochemical classification of groundwater, the groundwater samples from the three regions are characterized by high Ca concentrations and very low bicarbonate concentration, thus all the water sample have RSC values of less than 1.25 (Table 3) and are considered good for irrigation.

Magnesium hazard

Magnesium hazard is expressed as the ratio of Mg to Ca in water where the concentrations are in milliequivalents per liter. Though Ca and Mg are in the state of equilibrium in water, it is not the same in the soil system (Ravikumar et al. 2011). Mg ions affect the soil infiltration properties as they are about 50 % bigger than Ca ions and are not very strongly attracted to the clay particles (Hanson et al. 1999). This causes more water to be adsorbed between the Mg ions and clay particles thereby reducing the overall soil infiltration rates. Based on the Ca/Mg ratio, the irrigation water can be classified as safe (less than 1.5), moderate (1.5–3), and unsafe (greater than 3). Since the water samples from all the three regions were characterized by high Ca concentration, they fall within the safe to moderately safe zone for irrigation. All the groundwater samples from Hail fall within the safe zone whereas samples from Al Jawf and Tabuk fall within the safe and moderately safe zone (Table 3).

Conclusion

Samples from the Hail and Tabuk regions are characterized by the high concentration of Ca (cation) and Cl (anion); whereas, samples from Al Jawf are characterized by the dominance of Na and SO_4. K and HCO_3 are the least-dominant cations and anions in the three regions. Groundwater has been classified as Ca–Cl type, mixed Ca–Mg–Cl type, and Na–Cl type on the Piper

diagram. Evaporation and reverse ion exchange are the two major processes influencing the groundwater chemistry in the present study though reverse ion exchange process is more dominant as shown by Piper's plot, ionic relationships, the modified Piper's plot, chloro-alkaline indices, and saturation indices. The effects of evaporation as well as reverse ion exchange are most pronounced in the samples from Hail. The groundwater samples from the three regions are saturated with respect to aragonite/calcite and dolomite, which is a consequence of the evaporation dominant environment. Average fluoride concentrations in excess of 1.5 mg/l have been found in the groundwater in this study. Though it appears to be from geogenic sources, it requires further investigations to understand the exact nature of its occurrence. Nitrate concentration in the study area is probably due to use of fertilizers on the agriculture farms, but none of the samples showed the presence of nitrate in excess of 50 mg/l. The irrigation water quality assessment shows that the samples from the three regions are characterized by low SAR values (less than 10), moderate to very high salinity values (greater than 750 μS/cm), low RSC values (less than 1.25), and low to moderate Ca/Mg ratio (between 0 and 3). There will be no adverse impact on soil properties due to the use of this water for irrigation purposes as they are characterized by high salinity and low Ca/Mg ratios. The quality of irrigation water does not necessitate the use of additional amendments to improve aeration or soil permeability. However, the high salinity requires plants and crops which are salinity resistant to be grown or cultivated.

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