A pragmatic approach to study the groundwater quality suitability for domestic and agricultural usage, Saq aquifer, northwest of Saudi Arabia

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Abstract The present study deals with detailed hydrochemical assessment of groundwater within the Saq aquifer. The Saq aquifer which extends through the NW part of Saudi Arabia is one of the major sources of groundwater supply. Groundwater samples were collected from about 295 groundwater wells and analyzed for various physico-chemical parameters such as electrical conductivity (EC), pH, temperature, total dissolved solids (TDS), Na^+, K^+, Ca^{2+}, Mg^{2+}, CO_3^-, HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^-. Groundwater in the area is slightly alkaline and hard in nature. Electrical conductivity (EC) varies between 284 and 9,902 μS/cm with an average value of 1,599.4 μS/cm. The groundwater is highly mineralized with approximately 30 % of the samples having major ion concentrations above the WHO permissible limits. The NO_3^- concentration varies between 0.4 and 318.2 mg/l. The depth distribution of NO_3^- concentration shows higher concentration at shallow depths with a gradual decrease at deeper depths. As far as drinking water quality criteria are concerned, study shows that about 33 % of samples are unfit for use. A detailed assessment of groundwater quality in relation to agriculture use reveals that 21 % samples are unsuitable for irrigation. Using Piper's classification, groundwater was classified into five different groups. Majority of the samples show Mix-Cl-SO_4- and Na-Cl-types water. The abundances of Ca^{2+} and Mg^{2+} over alkalis infer mixed type of groundwater facies and reverse exchange reactions. The groundwater has acquired unique chemical characteristics through prolonged rock-water interactions, percolation of irrigation return water, and reactions at vadose zone.

Introduction

During the last three decades, the kingdom of Saudi Arabia has experienced a comprehensive development in all sectors together with increases in population and living standards. The annual national water demand has increased from 2,352 million cubic meters (MCM) in 1980 to more than 20,000 MCM in 2004 (FAO 2009). Irrigated agriculture consumes 88 % of the water with domestic demand accounting for 9 % and industry 3 %. The boom in desert agriculture in the 1980s resulted in rapid rise in water use to a point where agricultural consumption is about 10 times greater than the renewable water resources (FAO 2009). Groundwater is the major source of water for irrigation and also supports domestic and industrial water supply. Due to rise in

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agriculture production, groundwater has set a declining trend throughout the major aquifers of the country.

The Saq aquifer is one of the major groundwater sources that are located in the northwestern part of the Kingdom of Saudi Arabia. The groundwater resources of the Saq study area, covering 375,000 km^2, are intensively exploited (Fig. 1). The current rate of groundwater abstraction so far has exceeded the rate of groundwater recharge. As pumping wells tapping the various aquifers of the region are unevenly distributed, the consequences of this unbalanced groundwater exploitation vary from one part of the Saq study area to another. Schematically, water levels of the main aquifers have dropped sharply over the past three decades in areas where groundwater abstractions are concentrated but show little or no decline elsewhere (MWE 2008).

The absence of a declining trend in a specific aquifer or a specific area is not in itself a sign of groundwater sustainability. Due to its very large lateral and vertical extent, the multi-layer aquifer system of the Saq study area reacts slowly to any stresses imposed on it, and declining trends expand only gradually outside the abstraction areas and toward overlying or underlying aquifers. For a period from 1980 to 2006, the average annual groundwater decline in important aquifers like Saq, Tawil, and Kahfah aquifers was about 3, 1.77, and 1.5 m, respectively (MWE 2008).

Water resources safeguard policy requires periodic assessment of both groundwater quantity and quality. Quantitatively, the Saq aquifer has been exploited indiscriminately mostly for agricultural usages. The present study focuses on the assessment of groundwater quality and its suitability for domestic and agricultural purposes.

Geology and hydrogeological framework

The Arabian Peninsula can be divided into two main geological units (MWE 2008). The western part is
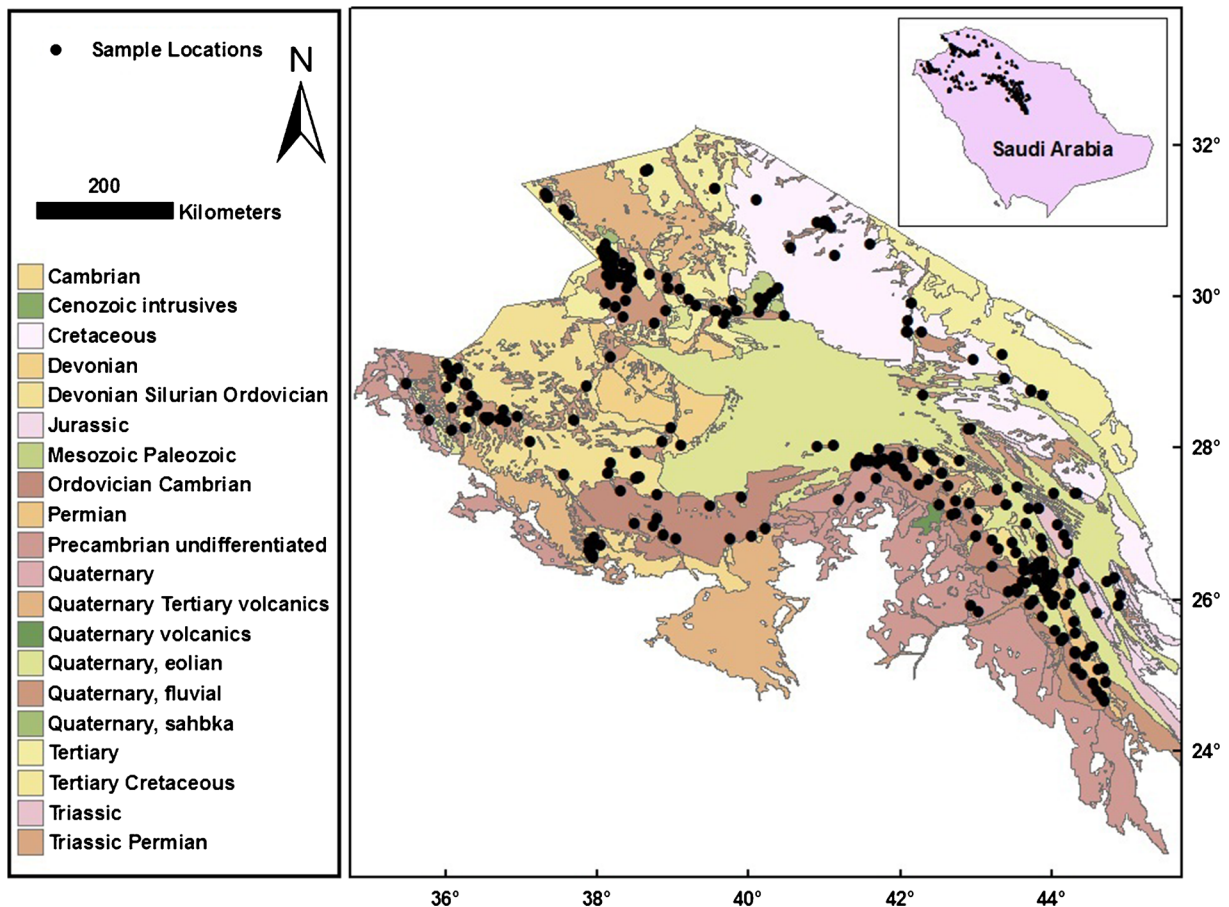

Fig. 1 Location, sampling locations, and geological map of Saq aquifer in northwestern part of Saudi Arabia

occupied by Precambrian rocks of the Arabian Shield. In the central and eastern parts of the peninsula, a succession of continental and shallow-marine sedimentary rocks of the Arabian Shelf overlies the Precambrian basement. This succession consists mainly of sandstone and limestone that are exposed in a great curved belt along the eastern margin of the shield. The western boundary of the area is marked by the contact between the Precambrian basement and the overlying sedimentary rocks of the Arabian Shelf. The sedimentary cover is composed of a thick succession of formations of Cambrian-Ordovician to Quaternary age. Tilting of the Precambrian basement resulted in a gentle dip of the sedimentary strata to the east. The Saq sandstone is found at the base of the sedimentary sequence and crops out in a strip adjacent to the basement, following the S shape of the Arabian Shield (Fig. 1). Moving away from the contact with the basement toward the east, the overlying formations appear one after the other in chronological order (MWE 2008). Predominant soil types of the study area are Calciorthid-rock outcrops-Torriorthents and Torripsamments-rock outcrops or sand dunes type. The former is basically loamy, arable soil founds at gently sloping alluvial plains, fan piedmonts, and interfluve area. However, the latter is typically represented by sand dunes; it is a mix of sand and rock outcrops and nonarable type (Water 1984).

At a regional level, groundwater recharge has been assessed at 2.5 mm/year for the Saq sandstone outcrops south of Tayma. At the scale of the entire Saq area, groundwater recharge most probably does not exceed 5 mm/year. Historical data on groundwater use are provided by Parsons-Basil (1969) and BRGM (1985). An updated evaluation of groundwater abstractions for the year 2005 has been realized as part of this study. The total volume of groundwater abstracted in the Saq area in 2005 (8,727MCM/year) equals a water column of 24 mm covering the entire Saq area (~370,000 km^2). This is five to 10 times higher than the recharge occurring during the same period and is therefore not sustainable (MWE 2008). There are seven aquifers or aquifer groups from bottom to top:

- Saq sandstone
- Kahfah sandstone
- Quwarah-Sarah sandstones
- Sharawra and Tawil sandstones
- Jubah sandstone
- Khuff limestone

- Secondary (Mesozoic)-Tertiary-Quaternary (STQ) sandstone and limestone

Two layers act regionally as aquitards but they contain units that are locally exploited as aquifer:

- Jauf limestone and sandstone;
- Unayzah and Berwath sandstones

Topography and climate

The highest elevations are encountered in the mountains along the western boundary, from the border with Jordan down to Al Ula, where harrats (basalt plateau) form the crest line at elevations above 1,800 m with Jabal al Juhayyir (36° 43′ 20″ E/27° 38′ 40″ N) reaching 2,111 m. The boundary of Saq basin, defined by the contact between the Saq sandstone and basement rocks, does not coincide with the crest line as the Saq sandstone is exposed west of the harrats (Tertiary basalt fields). As a result, along the western boundary of the Saq aquifer regional boundaries, the surface-water drainage basins do not match with the groundwater basin geometry. The terrains along the western boundary of the Saq basin are bordered to the east by the Tabuk and Al Ula valleys with flat valley bottoms at an elevation around 800 m. Farther east stretches a second ridge from the Jordanian border southward, passing east of Tabuk and then between Al Ula and Tayma, reaching elevations slightly above 1,000 m in the central part with peaks above 1,200 m in the northern and southern parts. The area east of this second ridge, representing 85 % of the Saq area, is characterized by a flat topography gently dipping eastward from elevations near 900 m in the west to below 400 m along the eastern boundary (MWE 2008).

The climate in the north and northwestern Saudi Arabia where the Saq aquifer is the dominant groundwater resource is arid with low annual rainfall. Nevertheless, some regional differences exist, with the lowest mean annual rainfall (less than 30 mm/year) being encountered in the western part of the area (Tabuk region) and the highest rainfall in the southeastern part (170 mm/year). With such a low rainfall and a potential evapotranspiration of nearly 2,400 mm/year, groundwater recharge can only occur where concentration of runoff waters coincides with favorable infiltration characteristics of the surface layers. The

temperature ranges from 43 to 48° C during daytime and 32 to 36° C during night time in summer. In winter, it sometime falls to 0°C.

Methodology

A total of 295 groundwater samples were collected from water wells in the Saq aquifer during the course year of 2013, NW Saudi Arabia (Fig. 1). Samples were collected in polyethylene bottles of 1 l capacity. Prior to their filling with sampled water, these bottles were rinsed to minimize the chance of any contamination. The samples preservation and the used analytical techniques were in accordance with the standard methods from the American Public Health Association (APHA 1995). 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 EC-meter, and a TDS-meter (Hanna Instruments, Michigan, USA). The sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) ions were determined by atomic absorption spectrophotometer (AAS). Bicarbonate (HCO_3^-) and chloride (Cl^-) were analyzed by volumetric methods. Sulfate (SO_4^{2-}) was estimated by the colorimetric and turbidimetric methods. Nitrate (NO_3^-) was measured by ionic chromatography. The accuracy of the chemical analysis was verified by charge balance errors, and samples above 5 % error were discarded.

Hydrochemical classification and groundwater evolution have been discussed using bivariate plots, Piper's plot, Gibb's plots, chloro-alkaline indices, and meteoric genesis indices. For drinking water quality assessment, the results were compared with the World Health Organization (WHO) standards. The suitability for agriculture use was assessed using sodium absorption ratio (SAR), sodium percentage (Na%), residual sodium concentration (RSC), Kelley's ratio, and magnesium hazard.

Results and discussion

General chemistry

The waters are slightly acidic to alkaline with pH values ranging from 6.4 to 9.6. Electrical conductivity (EC) ranges from 284 to 9,902 μS/cm, with an average of 1,599.4 μS/cm. About 31 % of the samples are crossing

the maximum permissible limit of EC (1,500 μS/cm). The large variation in EC values is attributed to geochemical evolution of groundwater through rock-water interaction during long resident time period and the anthropogenic influences. The total dissolved solids (TDS) were measured through summing up all major ions concentrations which range from 195.5 to 6,771.7 mg/l with an average value of 1,072 mg/l. Only 27 % of the sample has TDS value <500 mg/l. As per TDS classification, 29 % of the wells are brackish (TDS >1,000) water type and 44 % wells are fresh (TDS <1,000) water (Freeze and Cherry 1979) (Table 1).

The distribution of major ions in the groundwater is $Na^+>Ca^{++}>Mg^{++}>K^+$ and $Cl^->SO_4^{-2}>HCO_3^->NO_3^-$. The concentration of Na^+ shows a large variation from 3.8 to 1,640 mg/l, averaging 177.4 mg/l. About 23 % of samples have Na values greater than permissible limit of 200 mg/l for drinking water. The concentration of Ca^{2+} in the study area ranges from 17 to 820 mg/l with an average of 111.4 mg/l. As per WHO standards, 45 % of the samples from this study exceed the permissible limit of 75 mg/l. The major source of Ca^{2+} in the groundwater is due to ion exchange of minerals from

Table 1 Summary statics of groundwater quality parameters

	Min	Max	Average	Std. dev.
Depth	15	2,400	441.2	356.2
Temp	22.3	58.1	31.4	6.2
EC (μS/cm)	284	9,902	1,599.4	1,487.2
TDS (mg/l)	195.5	6,771.7	1,072.0	1,021.0
pH	6.4	9.6	7.5	0.4
Alkalinity	30	220	107.1	31.4
Ca (mg/l)	17	820	111.4	106.1
K (mg/l)	0.9	91	14.9	14.9
Mg (mg/l)	1.1	335.5	36.5	44.0
Na (mg/l)	3.8	1,640	177.4	212.8
Cl (mg/l)	12.9	2,622	295.9	367.3
SO4 (mg/l)	15.1	2,120	256.4	337.9
HCO3 (mg/l)	65	543	149.1	61.7
NO3 (mg/l)	0.4	318.2	30.3	38.9
Ht	74.48	2,980.7	428.2	421.8
%Na	6.81	83.12	45.8	11.8
SAR	0.14	17.53	3.4	2.5
Kelly ratio	0.06	4.83	0.9	0.5
RSC	−57.79	3.36	−6.1	8.3

rocks of this area. Further, this may also be due to the presence of $CaCO_3$ and $CaSO_4$ minerals present in the soil horizon, gypsum anhydrides, dolomite, etc. The concentration of Mg^{2+} ranges from 1.1 to 335.5 mg/l with an average value of 36.5 mg/l. Most of the Mg^{2+} concentrations (81 %) are within the desirable limit of 50 mg/l. The concentration of K^+ ranges from 0.9 to 91 mg/l with an average value of 15 mg/l.

The Cl^- concentration ranges from 12.9 to 2,622 mg/l, averaging 295.9 mg/l. About 45 % sample has Cl^- concentration more than the permissible limit of 200 mg/l. The SO_4 concentration range from 15.1 to 2,120 mg/l, with an average value of 256.4 mg/l. Out of the total 32 % sample has SO_4 concentration greater than the permissible limit of 200 mg/l. The HCO_3 concentration ranges from 65 to 543 mg/l with an average of 149.1 mg/l. The NO_3 concentration ranges from 0.4 to 318.2 with an average of 30.3 mg/l. As much as 19 % sample has more than the permissible NO_3 concentration (45 mg/l).

Hardness of groundwater results from the presence of divalent metallic cations of which concentration of Ca^{2+} and Mg^{2+} are most abundant in groundwater. Adopting Sawyer and McCarty (1967) classification criteria, only 9 % of the sample classify as moderately hard type. The remaining 50 and 41 % samples classify to "hard" and "very hard" water classes.

Hydrochemical classification

The classification of groundwater facies was done using Piper's diagram (Piper 1944). The ternary diagrams (Fig. 2) show Na^+, Ca^{+2}, mix cation type, and Cl^-, SO_4, mix-anion enriched trend. The plots of desirable data on the diamond-shaped field classify the groundwater types into five groups (Table 2).

Majority of sample (85 %) falls in groups I and II which show evolved groundwater type where unique chemical masking is achieved through rock-water interaction, ion exchange, and reverse ion exchange; reactions within unsaturated zones; increased resident time; and anthropogenic influences. The group III water types representing meteoric signatures or fresh recharged water constitutes only 5 % of the total samples. The location of the samples collected varies widely both vertically and spatially; therefore, they show greater variation in range for each parameter. The depth of samples varies from 15 to 2,400 m.

Hydrochemical evolution

The results of groundwater chemistry were analyzed to decipher chemical alteration and to mask of natural or meteoric characteristics of groundwater. This necessitates ions converted to equivalent weights and then plotting to reveal various correlations which are helpful to indicate possible source to groundwater chemistry. Gibbs (1970) plot was used to determine major processes controlling the groundwater chemistry. The data points on the Gibbs diagram (Fig. 3) suggests that groundwater chemistry is controlled principally by rock weathering and to some extent evaporation-crystallization is the dominant factor leading to increased salinity and therefore poor quality of groundwater (Subba Rao 2002; Srinivasamoorthy et al. 2008). This is expected, as evaporation greatly increases the concentrations of ions formed by chemical weathering of the rock, leading to higher salinity.

Ionic concentrations of major elements present in groundwater were analyzed for relative abundances and ionic affinity. Ionic abundance plot of alkalis with Ca + Mg is suggestive of mix type trends of concentrations as evident by moderate correlation ($r=0.57$). About 60 % of the total samples have alkali abundance, and the remaining samples have more Ca + Mg concentrations than alkalis (Fig. 4). Predominance of Ca and Mg over Na and K and abundances of Na with Ca concentration, individually (Fig. 4) are indicative of ion-exchange reactions (Subba Rao et al. 2012).

Relative abundance of anionic facies was examined (Fig. 4); where Cl + SO$_4$ is far more abundant than HCO$_3$. Ionic affinity relationships were tested first between ionic pairs having primary affinity. The plot of Ca + Mg concentrations against HCO$_3$ (Fig. 4) shows that majority of samples have excess Ca and Mg. Ca + Mg/HCO$_3$ ratio (<1) which can be used to present fresh recharge or meteoric nature of groundwater suggested that only nine samples from the different formations (five from Saq, two from Jauf, one from Tawil, and one from Kahfah) show meteoric nature. Nonetheless, predominance of Ca + Mg over HCO$_3$ could relate its genesis through extreme aridity and carbonate weathering (Al-Amry 2008), ion exchange at favorable lithology (Al-Bassam et al. 1997), and to some extent lack of recent recharge. Further, ion exchange in groundwater and host environment can be inferred through chloro-alkaline indices (CAI) using equivalent concentrations of Cl, Na, K, SO$_4$, HCO$_3$, CO$_3$, and NO$_3$
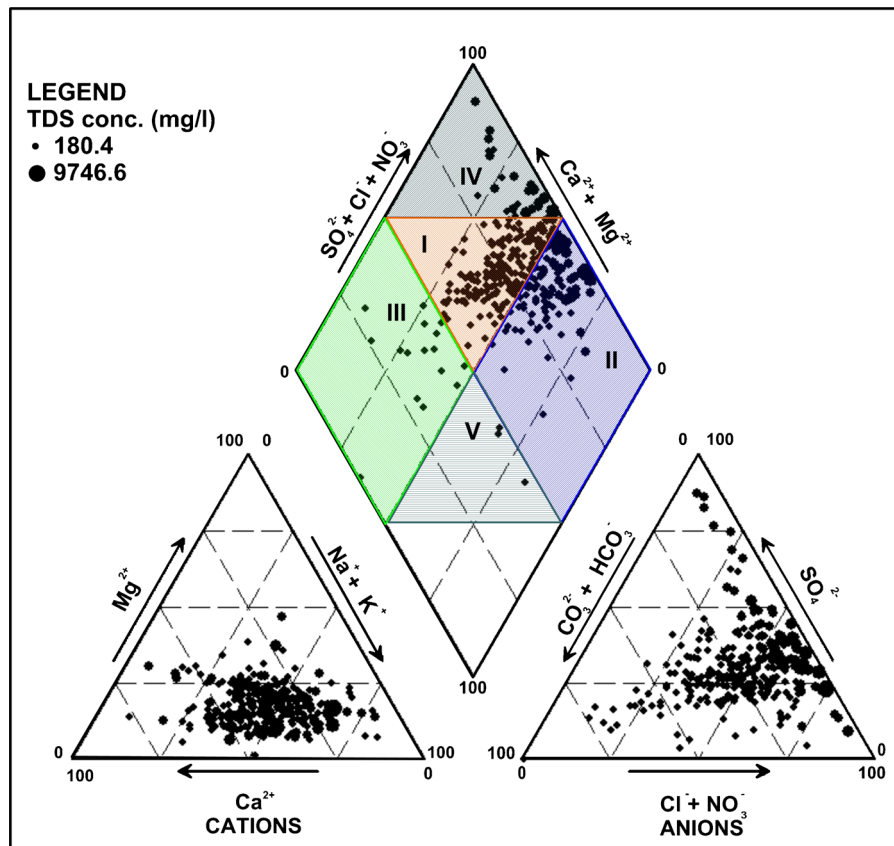
Fig. 2 Piper plot for groundwater facies classifications

(CAI-1 and CAI-2) (Schoeller 1965). The positive indices (in 96 % sample) decipher base exchange reactions,

Table 2 The water types via location in the Saq aquifer

Type	Composition	location
I	Mix Ca-Mg-Cl-SO$_4$	In the basaltic area, in the confined section, and to the north of the east part
II	Na-Cl	In the wadi outlets in the west and dominant in the outcrops in the east part of the study area.
III	Ca-HCO$_3$	In the outcrops and shallow wells in the west part of the study area and in some deep wells near the outcrops in the east part
IV	Ca-Cl	In the confined section near to the outcrops all over the study area
V	Mix Ca-Na-HCO$_3$	In the outcrops and deep wells of the west part, confined section near to southwest region, in the east part of the study area

i.e., exchange of Na and K in water with Mg and Ca at host environment (Schoeller 1965; Garcia et al. 2001). Base exchange reactions cause changes in the physical properties of soils causing deflocculating and permeability reduction (Todd 1980).

Alkalis have primary bonding affinity with Cl and SO$_4$; the present study shows good correlation with Cl + SO$_4$ ($r=0.88$) and suggests that almost all alkalis are consumed while bonding with Cl and SO$_4$ (Fig. 4) (Table 3) and rules out genesis of Na$^+$ from anthropogenic factors (Marghade et al. 2012). Further, a good correlation between alkalis with Cl and SO$_4$ indicates that this trend evolved from rocks rather than from anthropogenic origin (Sarin et al. 1989; Datta et al. 1996; Rao et al. 2002). The meteoric genesis index (MGI) expressed by Na$^+$ + K$^+$ − Cl$^-$/SO$_4^{2-}$, where all concentrations are in milliequivalents/liter, helps in determining whether groundwater source is of deep meteoric water percolation type (MGI<1) or shallow meteoric water percolation type (MGI>1) (Soltan 1998). The meteoric genesis indices demonstrated that most of the
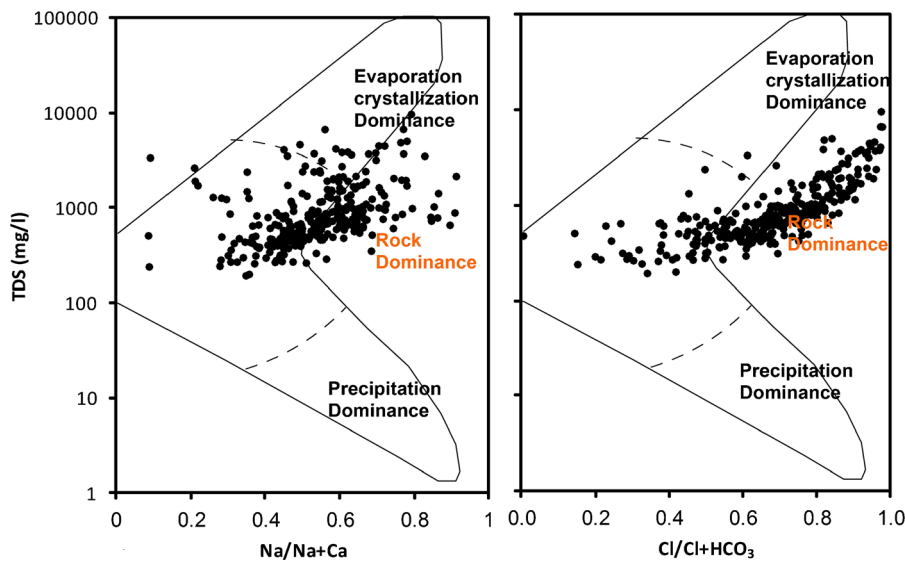
Fig. 3 Gibbs plot showing major processes controlling groundwater chemistry

samples (96 %) belong to a deep meteoric water percolation type. Further, plot of Na with Cl shows a very good correlation ($r=0.9$) indicating that halite dissolution could be the source of groundwater genesis. Samples away from 1:1 line on either sides are suggestive of excess concentrations and possibility to have secondary bonding affinity; Na with HCO_3 and Cl with Ca.

A good correlation ($r=0.75$) between the plots of Ca + Mg with SO_4 suggests a possibility of originating from source rocks containing dolomites and gypsum. Apart from geogenic processes, SO_4 enrichment may enter groundwater system through different anthropogenic activity including sewage pollution, industrial wastes, specialized fertilizers, etc. (Umar and Ahmed 2007, Umar et al. 2009). The spatial distribution of NO_3 further advocates the widespread anthropogenic influence on groundwater irrespective of lithology and depth.

Nitrate contamination

Due to the general reducing conditions at the deeper depths, NO_3^- is generally absent in deep and/or confined aquifers, with depth NO_3 is transformed into NO_2 and gaseous nitrogen by de-nitrification. This bacterial reaction is emphasized by a moderate increase in temperature as evident from the depth-temperature correlation ($r=0.76$) in Table 3. The concentration of NO_3^- can be used as a good indicator of interaction of land use pattern with the groundwater environment (Trojan et al.

2003, White et al. 2013). The NO_3^- concentration ranges from 0.4 to 318.2 mg/l, averaging 30.3 mg/l. A depth-wise NO_3^- distribution show gradual decrease in average concentration with depth (Fig. 5). The higher concentrations correspond with aquifers like STQ; shallow Saq; Kahfah; and alluvium of Al Qassim, Al Hail, Al Jawf, and Al Medina provinces.

A relatively good correlation of NO_3 with Cl and SO_4 (Table 3) may indicate a common origin i.e., use of fertilizers (NPK, gypsum, potassium fertilizers, etc.) and sewage pollution. A clear distinction of the contaminant sources i.e., agricultural and/or municipal is difficult to made (Gold et al. 1990). Landuse pattern can help relate the actual source of NO_3 contamination in many cases. Though, not necessarily a good correlation exists even they have the common origin as a variety of reactions are involved in soil horizon and vadose zone may dilute the proportion.

Suitability for irrigation use

The suitability of groundwater for irrigation is contingent on the effects of the mineral constituents of the water on both the plant and the soil (Richards 1954; Wilcox 1955). The general criteria for assessing the irrigation water quality includes estimates of electrical conductivity, sodium adsorption ratio (SAR), relative proportions of Na^+ expressed by %Na, and residual sodium carbonate (RSC). EC and Na^+ are particularly important in
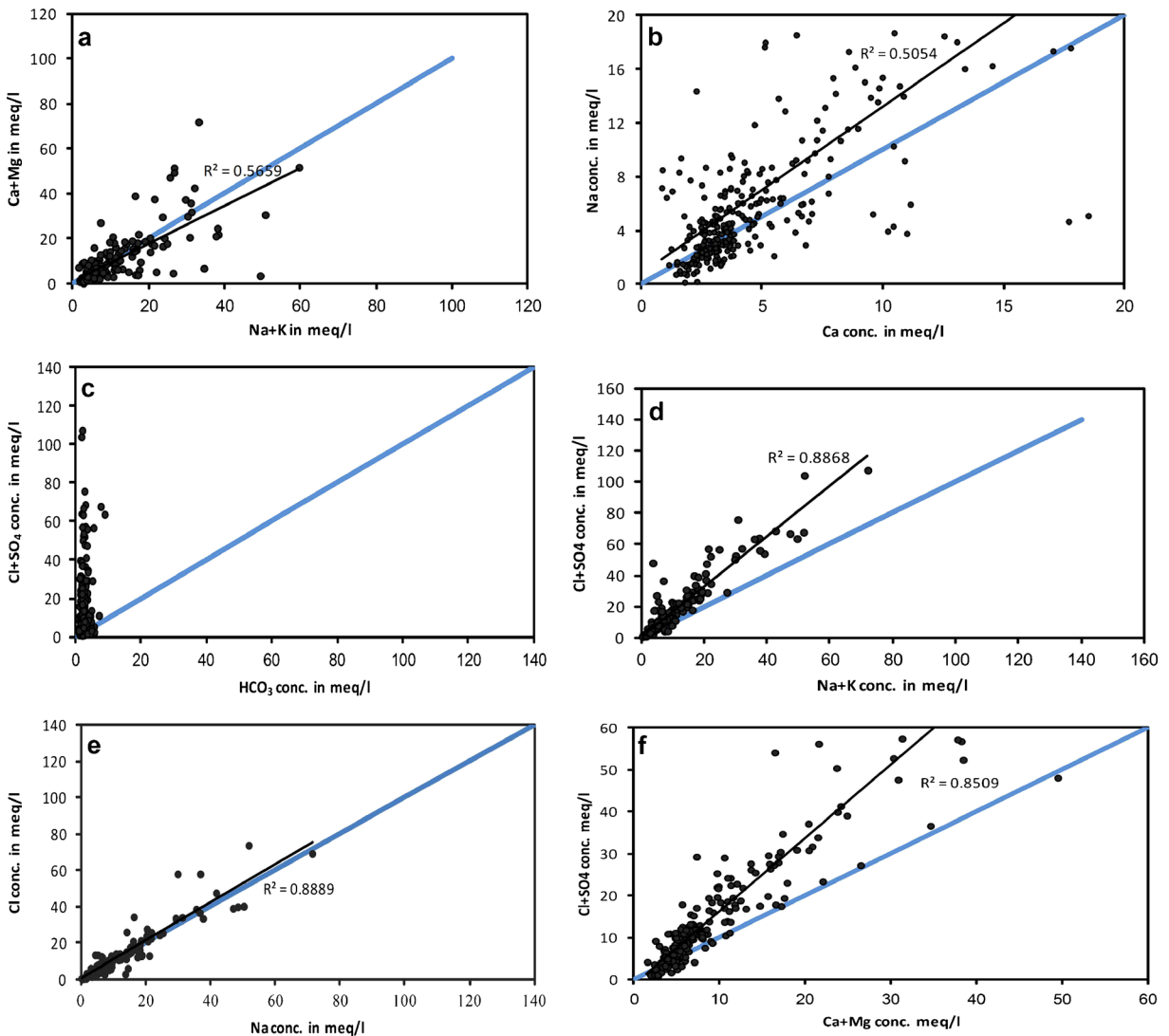
Fig. 4 Major ion chemistry of the Saq aquifer: **a** Alkalis relationship with Ca and Mg. **b** Ca versus Na relationship. **c** Relative abundance of weal (HCO_3) and strong ($Cl+SO_4$) acids. **d** Bonding affinity between alkalis and $Cl + SO_4$. **e** Bonding relationship of Na-Cl. **f** Relationship of Ca + Mg with $Cl + SO_4$

classifying irrigation water. The high salt contents in irrigation water cause osmotic pressure in soil solution (Thorne and Peterson 1954), whereas Na^+ reacts with soil to reduce permeability through ion exchange. Water quality criteria can be used as guidelines by farmers for selecting appropriate management practice to overcome potential salinity hazard, if the quality of available water would pose any problem for irrigation.

US salinity laboratory's salinity hazards map

The graphic presentation of EC and SAR is an important parameter for determining the suitability of groundwater for irrigation purposes. SAR is calculated as follows where all concentrations are given in milliequivalents/liter.

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

The salinity laboratory of the US Department of Agriculture recommends SAR because of its direct relation to adsorption of Na^+ by soil (Richards 1954). The plot of EC and SAR infers that 23 % samples fall in C2-S1 class which is generally considered as good for irrigation (Fig. 6). About 58 % sample falls in high

Table 3 Correlation coefficient

	Depth	Temp	EC	TDS	pH	Ca	K	Mg	Na	Cl	SO4	HCO3	NO3	%Na	SAR	PI
Depth	1.00															
Temp	0.76	1.00														
EC	−0.13	−0.07	1.00													
TDS	−0.14	−0.11	0.94	1.00												
pH	−0.23	−0.21	−0.14	−0.16	1.00											
Ca	−0.18	−0.14	**0.79**	**0.87**	−0.13	1.00										
K	0.35	0.43	0.31	0.29	−0.18	0.10	1.00									
Mg	−0.12	−0.11	**0.81**	**0.86**	−0.13	**0.78**	0.23	1.00								
Na	−0.14	−0.11	**0.92**	**0.95**	−0.13	**0.71**	0.32	**0.72**	1.00							
Cl	−0.15	−0.11	**0.91**	**0.93**	−0.11	**0.79**	0.28	**0.75**	**0.94**	1.00						
SO4	−0.14	−0.11	**0.81**	**0.89**	−0.16	**0.84**	0.21	**0.87**	0.76	**0.68**	1.00					
HCO3	0.18	0.15	0.27	0.29	−0.15	0.10	0.36	0.28	0.29	0.19	0.20	1.00				
NO3	−0.19	−0.19	0.52	0.57	−0.16	0.55	−0.05	0.33	0.57	0.54	0.44	0.08	1.00			
%Na	0.20	0.26	0.32	0.25	−0.05	−0.06	0.49	0.03	0.44	0.32	0.07	0.25	0.11	1.00		
SAR	−0.03	0.02	0.81	**0.80**	−0.11	0.49	0.45	0.53	**0.91**	0.81	0.60	0.35	0.45	**0.73**	1.00	
PI	0.24	0.24	−0.19	−0.25	0.03	−0.53	0.19	−0.40	−0.03	−0.14	−0.40	0.20	−0.13	0.65	0.22	1.00

Bold entries are indicative of good correlations

salinity hazard corresponding with low to medium SAR which is considered as permissible for irrigation. About 19 % sample falls in very high salinity hazard and is considered unsuitable for irrigation.

Sodium percentage versus EC plot (Wilcox diagram)

Sodium percentage (Na%) is estimated as follows where concentrations are measured in milliequivalents/liter:

$$Na\% = \frac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+} + Mg^{2+}} \times 100$$

The estimates of sodium percentage (Na %) ranges from 6.8 to 83.1 with an average value of 46 (Table 1). The majority of samples (87 %) have Na% values between 20 and 60 corresponding with good to permissible class. Wilcox (1955) diagram relates plot of Na% and EC to designate irrigation water quality. Figure 7 infers that 65 % samples falls within excellent to permissible category of irrigation water use. About 12 and 10 % samples are classified as permissible to doubtful and doubtful to unsuitable. However, about 13 % of the water samples have high EC values making it unsuitable for irrigation use (Table 4).
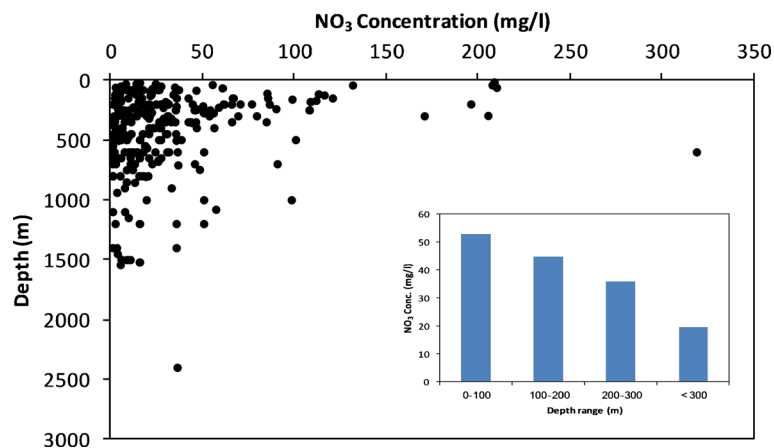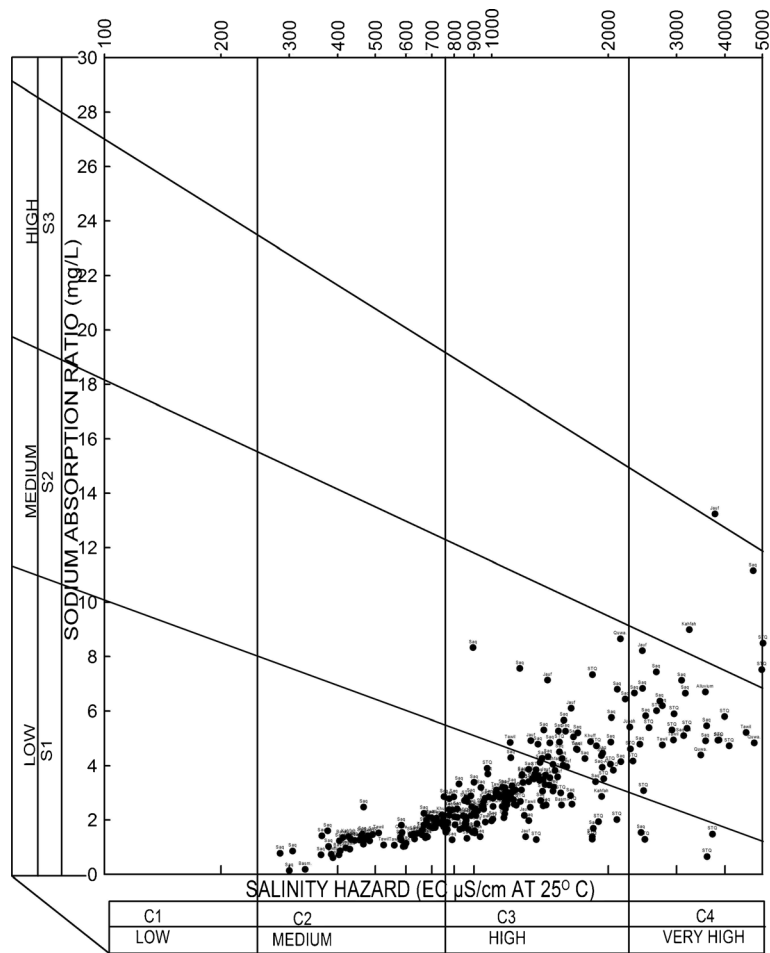

Fig. 5 NO₃ concentration versus well depth

Fig. 6 Classification of irrigation waters by USSL (after Richards 1954)

Residual sodium carbonate (RSC)

The water having excess of carbonate and bicarbonate over the alkaline earth mainly calcium and magnesium, in excess of allowable limits affects agriculture unfavorably (Eaton 1950; Richards 1954). The residual sodium carbonate is shown in the following equation:

$$RSC = (CO_3 + HCO_3) - (Ca^{+2} + Mg^{+2})$$

where, all values of cations and anions are expressed in milliequivalents/liter. Organic matter is vital for the agricultural productivity; high concentration of HCO_3^- leads to an increase in pH values causing the dissolution of organic matter. Thus, the residual sodium carbonate is used to distinguish between the different water classes for irrigation purposes. Due to high concentration of Ca and Mg, about 98 % sample qualify in safe category

(RSC <1.25), while marginal (RSC 1.25–2.5) and unsuitable (RSC >2.5) categories are represented by two samples each (Table 4).

Kelley's ratio

Kelley et al. (1940) have suggested that the sodium problem in irrigational water could very conveniently be worked out on the basis of the values of Kelley's ratio.

$$Kelley's\ Index(KI) = \frac{Na^+}{Ca^{2+} + Mg^{2+}}$$

A Kelley's index of more than one indicates an excess level of sodium in waters. Hence, waters with a Kelley's index less than one are suitable for irrigation, while those with a ratio more than one are unsuitable.
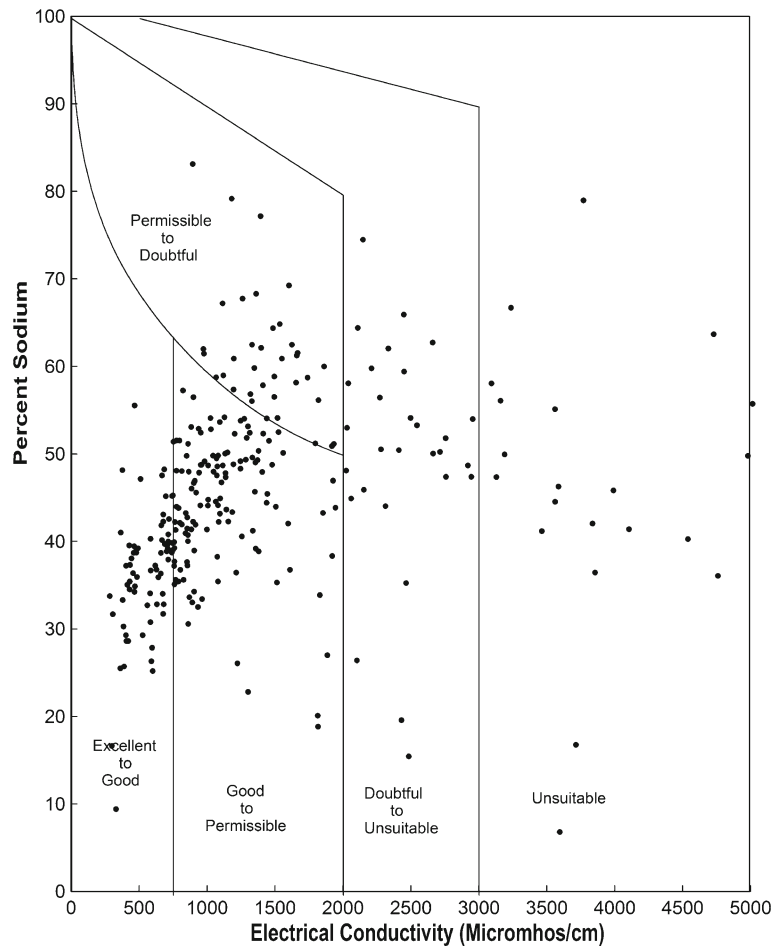
Fig. 7 Classification of irrigation waters using Wilcox diagram

Kelley's index in the present study varied from 0.1 to 4.8, and about 29 % water samples are unsuitable for irrigation according to Kelley's index (Table 4).

Magnesium hazard

Generally, Ca^{2+} and Mg^{2+} maintain a state of equilibrium in most waters, although in soil system, Ca^{2+} and Mg^{2+} do not behave equally and Mg^{2+} deteriorates soil structure particularly when waters are sodium dominated and highly saline (Ravikumar et al. 2011). High level of Mg^{2+} is usually due to the presence of exchangeable Na^+ in irrigated soils. In equilibrium, more Mg^{2+} present in water will adversely affect the soil quality rendering it alkaline resulting in decreased and adversely affected crop yields. Based on the residual Mg/Ca ratio, the groundwater samples can be classified as safe (<1.5), moderate (1.5 to 3.0), and unsafe (>3) for irrigation. In the present study, 96 % sample classifies to be in safe

category and the remaining samples show groundwater moderate suitability for irrigation based on Mg hazard (Table 4).

Conclusion

The distribution of major ions in the groundwater is as follows: $Na^+ > Ca^{++} > Mg^{++} > K^+$ and $Cl^- > SO_4^{-2} > HCO_3^- > NO_3^-$. Groundwater of the Saq aquifer is of evolved type with mix abundances of ionic concentrations. Alkalis are slightly more abundant than alkaline earth, while Cl and SO_4 dominate HCO_3 and NO_3. As far as domestic suitability of groundwater is concerned, higher concentrations of Ca^{2+}, Cl^-, Na^+, and SO_4^{2-} make about 30 % of the groundwater samples unsuitable for drinking purposes. Similarly, about 30 % of the samples have TDS value above the maximum permissible limit (>1,000 mg/l). The suitability for irrigation

Table 4 Classification of groundwater for irrigation use

Parameters	Range	Water class	Samples
Na% after Wilcox (1995)	<20	Excellent	7
	20–40	Good	88
	40–60	Permissible	168
	60–80	Doubtful	31
	>80	Unsuitable	1
Alkalinity Hazard (SAR)	<10	Excellent	287
	10–18	Good	8
	18–26	Doubtful	–
	>26	Unsuitable	–
EC	<250	Excellent	–
	250–750	Good	68
	750–2.000	Permissible	164
	2,000–3,000	Doubtful	29
	>3,000	Unsuitable	34
RSC	<1.25	Good	291
	1.25–2.50	Doubtful	4
	>2.5	Unsuitable	–
Residual Mg/Ca ratio	<1.5	Safe	285
	1.5–3.0	Moderate	10
	>3.0	Unsafe	–
Kelley's ratio	<1	Safe	209
	>1	Unsafe	86

use was examined through using SAR, EC, Na%, RSC, Mg/Ca ratio, and Kelley's ratio. Overall, 79 % samples are considered suitable for irrigation use, while the remaining 21 % are classified as doubtful to unsuitable for irrigation uses. Using Piper's approach, groundwater has been classified into five hydrochemical groups with each group having its unique chemical characteristics. Various bi-variate plots suggested the genesis of groundwater which is acquired mainly through ion exchange, rock-water interaction, evaporation-crystallization reactions within the thick vadose zone, contamination through irrigation return water, sewage pollution, etc. The present study indicates that albeit natural factors controlling the groundwater chemistry of Saq aquifer, anthropogenic impacts in the form of agricultural activities are influencing the general groundwater chemistry. The fact is advocated by the presence of high concentrations of NO_3, Cl, and SO_4 beneath agricultural tracts. The study recommends that strict mitigation plans should be adopted in the areas with poor groundwater quality to check further deterioration.

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