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ORIGINAL ARTICLE

Hydrochemical processes governing groundwater quality of sedimentary aquifers in Central Saudi Arabia and its environmental implications

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Abstract The present study deals with the interpretation of the major processes governing the groundwater chemistry in parts of Qassim and Riyadh province of Saudi Arabia. The study area that is dominated by agricultural activities is represented by a multi-layered aquifer system with sedimentary formations ranging from Cambrian to the Quaternary present as outcrops. Groundwater samples from 97 agricultural bore wells in the area were collected and analyzed for 16 physio-chemical parameters. The evaluation of the main hydrochemical processes affecting the groundwater quality was carried out by interpreting the ionic relationships and hydrochemical facies analysis. The interpretation pointed toward evaporation, gypsum dissolution and ion exchange as main factors controlling the major ion groundwater chemistry. The piper plot showed SO_4–Cl type of groundwater with majority of the samples falling in the zone of permanent hardness due to the formation of non-carbonate salts. Principal component analysis that helps to understand the underlying natural and anthropogenic factors controlling the groundwater chemistry in an area was used in the present study, based on which four principal components (PCs) were extracted. The first PC as expected was dominated by the major ions and was attributed to natural processes, whereas the extracted components (mainly heavy metals) in PC 2, 3 and 4 pointed toward anthropogenic activities playing an active role in affecting the trace element hydrochemistry.

Keywords Arid regions · Saudi Arabia · Ion exchange · Gypsum dissolution · Principal component analysis

Introduction

Arid and semi-arid regions of the world occupy about 30 % of the earth's surface (Dregne 1991) and include major parts of Africa, the Middle-east, Central Asia, Australia, Western USA, southern parts of South America and parts of Europe. Rainfalls in arid regions are rare and are normally of short duration and high intensity, if at all they occur (Martínez-Mena et al. 1998; Osterkamp and Friedman 2002). The low rainfall and high evaporation rates result in a practically negligible recharge from precipitation in these regions (Qin et al. 2011) and often leads to the common problem of groundwater salinization (Umar and Absar 2003). Over-exploitation of the available limited groundwater resources have led to declining water levels and desertification across many arid regions of the world (Qi and Luo 2006). In the absence of plentiful surface water supplies, groundwater resources form the single most important source of fresh water supplies in these regions,

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especially Saudi Arabia (Scanlon et al. 2006; Zaidi and Kassem 2012; Kolsi et al. 2013).

Saudi Arabia is the largest country in the world with no lakes or rivers (Llamas and Custudio 2003), and over 80 % of the water supply comes from the non-renewable (fossil) groundwater aquifers (ESCWA 2001). Deteriorating groundwater quality (due to natural or anthropogenic activities) can further restrict the usage of this non-renewable resource, thus leading to water stress which is already high for Saudi Arabia (Gleeson et al. 2012).

The present study is an attempt to understand the factors affecting the groundwater quality in the region, which is dominated mostly by agricultural activities, by using the classical hydrochemical interpretation technique (groundwater facies analysis, ionic relationships) and the statistical technique of principal component analysis (PCA). PCA reduces the dimensions of the available data and helps in deciphering the underlying factors that govern the overall groundwater quality.

Hydrogeochemical processes affecting the groundwater chemistry of an area using ionic relationships and groundwater facies analysis have been carried out by many workers (Alaya et al. 2014; Varol and Davraz 2014; Chaudhuri and Ale 2014). Multivariate statistical analysis, mainly PCA, has been used effectively across many regions of the world to identify the various geogenic and anthropogenic factors that affect the groundwater chemistry of an area (Galazoulas and Petalas 2014; Salman et al. 2014; Parizi and Samani 2013).

Study area description

The study area is located between latitudes 25°N and 26.5°N and longitude 43.25°E and 46.25°E and forms a part of the Riyadh and Qassim province of Saudi Arabia (Fig. 1). The average annual precipitation in the region is less than 150 mm. The region is characterized by a high diurnal range of temperature which averages from 43–28 °C during summers and 21–9 °C during winters. Temperatures falling up to 0 °C are quite common in the area during winters. The mean elevation of the area is 705 m amsl. The higher elevations are present in the south western corner (pre-cambrian basement out crops) and the central region (Jurassic limestone formations).

Geological and hydrogeological settings

The geological formations in the study area range from the Precambrian basement rocks to the quaternary eolian deposits (Fig. 1). The Precambrian granitic gneisses are exposed in the south west corner of the study. The formations become progressively younger as one moves in the eastward direction. Major portion of the study area is occupied by the Paleozoic and Mesozoic sedimentary rocks comprising mainly of sandstone, limestone, shale and gypsum. Cenozoic sedimentary formations are exposed in the eastern part of the area. The quaternary surficial deposits consisting mainly of eolian sand, silt and gravel are found throughout the study covering the older sedimentary formations. The generalized stratigraphic sequence based on litholog information from previous studies (MoWA 1980, 2008) and surface geological mapping by Saudi Geologic Survey showing the prominent lithology of each formation have been presented in Table 1.

The study area represents a typical multilayered aquifer system that is mostly under confined conditions (unconfined only in areas of surface outcrops). Water samples were collected from individual farms where the water is used mainly for agricultural activities. The region is well known as the center for agricultural activities in Saudi Arabia (Al-Bassam 2006). Though Saq, Tabuk, Minjur and Dhruma, Ummer Radhuma and the Neogene formations are the principal aquifer present in the study, but individual farmers rely on wells drilled in formations, which can meet their daily agricultural water demands at a minimal cost. The depth of the wells seldom exceed 100 m and tap the sedimentary outcrops that act locally as aquifers (Khuff, Jilh, Marrat, Tuwaiq, Hanifa, Jubaila and Arab) where the groundwater is easily accessible and economically viable to the local farmers. The number of wells (from which the water samples were collected) tapping the different sedimentary formations and their respective hydrological parameters (Transmissivity and Storativity) have been presented in Table 1. All the water samples were collected from agricultural farms, but since most of the wells were sealed from the top after the placement of the pumping units, it was not possible to monitor the water levels. However, the discussion with the farmers in the field suggested that the water level was in excess of 50 m in all the wells.

Sampling and analytical methods

A total of 103 groundwater samples were collected in September, 2013, from the study area (Fig. 1). All the samples were collected from agricultural farms. The samples were collected in polyethylene bottles of 1-l capacity by pumping the bore wells. Care was taken to pump the bore wells for sufficient time to get rid of the water in the well bore storage, before collecting the samples. Prior to their filling with sampled water, the plastic bottles were rinsed to minimize the chance of any contamination. The sample preservation and the used analytical techniques

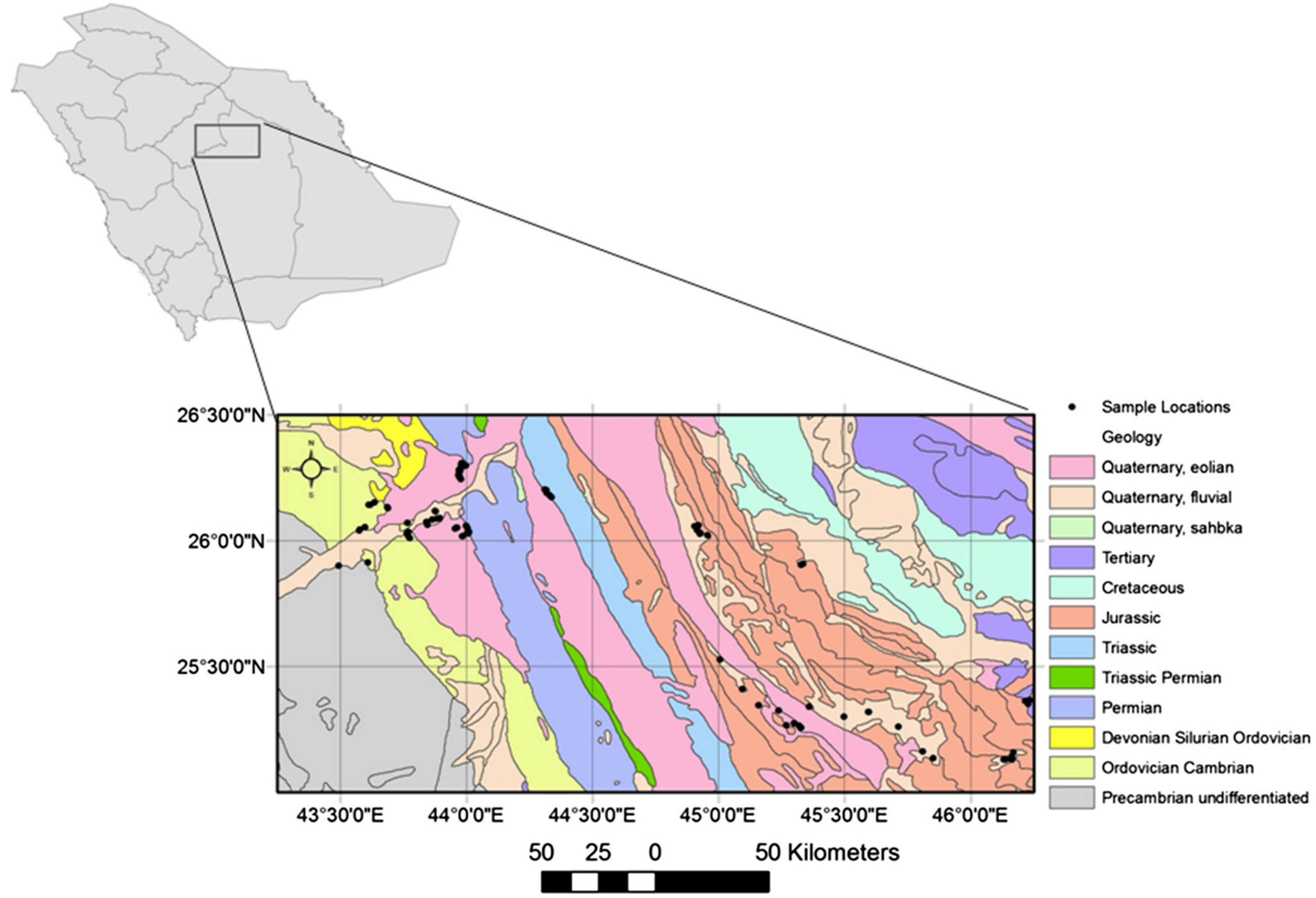

Fig. 1 Study area location, geology and the location of the collected groundwater samples

were in accordance with the standard methods from 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 analytical determination of the minor and trace elements was carried out by ICP-MS (inductively coupled plasma-mass spectrometer): NexION 300 D (PerkinElmer, USA).

After calculating the charge balance error, samples showing more than 5 % error were excluded from the results. The final number of samples include in the interpretation is 97. The results of the analysis were then interpreted using various ionic relationships and trilinear plot (Piper) to understand the major processes governing the groundwater chemistry.

The statistical analysis used in the present study comprises of PCA. It is one of the frequently used procedures for the multivariate statistical analysis of groundwater quality data, which helps in inferring the natural or anthropogenic processes controlling the groundwater chemistry of a given area (Güler et al. 2012; Kolsi et al. 2013; Nazzal et al. 2013; Loni et al. 2014). PCA is basically a variation reduction procedure wherein a number of observed/measures parameters can be transformed into a small number of artificial variables known as principal components (PCs). The extracted PCs account for most of the variance in the observed parameters and can be interpreted as an independent factor governing a given phenomenon (Kolsi et al. 2013).

The number of PCs extracted is actually equal to the number of parameters involved; however, the Kaiser criterion (Kaiser 1960), which takes into account PCs whose Eigen values greater than 1, is frequently employed (Kolsi et al. 2013; Qin et al. 2013). Varimax rotation is generally applied to all the extracted principal components to reduce

Table 1 Generalized geology of the study area including the formations tapped by the sampled bore and aquifer parameter of each formation

Age	Formation	Generalized geology	No. of sampled wells	Aquifer properties	
				T (m^2/s)	*S*
CENOZOIC					
Quaternary	Surficial Deposits	Gravel, sand and silt			
Miocene and Pliocene	Kharj	Limestone, lacustrine limestone, gypsum and gravel	3	1.5×10^{-4}	NA
Miocene and Pliocene	Hadrukh	Calcareous, silty sandstone, sandy limestone; local chert			
Paleocene	Ummer Radhuma	Limestone, dolomitic limestone and dolomite			
MESOZOIC					
Cretaceous	Aruma	Limestone and subordinate dolomite and shale			
Upper Jurassic	Arab	Calcarenite, calcarenitic and aphanitic limestone, dolomite and some anhydrite	1	1.7×10^{-3} to 7.2×10^{-3}	1.3×10^{-4}
Upper Jurassic	Jubaila	Aphanitic limestone and dolomite; subordinate calcarenite and calcarenitic limestone	3		
Middle Jurassic	Hanifa	Aphanitic limestone, calcarenitic limestone and calcarenite	5		
Middle Jurassic	Tuwaiq	Aphanitic limestone and subordinate calcarenite and calcarenitic limestone	1		
Lower Jurassic	Dhruma	Aphanitic limestone and shale; subordinate calcarenite	12	1×10^{-2} to $1.6x10^{-2}$	1.3×10^{-4}
Lower Jurassic	Marrat	Shale and aphanitic limestone; subordinate sandstone	9		
Upper Triassic	Minjur	Sandstone, aphanitic limestone and shale; subordinate gypsum			
Middle/Upper Triassic	Jilh	Sandstone, aphanitic limestone and shale; subordinate gypsum	5	2.5×10^{-5} to 4.5×10^{-4}	5×10^{-5} to 2×10^{-4}
Lower Triassic	Sudair	Red and green shale			
PALAEOZOIC					
Upper Permian	Khuff	Limestone and shale	29	1×10^{-3}	
Devonian	Jauf	Limestone, shale and sandstone			
Ordovician/Silurian	Tabuk	Sandstone and shale	2	4×10^{-4} to 1.5×10^{-4}	2.7×10^{-4} to $2.5x10^{-3}$
Cambrian/Ordovician	Saq	Sandstone. Includes a zone of several thin layer of shale	25	4×10^{-4} to 2.7×10^{-2}	2.5×10^{-5} to 6.2×10^{-5}
PRE-CAMBRIAN					
	Basement	Genissic gray granites; subordinate younger granites	2	NA	NA

Lithological information has been taken from Powers et al. (1966) and aquifer parameters have been taken from Saudi Water Atlas, (1984)

NA data not available

the contribution of the variables that are not significant (Closs and Nichol 1975).

The first PC accounts for the greatest variability (Webster 2001), which can be seen on the scree plot. The factor loading or the PC score associated with each of the variables in a given principal components is the correlation between the original variable and the factor and gives an idea about the processes that control the data variability (Hu et al. 2012). A factor loading close to ±1 indicates a strong correlation between the given variable and the factor. The variables that show loadings of greater than 0.5 are generally considered to be significant. The detailed mathematics behind PCA is available in numerous published works (Davis 2002; Yidana et al. 2010). The statistical software used in the present study was the SPSS® 17 software package.

Results and discussion

General groundwater chemistry

The pH value for the analyzed samples ranged from 6.68 (slightly acidic) to 8.00 (slightly basic) with an average value of 7.15. The pH value prescribed by WHO (1997) for drinking purpose is in the range of 6.5–8.5, and the groundwater in the study area falls within this prescribed limit.

The major ion relationship in the analyzed water samples are as follows: $SO_4 > Cl^- > Ca^{2+} > Na+ > HCO_3^- > K^+ > Mg^{2+} > NO_3^-$. The average concentration of all the major ions exceeds the maximum permissible limits. Box and whisker plot for the major ion concentration and trace elements are shown in Fig. 2a, b. The plots represents the lower quartile, median, upper quartile, mean, maximum and minimum values for the major ions and trace elements.

TDS shows the maximum interquartile range. Among the cations, Ca^{2+} shows the maximum interquartile range followed by Na^+, K^+ and Mg^{2+}. SO_4^{2-} shows the maximum interquartile range followed by Cl^-, HCO_3^- and NO_3^- among the anions.

Hydrochemical evaluation

The TDS content of the samples ranges from 1,015 to 18,970 mg/l with an average of 7,214 mg/l. The rate of evaporation, rock composition and chemical composition of rain water controls the overall chemistry of the groundwater in a given area (Gibbs 1970). The log of TDS versus Na^+/Na^++Ca^{2+} and $Cl^-/Cl^-+HCO_3^-$ of the analyzed samples from the study area is plotted on the Gibbs diagram. Though the Gibbs plots (Fig. 3a) indicates that evaporation is the major dominating factor controlling the overall water chemistry of the region, the plot of Na/Cl versus EC indicates that it is not completely true in the present case. In general if evaporation is the major process governing the groundwater chemistry of a given area, Na/Cl versus EC plot should be a straight line, indicating that the Na/Cl ratio remains constant with increasing salinity (Jankowski and Acworth 1997; Mrazovac et al. 2012). Though weakly correlated, the Na/Cl ratio shows an increase with increasing salinity (Fig. 3b).

The Ca^{2+}/Mg^{2+} versus HCO_3^-/SO_4^{2-} scatter plot should be a 1:1 line if the dissolution of calcite, dolomite, anhydrite and gypsum is the dominating reactions (Venugopal et al. 2009). Excess of HCO_3^- and SO_4^{2-} will indicate ion exchange, whereas excess of $Ca^{2+}+Mg^{2+}$ will indicate reverse ion exchange (Fisher and Mullican 1997; Belkhiri et al. 2012). In the present study, the samples are distributed on the 1:1 equiline as well as on either side of the line (Fig. 4a), indicating that ion exchange as well as some reverse ion exchange reactions is taking place in the study area. Reverse ion exchange normally occurs in the presence of clays/shale with exchangeable Calcium. The reaction can be represented as follows:

$$2Na^+ + Ca^-Clays = Na^{2-}Clay + Ca^{2+}$$

Ca, Mg and Na take part in ion exchange reactions can be validated by the plot of $Na^+–Cl^-$ versus $(Ca^{2+}+Mg^{2+})–(HCO_3^-+SO_4^{2-})$. If ion exchange is the main process in the system, the plot should form a slope of −1.0 (Fisher and Mullican 1997; Rajmohan and Elango 2004). In the present case (Fig. 4b), it is −1.06 indicating that Ca, Mg and Na concentrations are interrelated through ion exchange process.

On the Na versus Cl plot, the 1:1 equiline indicates the halite dissolution. However, in Fig. 5a, the data points are scattered on either side of the halite dissolution line. Na^+ ions behave conservatively and are not used up in biological processes. Excess Na is indicative of groundwater mixing and cation exchange reactions (Umar et al. 2009). Further cation exchange reactions will increase the concentration of Na relative to Cl due to the release of Na from cation exchange sites (Neal and Kirchner 2000). At the same time, a high ratio of Na^+/Cl^- is also indicative of silicate weathering (Mayback 1987); however, silicate weathering is also accompanied by the domination of bicarbonate ions in the groundwater (Elango and Kannan 2007). In the present study, the bicarbonate ion concentrations are very low; therefore, the possibility of silicate weathering can be ruled out, thereby pointing more toward cation exchange. The excess of Cl over Na as observed in a few samples falling far above the 1:1 equiline (Fig. 5a) can be attributed to the removal of Na from the groundwater as a result of reverse ion exchange.

The ionic relationship between Ca and SO_4 (Fig. 5b) shows good correlation with many samples falling along the 1:1 equiline (pointing toward gypsum dissolution). However, in certain samples, there is excess of SO_4, while in others there is excess of Ca. They combine with the excess of Cl and Na to form calcium chloride ($CaCl_2$) and sodium sulfate (Na_2SO_4) type of groundwater.

Water type

The major ions were plotted in the Piper Diagram (Fig. 6) to understand the main groundwater facies occurring in the region. The groundwater in the study area is represented by an evolved type of facies where the lack of recent groundwater recharge coupled with evaporation and rock–water interaction has resulted in the groundwater losing its initial meteoric signature. The cationic triangle is dominated by the presence of Ca^{2+} ions followed by Na^+ ions. The anionic triangle is dominated by the presence of SO_4^{2-} ions followed by Cl^- ions. On the diamond of the piper diagram, majority of the samples fall within the Cl–SO_4 type of groundwater facies, whereas few samples fall

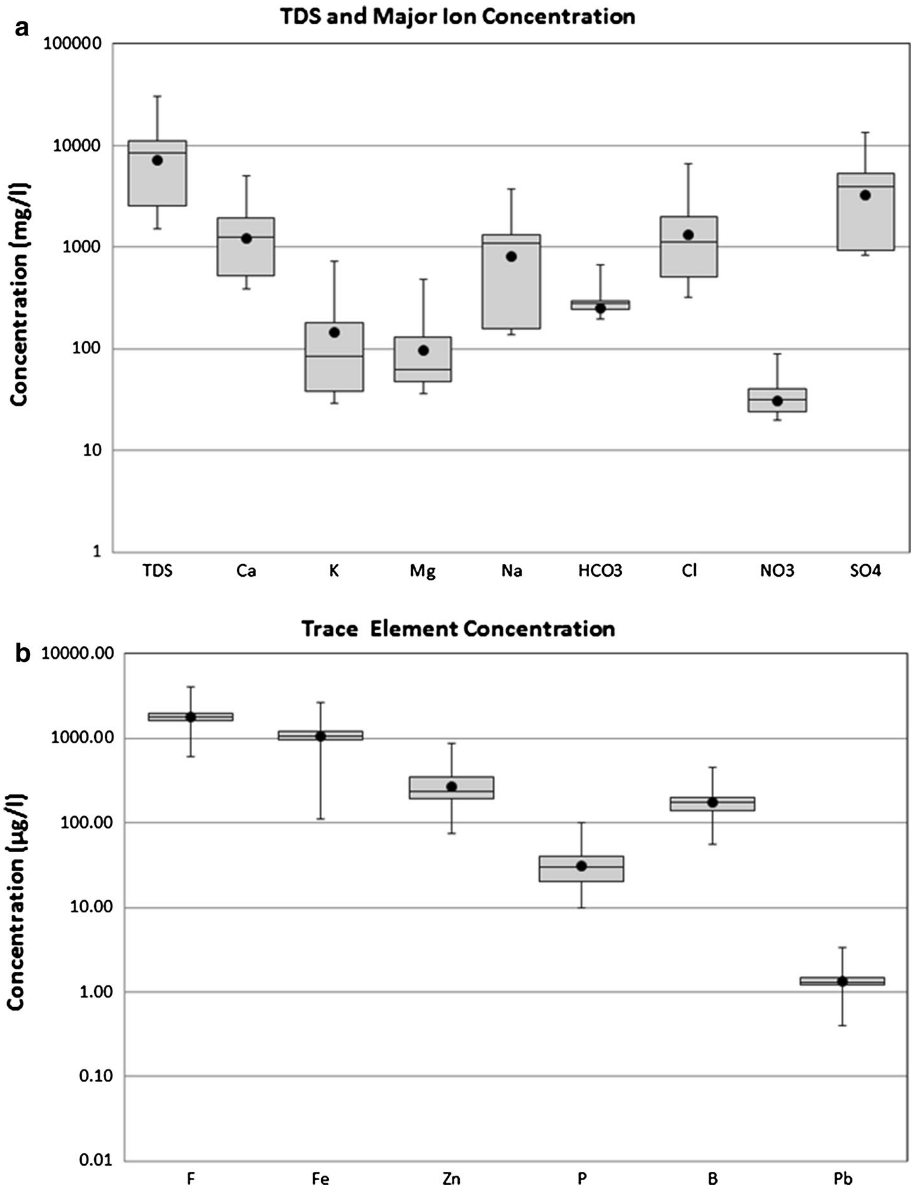

Fig. 2 **a** Box plot for TDS and major ion concentration. **b** Box plot for trace element concentration

within the Ca(Mg)–Cl(SO_4) facies. A closer look at the facies shows that the samples are in general dominated by the presence of Ca^{2+} and SO_4^{2-} ions. The detailed groundwater facies and the number of samples falling within each facies have been given in Fig. 6. Ca–Na–SO_4–Cl type of groundwater facies is the most dominant type of facies occurring in the area with 73 samples falling within this class. The Ca–Na–SO_4–Cl type and the Ca–SO_4–Cl type (8 samples) represent the groundwater samples that are influenced by rock–water interaction (mainly gypsum dissolution and ion exchange). The Ca–Cl–SO_4 facies (6 samples) and the Ca–Na–Cl–SO_4 (1 sample) are represented by reverse ion exchange process. The Na–Ca–Cl–SO_4 type (1 sample) is influenced by the evaporation process, whereas the Na–Ca–SO_4–Cl type (8 samples) represents the facies that is influenced by evaporation as well as the ion exchange process. All the groundwater samples fall within the zone of permanent hardness due to the formation of non-carbonate salts. Table 2 shows the formation-wise distribution of the number of samples falling within each water class. Khuff aquifer shows the maximum variability with samples falling within each of the six water types. The water samples showing reverse ion exchange (Ca–Cl–SO_4 type) are characterized by the presence of shale in the geological formation (Table 2).

Irrigation water quality

The sodium adsorption ratio (SAR) versus electrical conductivity (EC) diagram (Fig. 7) is an informative plot for

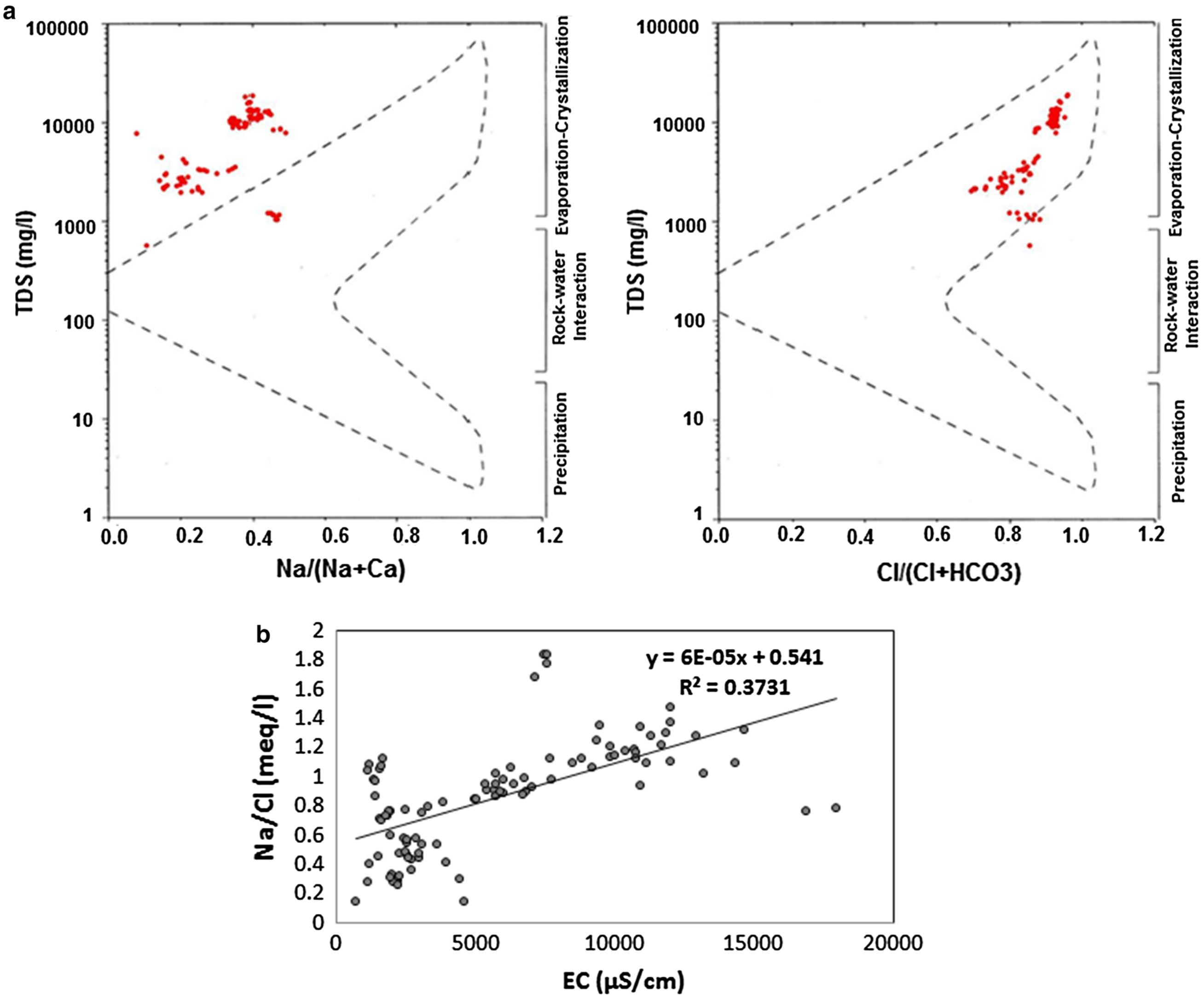

Fig. 3 **a** Gibbs plot showing the dominant factor controlling the groundwater chemistry. **b** Na/Cl versus EC plot

determining the suitability of the groundwater for agriculture. Sodium readily replaces other cations present in the soil, resulting in sodium hazard. The SAR gives an idea about the degree of this replacement and is expressed as

$$\frac{\mathrm{Na}}{\sqrt{\frac{(\mathrm{Ca}+\mathrm{Mg})}{2}}}$$

The average SAR values of the groundwater is less than 10 (7.65), which renders it fit for irrigation; however, on the basis of SAR versus EC plot, the agricultural water quality can be divided into four types that include (i) high salinity—low alkalinity type, (ii) very high salinity—low alkalinity type, (iii) very high salinity—high alkalinity type and (iv) very high salinity—very high alkalinity type. Based on the EC values, the agricultural water quality ranges from highly to very highly saline and is not suitable for irrigation purpose. The average EC value is 5,843 µ/cm and falls within the very high salinity hazard range.

The concentration of NO_3 in natural groundwater may vary up to 10 mg/l; however, the presence of anthropogenic activities (agriculture/septic systems/animal manure) can elevate its concentration (Widory et al. 2004) much beyond the WHO permissible limit of 50 mg/l (WHO 1997). Though the nitrate value ranges from 4 to 49 mg/l in the study area with an average of 31 mg/l which is well below the maximum permissible limit, its possible source is mainly attributed to the extensive use of fertilizers in the region (Nazzal et al. 2014).

Trace element chemistry

Among the trace element/minor ion, fluoride shows the maximum concentration with an average of 1.767 mg/l, whereas lead has the lowest concentration with an average

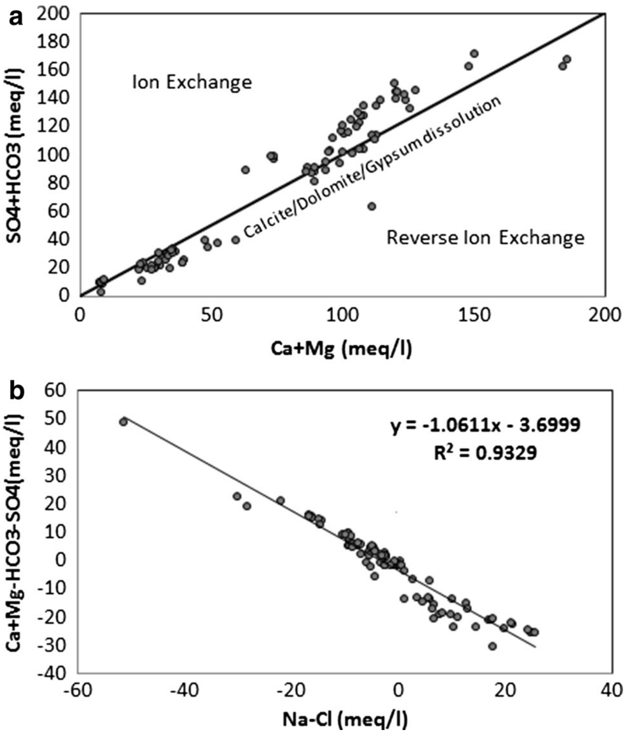

Fig. 4 **a** SO_4+HCO_3 versus Ca+Mg plot. **b** Ca+Mg–HCO_3–SO_4 versus Na–Cl plot

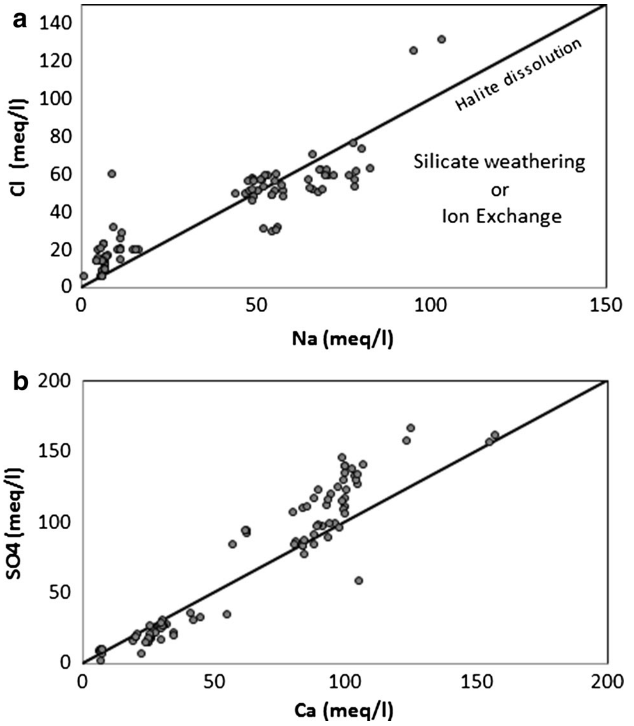

Fig. 5 **a** Cl versus Na plot. **b** SO_4 versus Ca plot

of 1.37 µg/l. The trace element concentrations in the analyzed samples are as follows: $F^{-}>Fe^{3+}>Zn^{2+}>B^{3+}>P^{3-}>Pb^{2+}$.

The fluoride (F) levels in the collected water sample exceed the maximum permissible limit of 1.5 mg/l with a mean value of 1.76 mg/l. The exact cause and nature of the occurrence of fluoride need to be investigated. Small quantities of fluoride may be present in the groundwater due to the dissolution of fluorite-bearing minerals such as apatite, fluorite and some mica (Weinstein and Davison 2004; Chae et al. 2007). However, the enrichment of fluoride in groundwater has also been attributed to anthropogenic activities (Ramanaiah et al. 2006; Brindha et al. 2010).

Iron (Fe) is one of the eight most abundant elements found in the earth's crust and can easily contaminate groundwater. Though it is an essential element for healthy human growth, its presence in quantities in excess of the WHO prescribed limits of 300 µg/l makes it unfit for human consumption (WHO 2011). The average value for the iron in the ground water samples is 1069.87 µg/l, which is much above the prescribed limit for drinking water.

Zinc (Zn) is an essential micronutrient, which is important from human growth and its concentration in groundwater from geogenic sources seldom increases 100 µg/l (WHO 2011). Zinc concentration in the groundwater samples of the study area has an average value of 270.18 µg/l).

Phosphorous (P) concentrations in natural groundwater seldom exceed 0.02 mg/l; however, in the present case, it is much higher than this value. The average value in the analyzed samples is 0.03 mg/l.

Boron (B) can be a health hazard if it is present in excess of 500 µg/l (WHO 1997), and the enhanced concentrations can be attributed to anthropogenic influences or from hydrothermal influences on infiltrating water or mineral weathering, dissolution of evaporates or sea water intrusion (Ravenscroft and McArthur 2004). The average concentration of boron in the analyzed samples is 174.33 µg/l, which is below the prescribed limits.

Concentrations of lead (Pb) in natural groundwater seldom exceed 5 µg/l; however, higher concentrations reaching up to 100 µg/l can be found in areas where Pb is being used in plumbing fixtures (WHO 2011). Exposure to groundwater containing more than 10 µg/l can have severe health consequences, especially for infants and children. The average lead concentration in the study area is about 1.37 µg/l.

Principal component analysis

The multivariate statistical technique used in the present study was PCA. The SPSS (version 17) package was used to extract the principal components on 16 measured water-quality parameters (variables). The parameters included are EC, TDS, Na, K, Mg, Ca, HCO_3, SO_4, Cl, NO_3, F, Fe, Pb,

Fig. 6 Piper plot for the analyzed groundwater samples

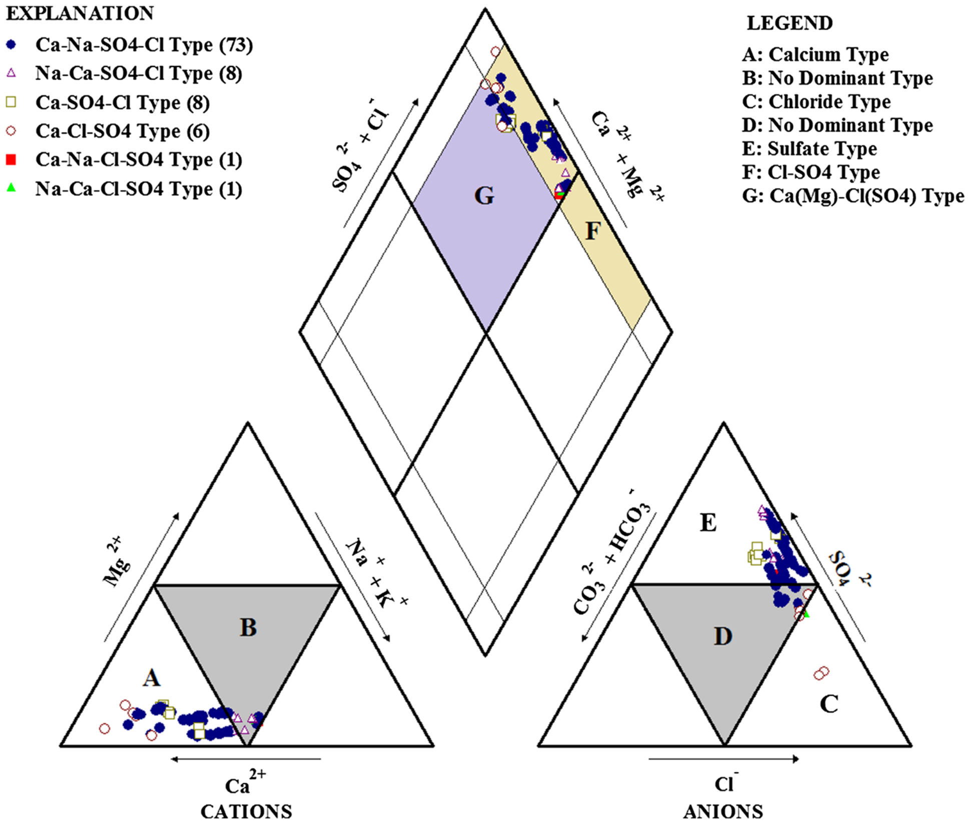

Table 2 Formation wise water type distribution for each sample

Name of formation	Generalized lithology	Number of samples falling in each water type					
		Type 1	Type 2	Type 3	Type 4	Type 5	Type 6
KHARJ (3)	Limestone, lacustrine limestone, gypsum and gravel	2		1			
ARAB (1)	Calcarenite, calcarenitic and aphanitic limestone, dolomite and some anhydrite			1			
JUBAILA (3)	Aphanitic limestone and dolomite; subordinate calcarenite and calcarenitic limestone	1	2				
HANIFA (5)	Aphanitic limestone, calcarenitic limestone and calcarenite	5					
TUWAIQ (1)	Aphanitic limestone; subordinate calcarenite and calcarenitic limestone	1					
DHRUMA (12)	Aphanitic limestone and shale; subordinate calcarenite	12					
MARRAT (9)	Shale and aphanitic limestone; subordinate sandstone	7			2		
JILH (5)	Sandstone, aphanitic limestone and shale; subordinate gypsum	4		1			
KHUFF (29)	Limestone and shale	23	2	1	1	1	1
TABUK (2)	Sandstone and shale	2					
SAQ (25)	Sandstone. Includes a zone of several thin layer of shale	14	4	4	3		
GRANITIC GNEISS (2)	Genissic gray granites; subordinate younger granites	2					

Type 1 Ca–Na–SO_4–Cl, *Type 2* Na–Ca–SO_4–Cl, *Type 3* Ca–SO_4–Cl, *Type 4* Ca–Cl–SO_4, *Type 5* Ca–Na–Cl–SO_4, *Type 6* Na–Ca–Cl–SO_4

Numbers in bracket shows the collected water samples from the respective formation

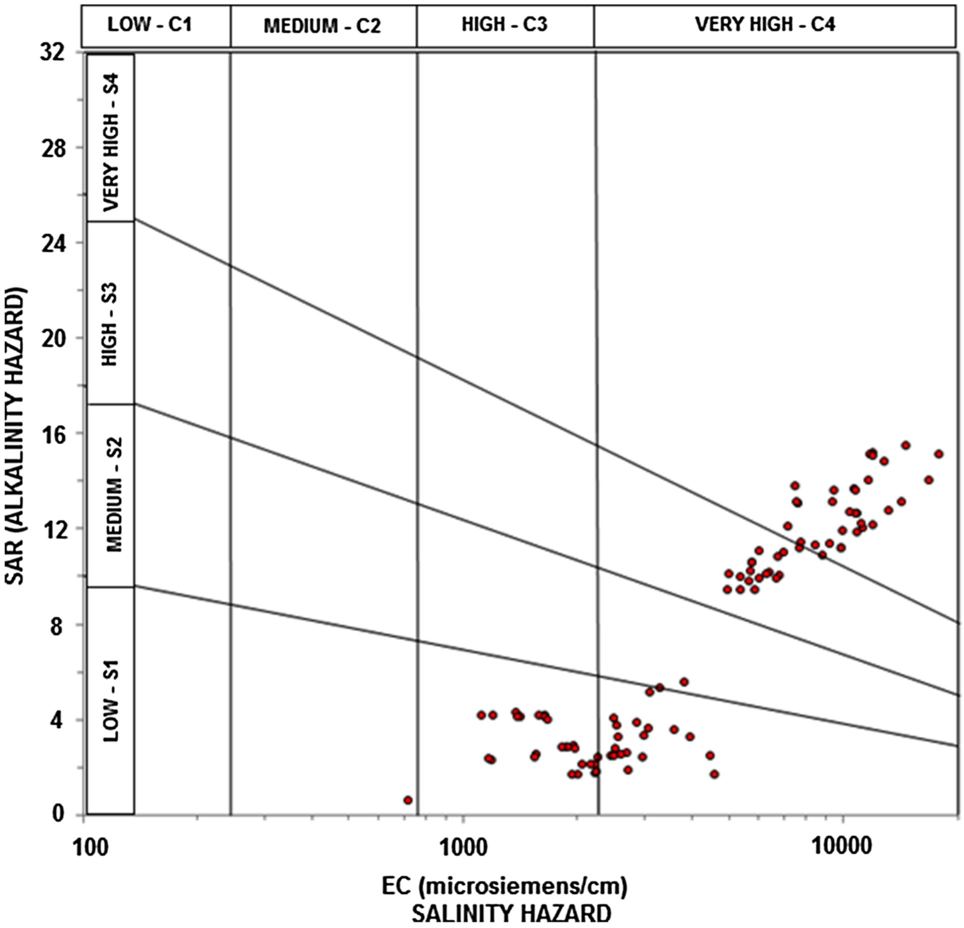

Fig. 7 SAR versus EC diagram showing the suitability of water for irrigation

P, B and Zn. Kaiser criterion that eliminates all PCs with eigen values less than 1 was used along with varimax rotation to reduce the contribution of parameters with minor significance. Four principal components (PC) that accounted for approximately 72.9 % of the data variability were extracted. Table 3 shows the variables and the extracted principal components

The very high TDS values (average 7174.36 mg/l) and EC (average 5842.68 μ/cm) are reflected in the PCA as the first principal component is dominated by the major ions. This PC accounts for 47.5 % of the total data variability. In all, the PC consists of 9 variables that include TDS, EC, Na, K, Mg, Ca, HCO_3, SO_4 and Cl^- with loadings ranging from 0.748 to 0.991. The high factor loadings of EC, TDS and the major ions are mainly attributed to the processes related with gypsum dissolution, evaporation and ion exchange and reverse ion exchange. In short, PC 1 reflects the natural processes that have affected the groundwater quality in the region.

PC2 accounts for 9.8 % of the total principal component variability and is represented by significant loadings of F, P and Pb with factor loadings ranging from 0.507 to 0.692. The F values in the water-quality analysis shows an average concentration of 1.77 mg/l that is more than WHO prescribed maximum permissible limit for drinking water. The high values of F can be attributed to geogenic as well as anthropogenic causes. Groundwater with elevated F concentrations has been reported by many workers in arid regions with high rates of evapotranspiration and low rainfall (Gao et al. 2007; Naseem et al. 2010). Rock water interaction involving the dissolution of fluoride-bearing minerals such as muscovite and biotite which are commonly found in sedimentary rock formation can be one of the possible sources. High fluoride concentrations can also be a result of anthropogenic activities such as application of phosphatic fertilizers (Brunt et al. 2004; Chen et al. 2010), which is quite frequent in the study area. To ascertain the exact cause of F in the study area, further investigations (rock mineralogy, temporal variations in fluoride levels) are required.

The high loading of P in PC2 can be a result of the anthropogenic activities as geogenic processes seldom result in phosphorous concentrations in excess of 0.02 mg/l. The elevated concentrations of phosphorus can be derived from point sources such as the use of laundry detergent in

Table 3 Loading of the 16 physico-chemical parameters on the first 4 principal components for 97 groundwater samples

Variable	PC1	PC2	PC3	PC4
EC	**0.957**	−0.014	−0.013	0.034
TDS	**0.991**	0.016	0.052	0.021
Ca	**0.969**	0.014	0.113	−0.008
K	**0.768**	0.005	−0.2	0.22
Mg	**0.877**	0.045	−0.164	0.071
Na	**0.955**	0.009	0.054	0.024
HCO_3	**0.748**	0.115	0.268	−0.203
Cl	**0.947**	−0.013	0.096	0.02
SO_4	**0.981**	0.024	0.026	0.023
NO_3	0.08	0.362	**0.663**	−0.16
F	0.118	**0.507**	0.173	−0.155
Fe	0.154	0.173	0.198	**0.836**
Zn	0.05	0.321	**−0.796**	−0.168
P	−0.022	**0.692**	−0.101	0.235
B	0.027	0.206	0.311	−0.487
Pb	−0.055	**0.665**	−0.035	−0.027
Eigen values	7.614	1.57	1.377	1.103
% of variance explained	47.585	9.814	8.606	6.892
% cumulative variance	47.585	57.399	66.005	72.897

Extraction Method: Principal Component Analysis

Rotation Method: Varimax with Kaiser Normalization

Values in bold represent significant factor loadings

domestic use or from diffuse sources such as the use of phosphate fertilizers on agricultural lands (Chen et al. 2010; Sharifi and Sinegani 2012).

Pb is the third important parameter, which shows a high factor loading in PC2. The corrosion of old galvanized pipes, especially those made of brass can also be an important source of lead in the analyzed samples (Lytle and Schock 1997; Schock 1990; Gardels and Sorg 1989). The elevated concentrations in the study area are mainly attributed to the use of old plumping fixtures mainly in the form of pipes that are used to pump up the water from the boreholes and have undergone considerable corrosion with time.

PC3 shows 8.6 % of the total principal component variability and is dominated by significant positive factor loading of NO_3 (0.663) and negative loading for Zn (−0.796).

Under natural conditions, the nitrate concentration in groundwater seldom exceeds 10 mg/l (Widory et al. 2004); however, its concentration is often elevated by anthropogenic activities that involve the use of nitrogenous compounds such as mineral fertilizers and as by-products of organic compounds from agriculture, septic systems and animal manure (McLay et al. 2001; Squillace et al. 2002; Pastén-Zapata et al. 2014). Nitrate is one of the most important contaminants of groundwater, especially in agricultural areas, and points toward anthropogenic sources (Alabdula'aly et al. 2010; Qin et al. 2013; Nazzal et al. 2014). The average concentration of nitrate in the study area is 31 mg/l that though less than the maximum permissible limit for drinking water (50 mg/l), but shows enrichment mainly due to the application of mineral fertilizers in the agricultural farms.

The concentration of Zn in natural groundwater varies from 0.1 to 0.5 mg/l and is not a health concern (WHO 1997). The natural occurrences of zinc in groundwater may be dependent on the weathering conditions (Singh et al. 2010). High zinc concentrations may also be associated with the use of nitrate fertilizers that may contain up to 1 % of Zn as a micronutrient (Güler et al. 2010). However, the negative loading of Zn in the present case suggests that Zn concentrations are higher in areas where the nitrate concentrations are low and vice versa, thereby suggesting a different source of Zn enrichment (other than fertilizers). Studies have shown that brass plumbing fixtures can be a major source of copper, nickel and zinc (Kimbrough 2001, 2007, 2009) in the pumped/supplied water. The average concentration of Zn in the analyzed samples is about 0.27 mg/l and is mainly related to the dissolution from plumbing fittings.

The fourth PC that is dominated by a high factor loading of Fe (0.836) represents 6.89 percent of the total principal component variability. Iron concentrations are very high in the study area with average values of 1.767 mg/l that is much higher than the prescribed limits of 0.3 mg/l. Iron occurs naturally in all the groundwater derived mainly from the weathering of silicate minerals. The high concentrations in groundwater can be attributed low dissolved oxygen content in groundwater as a result of which reductive dissolution of iron oxides/hydroxides found in the sediments may take place (Güler et al. 2012). Anthropogenic causes such as corrosion of steel and iron pipes in the water distribution system (WHO 2011), acid mine drainage (Bigham et al. 1996; Gagliano et al. 2004) and leachate from landfills (Fletcher 2002) can also cause iron enrichment in the natural groundwater. The high concentration of iron in the study area could possibly be a mix of geogenic and anthropogenic sources.

Conclusion

Hydrochemical investigations of the groundwater samples in the study area indicate that rock–water interaction as well as evaporation has played a major role in the evolution of the groundwater chemistry. Piper plot of the analyzed sample indicates six types of groundwater facies dominated mainly by the presence of sulfates and chlorides. The water is not suitable for domestic use owing to its very high salinity and the high concentrations of major ions, which are above the maximum permissible limits. Though the SAR values for the collected groundwater samples range from low to very high, but the high to very high salinity values render it unfit for agricultural use.

PCA was carried out to understand geological or anthropogenic processes responsible for the hydrochemical variability in the collected samples. Based on the analysis, four principal components were extracted. The first principal component was dominated by the high factor loadings of all the major ions indicating a geogenic source for their enrichment in the groundwater of the area. The main processes involved are rock–water interaction and evaporation and crystallization resulting in a high TDS content and salinity in the samples. The second principal component was characterized by the significant factor loadings of fluoride, phosphorous and lead, indicating a mixed source. The third component that again highlights the anthropogenic activities is shown by the high factor loadings of nitrate and zinc. The fourth principal component is highlighted by the presence of geogenic as well as anthropogenic factors responsible for the occurrence of iron in the groundwater.

The overall results of the study reveal the fact that both geogenic and anthropogenic sources contribute to the groundwater chemistry. The geogenic factors include dissolution, ion exchange and evaporation. Some samples are also characterized by reverse ion exchange. The main anthropogenic factor affecting groundwater quality is the application of inorganic fertilizers on agricultural farms, which has led to the high concentrations of nitrate and phosphorous. Anthropogenic factors such as use of old and corroded plumbing fixtures are mainly responsible for the high concentrations of lead, zinc and iron.

Policies should be made to regulate and restrict the amount of inorganic fertilizers to be used in the farms. A periodic inspection of the pumping units should be made mandatory so as to avoid the high concentrations of elements such as lead, zinc and iron in the pumped water. The origin of fluoride in the groundwater of the study area needs to be further investigated. Finally, a groundwater monitoring network for the periodic assessment of groundwater quality should be made.

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References

Alabdula'aly AI, Al-Rehaili AM, Al-Zarah AI, Khan MA (2010) Assessment of nitrate concentration in groundwater in Saudi Arabia. Environ Monit Assess 161(1–4):1–9

Alaya MB, Saidi S, Zemni T, Zargouni F (2014) Suitability assessment of deep groundwater for drinking and irrigation use in the Djeffara aquifers (Northern Gabes, south-eastern Tunisia). Environ Earth Sci 71(8):3387–3421

Al-Bassam AM (2006) Evaluation of ground water quality in Al-Qassim area, Saudi Arabia, using cluster and factor analyses. Kuwait J Sci Eng 33(2):101–121

APHA (1995) Standard methods for the examination of water and wastewater, 19th edn. American Public Health Association, Washington DC

Belkhiri L, Mouni L, Tiri A (2012) Water–rock interaction and geochemistry of groundwater from the Ain Azel aquifer, Algeria. Environ Geochem Health 34(1):1–13

Bigham JM, Schwertmann U, Traina SJ, Winland RL, Wolf M (1996) Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochim Cosmochim Acta 60(12):2111–2121

Brindha K, Rajesh R, Murugan R, Elango L (2010) Natural and anthropogenic influence on the fluoride and nitrate concentration of groundwater in parts of Nalgonda district, Andhra Pradesh, India. J Appl Geochem 12(2):231–241

Brunt R, Vasak L, Griffioen J (2004) Fluoride in groundwater: probability of occurrence of excessive concentrations on global scale. International Groundwater Resources Assessment Centre (AGRAC) Report SP 2004–2

Chae GT, Yun ST, Mayer B, Kim KH, Kim SY, Kwon JS, Kim K, Koh YK (2007) Fluorine geochemistry in bedrock groundwater of South Korea. Sci Total Environ 385(1):272–283

Chaudhuri S, Ale S (2014) An appraisal of groundwater quality in Seymour and Blaine aquifers in a major agro-ecological region in Texas, USA. Environ Earth Sci 71(6):2765–2777

Chen X, Wo F, Chen C, Fang K (2010) Seasonal changes in the concentrations of nitrogen and phosphorus in farmland drainage and groundwater of the Taihu Lake region of China. Environ Monit Assess 169(1–4):159–168

Closs LG, Nichol I (1975) The role of factor and regression analysis in the interpretation of geochemical reconnaissance data. Can J Earth Sci 12(8):1316–1330

Davis JC (2002) Statistics and data analysis in geology, 3rd edn. Wiley, New York ISBN-9780471172758

Dregne HE (1991) Global status of desertification. Ann Arid Zone 30:179–185

Elango L, Kannan R (2007) Rock–water interaction and its control on chemical composition of groundwater. Dev Environ Sci 5:229–243

ESCWA (2001) The role of desalinated water in augmentation of the water supply in selected ESCWA member countries, Report No. E/ESCWA/ENR/2001/19, United Nation, New York

Fisher RS, Mullican WF (1997) Hydrochemical evolution of sodium-sulphate and sodium-chloride groundwater beneath the northern Chihuahuan desert, Trans-Pecos, Texas, USA. Hydrogeol J 5:4–16

Fletcher T (2002) Neighbourhood change at Love Canal: contamination, evacuation and resettlement. Land Use Policy 19:311–323

Gagliano WB, Brill MR, Bigham JM, Jones FS, Traina SJ (2004) Chemistry and mineralogy of ochreous sediments in a constructed mine drainage wetland. Geochim Cosmochim Acta 68(9):2119–2128

Galazoulas EC, Petalas CP (2014) Application of multivariate statistical procedures on major ions and trace elements in a multilayered coastal aquifer: the case of the south Rhodope coastal aquifer. Environ Earth Sci 72(10):4191–4205

Gao X, Wang Y, Li Y, Guo Q (2007) Enrichment of fluoride in groundwater under the impact of saline water intrusion at the salt lake area of Yuncheng basin, northern China. Environ Geol 53(4):795–803

Gardels MC, Sorg TJ (1989) Laboratory study of the leaching of lead from water faucets (No. PB-90-104498/XAB; EPA-600/J-89/

086). Environmental Protection Agency, Cincinnati, OH (USA). Drinking Water Research Divison

Gibbs RJ (1970) Mechanisms controlling world's water chemistry. Science 170:1088–1090

Gleeson T, Wada Y, Bierkens MF, van Beek LP (2012) Water balance of global aquifers revealed by groundwater footprint. Nature 488(7410):197–200

Güler C, Alpaslan M, Kurt MA, Temel A (2010) Deciphering factors controlling trace element distribution in the soils of Karaduvar industrial-agricultural area (Mersin, SE Turkey). Environ Earth Sci 60(1):203–218

Güler C, Kurt MA, Alpaslan M, Akbulut C (2012) Assessment of the impact of anthropogenic activities on the groundwater hydrology and chemistry in Tarsus coastal plain (Mersin, SE Turkey) using fuzzy clustering, multivariate statistics and GIS techniques. J Hydrol 414:435–451

Hu S, Luo T, Jing C (2012) Principal component analysis of fluoride geochemistry of groundwater in Shanxi and Inner Mongolia, China. J Geochem Explor 135:124–129

Jankowski J, Acworth RI (1997) Impact of debris-flow deposits on hydrogeochemical processes and the development of dryland salinity in the Yass River catchment, New South Wales, Australia. Hydrogeol J 5(4):71–88

Kaiser HF (1960) The application of electronic computers to factor analysis. Educ Psychol Meas 20:141–151

Kimbrough DE (2001) Possible role of brass corrosion and the USEPA's lead and copper rule monitoring program. J Am Water Works Assoc 93(9):81–91

Kimbrough DE (2007) Brass corrosion as a source of lead and copper in both traditional and all-plastic distribution systems. J Am Water Works Assoc 99(8):70–76

Kimbrough DE (2009) Source identification of copper, lead, nickel, and zinc loading in wastewater reclamation plant influents from corrosion of brass in plumbing fixtures. Environ Pollut 157(4):1310–1316

Kolsi SH, Bouri S, Hachicha W, Dhia HB (2013) Implementation and evaluation of multivariate analysis for groundwater hydrochemistry assessment in arid environments: a case study of Hajeb Elyoun-Jelma, Central Tunisia. Environ Earth Sci 70:2215–2224

Llamas R, Custudio E (2003) Intensive use of groundwater: challenges and opportunities. A.A. Balkema Publishers, Lisse

Loni OA, Zaidi FK, Alhumimidi MS, Alharbi OA, Hussein MT, Dafalla, AlYousef KA, Kassem OMK (2014) Evaluation of groundwater quality in an evaporation dominant arid environment; a case study from Al Asyah area in Saudi Arabia. Arab J Geosci. doi:10.1007/s12517-014-1623-4

Lytle DA, Schock MR (1997) An investigation of the impact of alloy composition and pH on the corrosion of brass in drinking water. Adv Environ Res 1(2):213–233

Martínez-Mena M, Albaladejo J, Castillo V (1998) Factors influencing surface runoff generation in a Mediterranean semi-arid environment: Chicamo watershed, SE Spain. Hydrol Process 12:741–754

Mayback M (1987) Global chemical weathering of surficial rocks estimated from river dissolved loads. Am J Sci 287:401–428

McLay CDA, Dragten R, Sparling G, Selvarajah N (2001) Predicting groundwater nitrate concentrations in a region of mixed agricultural land use: a comparison of three approaches. Environ Pollut 115(2):191–204

MoWA (1980) Umm Er Radhuma study. Unpublished report, Ministry of Agriculture and Water, Kingdom of Saudi Arabia

MoWE (2008) Investigations for updating the groundwater mathematical models of the Saq and overlying aquifers. Unpublished report, Ministry of Water and Electricity, Kingdom of Saudi Arabia

Mrazovac S, Vojinović-Miloradov M, Matić I, Marić N (2012) Multivariate statistical analyzing of chemical parameters of groundwater in Vojvodina. Chemie der Erde-Geochemistry. 73(2):217–225

Naseem S, Rafique T, Bashir E, Bhanger MI, Laghari A, Usmani TH (2010) Lithological influences on occurrence of high-fluoride groundwater in Nagar Parkar area, Thar Desert, Pakistan. Chemosphere 78(11):1313–1321

Nazzal Y, Ghrefat H, Rosen MA (2013) Application of multivariate geostatistics in the investigation of heavy metal contamination of roadside dusts from selected highways of the Greater Toronto Area, Canada. Environ Earth Sci 71(3):1409–1419

Nazzal Y, Ahmed I, Al-Arifi NS, Ghrefat H, Zaidi FK, El-Waheidi MM, Batayneh A, Zumlot T (2014) A pragmatic approach to study the groundwater quality suitability for domestic and agricultural usage, Saq aquifer, northwest of Saudi Arabia. Environ Monit Assess 186(8):4655–4667

Neal C, Kirchner JW (2000) Sodium and chloride levels in rainfall, mist, stream water and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls. Hydrol Earth Syst Sci Dis 4(2):295–310

Osterkamp WR, Friedman JM (2002) The disparity between extreme rainfall events and rare floods—with emphasis on the semi-arid American West. J Hydrol Processes 14:2817–2829

Parizi HS, Samani N (2013) Geochemical evolution and quality assessment of water resources in the Sarcheshmeh copper mine area (Iran) using multivariate statistical techniques. Environ Earth Sci 69(5):1699–1718

Pastén-Zapata E, Ledesma-Ruiz R, Harter T, Ramírez AI, Mahlknecht J (2014) Assessment of sources and fate of nitrate in shallow groundwater of an agricultural area by using a multi-tracer approach. Sci Total Environ 470:855–864

Powers RW, Ramirez LF, Redmond CD, Elberg EL (1966) Geology of the Arabian peninsula. Geol Surv Prof Paper 560:1–147

Qi SZ, Luo F (2006) Hydrological indicators of desertification in the Heihe River Basin of arid northwest China. J Human Environ 35(6):319–321

Qin D, Qian Y, Han L, Wang Z, Li C, Zhao Z (2011) Assessing impact of irrigation water on groundwater recharge and quality in arid environment using CFCs, tritium and stable isotopes, in the Zhangye Basin, Northwest China. J Hydrol 405(1):194–208

Qin R, Wu Y, Xu Z, Xie D, Zhang C (2013) Assessing the impact of natural and anthropogenic activities on groundwater quality in coastal alluvial aquifers of the lower Liaohe River Plain, NE China. Appl Geochem 31:142–158

Rajmohan N, Elango L (2004) Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins, Southern India. Environ Geol 46(1):47–61

Ramanaiah SV, Mohan SV, Rajkumar B, Sarma PN (2006) Monitoring of fluoride concentration in ground water of Prakasham district in India: correlation with physico-chemical parameters. J Environ Sci Eng 48(2):129–134

Ravenscroft P, McArthur JM (2004) Mechanism of regional enrichment of groundwater by boron: the examples of Bangladesh and Michigan, USA. Appl Geochem 19(2004):1413–1430

Salman AS, Zaidi FK, Hussein MT (2014) Evaluation of groundwater quality in northern Saudi Arabia using multivariate analysis and stochastic statistics. Environ Earth Sci. doi:10.1007/s12665-014-3803-7

Scanlon BR, Keese KE, Flint AL, Flint LE, Gaye CB, Edmunds WM, Simmers I (2006) Global synthesis of groundwater recharge in semi-arid and arid regions. Hydrol Process 20:3335–3370

Schock MR (1990) Causes of temporal variability of lead in domestic plumbing systems. Environ Monit Assess 15(1):59–82

Sharifi Z, Sinegani AAS (2012) Assessment of arsenic, nitrate and phosphorus pollutions in shallow groundwater of the rural area in Kurdistan province (Iran). Curr World Environ 7(2):233–241

Singh SK, Singh CK, Mukherjee S (2010) Impact of land-use and land-cover change on groundwater quality in the Lower Shiwalik hills: a remote sensing and GIS based approach. Cent Eur J of Geosci 2(2):124–131

Squillace PJ, Scott JC, Moran MJ, Nolan BT, Kolpin DW (2002) VOCs, pesticides, nitrate, and their mixtures in groundwater used for drinking water in the United States. Environ Sci Technol 36(9):1923–1930

Umar R, Absar A (2003) Chemical characteristics of groundwater in parts of the Gambhir River basin, Bharatpur District, Rajasthan, India. Environ Geol 44(5):535–544

Umar R, Ahmed I, Alam F, Khan MMA (2009) Hydrochemical characteristics and seasonal variations in groundwater quality of an alluvial aquifer in parts of Central Ganga Plain, Western Uttar Pradesh, India. Environ Geol 58:1295–1300

Varol S, Davraz A (2014) Assessment of geochemistry and hydrogeochemical processes in groundwater of the Tefenni plain (Burdur/Turkey). Environ Earth Sci 71(11):4657–4673

Venugopal T, Giridharan L, Jayaprakash M, Periakali P (2009) Environmental impact assessment and seasonal variation study of the groundwater in the vicinity of River Adyar, Chennai, India. Environ Monit Assess 149(1–4):81–97

Water Atlas of Saudi Arabia (1984) Ministry of Agriculture and Water in cooperation with the Saudi Arabian–United States Joint Commission on Economic Cooperation, Ministry of Agriculture and Water, p 112

Webster R (2001) Statistics to support soil research and their presentation. Eur J Soil Sci 52(2):331–340

Weinstein LH, Davison A (2004) Fluoride in the environment: effects on plants and animals. CABI Publishing, Wallingford

WHO (1997) Guidelines for drinking-water quality: Surveillance and control of community supplies, vol 3. World Health Organization, Switzerland

WHO (2011) Guidelines for drinking-water quality, 4th edn. World Health Organization, Switzerland (ISBN: 9789241548151)

Widory D, Kloppmann W, Chery L, Bonnin J, Rochdi H, Guinamant JL (2004) Nitrate in groundwater: an isotopic multi-tracer approach. J Contam Hydrol 72(1):165–188

Yidana SM, Banoeng-Yakubo B, Akabzaa TM (2010) Analysis of groundwater quality using multivariate and spatial analyses in the Keta basin, Ghana. J Afr Earth Sci 58(2):220–234

Zaidi FK, Kassem OMK (2012) Use of electrical resistivity tomography in delineating zones of groundwater potential in arid regions: a case study from Diriyah region of Saudi Arabia. Arab J Geosci 5(2):327–333