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ORIGINAL ARTICLE

Water quality assessment and hydrochemical characterization of Zamzam groundwater, Saudi Arabia

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Abstract This study focuses on chemical and microbial analyses of 50 Zamzam water samples, Saudi Arabia. The soluble ions, trace elements, total colony counts, total coliform group, and *E. coli* were determined and compared with WHO standards. The obtained results indicated that the dissolved salts, soluble cations and anions, Pb, Cd, As, Zn, Cu, Ni, Co, Fe, Mn, Cr, PO_4^{3-}, NO_2^-, Br^-, F^-, NH_4^+, and Li^+, were within permissible limits for all samples. Yet, 2% of waters contain NO_3^- at slightly high concentration. The water quality index (WQI) reveals that 94% of the samples were excellent for drinking (class I). While the remaining was unsuitable due to total coliform group contamination "class (V)". Durov diagram suggest no clear facies and dominant water type can be noted. It indicates mixing processes of two or more different facies might be occurring in the groundwater system. All studied waters were undersaturated with respect to halite, gypsum, fluorite, and anhydrite. These minerals tend to dissolve and increase water salinity. A direct relationship between Zamzam water salinity and rainfall is recorded. The water salinity fluctuated between 4500 mg L^{-1} (year 1950) and 500 mg L^{-1} (year 2015) based on rainfall extent. The approach applied can be used to similar groundwater worldwide.

Keywords Zamzam · Groundwater quality · Water quality index · AquaChem software

Introduction

It is unnecessary to say that the quality of water is the most significant concerns of human health, especially in arid environment (Al-Omran et al. 2012). Sometime, humans have to use water contaminated by disease vectors, pathogens, or improper concentrations of toxins (William and Frank 2000). Using this water may lead to various diseases and sometimes death. Monitoring drinking groundwater is essential to confirm its safety (USEPA 2007). The hydrochemical and microbial analyses of groundwater have a substantial role in assessing water quality (Tiwari 2011). Countless people drink Zamzam groundwater in Saudi Arabia (Shomar 2012). According to Arab historians, the Zamzam well has been in use for around 4000 years (Khalid et al. 2014). The major solute chemistry reveals that the water contains high concentration of calcium and its water type is calcium carbonate type. The water is alkaline and the distributions of major salts are: magnesium bicarbonate, magnesium sulfate, sodium and potassium chloride (Shomar 2012; Al-Gamal 2009). The long residence time with aquifer materials of basic lava origin (basalt) led to the formation of ferro-magnesium minerals, soluble calcium and magnesium, in water (Al-Gamal 2009). Shomar (2012) reported that the Zamzam water contains high concentration of As and NO_3 and set above permission limit of WHO; on the other hand, Al Nouri et al. (2014)

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reported that the Zamzam water is free of As contaminations and its concentration sets within permissible limits according to WHO (2011) and SASO (1984). Griffin et al. (2007) reported that the Zamzam water contains high concentration of Fluoride and some other element. Mashat (2010) reported that the Zamzam water has no sign of biological growth due to it is naturally pure and salt-sterilized contents. In 1971, the ministry of agriculture and water resources sent Zamzam water samples to the European laboratories to test its potability. The results indicated that the water can be considered suitable for drinking; nevertheless, it contains slightly high concentration of fluoride, calcium, and magnesium (The annual report of the ministry of agriculture and water resources 1971). Calcium and magnesium in water and food are known to have antitoxic activity. They can help prevent the absorption of some toxic elements such as lead and cadmium from the intestine into the blood, either via direct reaction leading to formation of a non-absorbable compound or via competition for binding sites (Kozisek 2004). In addition, the WHO (1980) concluded that the populations supplied with low-mineral water may be at a higher risk in terms of adverse effects from exposure to toxic substances compared to populations supplied with water containing adequate mineral and hardness. Furthermore, the low mineral water and low TDS may cause salts to be leached from the human body. Shomar (2012) reported that the top 14 m of the Zamzam well is excavated in the sandy alluvium of the Wadi Ibrahim; however, the lower 17 m is located in the diorite bedrock. A 0.5-m-thick highly permeable weathered rock located between the alluvium and bedrock was observed. Most of the alluvial section of the well is lined with stone except for the uppermost 1 m, which has a reinforced concrete collar. The water enters to Zamzam well from alluvial section and at depth 13 m from surface. In attempting to test the well flow rate, a pumping machine at 8000 L s^{-1} was operated for more than 24 h. This test showed a decrease in the level of water by about 10 m and then the water level stopped receding. The water level recovered to its approximately original surface just after 11 min after pumping had stopped (ZSRC 2011). The aquifer feeding the Zamzam well appears to recharge from rock fractures in adjacent mountains around Mecca (Makkah). Therefore, the well taps groundwater primarily from the spring-fed alluvium and to a lesser extent from water percolating up through the permeable, weathered fresh bedrock (ZSRC 2011). This study aims to investigate the chemical and microbiological composition of Zamzam water, assess Zamzam waters for drinking purposes, and finally classify the hydrochemical characterization of Zamzam well.

Materials and methods

Study area

Mecca city is located in western part of Saudi Arabia about 70 km to the south of the city of Jeddah on the coast of the Red Sea. Mecca is bound by latitudes 21°26′48″N and longitudes 39°53′46″E with an elevation of about +1399 ft (Al-Gamal 2009) (Fig. 1). The city of Mecca contains AlMsgied Alharam. The Ka'ba Amosharafa is located inside the Alharam and Zamzam well located at about 20 m east of the Ka'ba (Fig. 2) (Koshak 1983). Al-Gamal (2009) recorded that the recharge of Zamzam well may have occurred during the last Holocene humid period and that the aquifer is now discharging ancient groundwater resources.

Chemical and microbiological analysis

Fifty water samples were collected from different locations in Saudi Arabia (Supplementary Table 1). Three samples were collected from the original well in Mecca, 13 samples from taps connected to the original well, ten samples from ice box filled with Zamzam water inside and outside Alharam in Mecca, three samples from Zamzam bottled Water Company in Mecca, 15 samples from Al-Madenah Almonawara, and six samples from Riyadh city. The Zamzam waters of Al-Madenah were transported from Mecca by government; however, Riyadh Zamzam waters were transported from bottled water company in Mecca by traders and sold in supermarkets and food stores in Riyadh. All samples were gathered, stored in ice box, and transported to King Saud University labs for analyses.

Microbiological analysis

Several microbiological estimations were conducted in this study, including the total colony counts, total coliform group, and *E. coli*. The total numbers of colony were determined by nutrient agar method; however, the coliform group and *E. coli* were determined by Colilert (defined substrate) method as described by Eckner (1998) and Maheux et al. (2008).

Chemical analysis

The water electrical conductivity (EC) in dS m^{-1} was measured using EC meter at 25 °C (Test kit Model 1500-20, Cole and Parmer); however, the pH was measured by pH meters (CG 817) (APHA 1998). In Addition, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), lithium (Li^{+}), potassium (K^{+}), ammonium ($NH_4{}^{+}$), fluoride (F^{-}), bromide

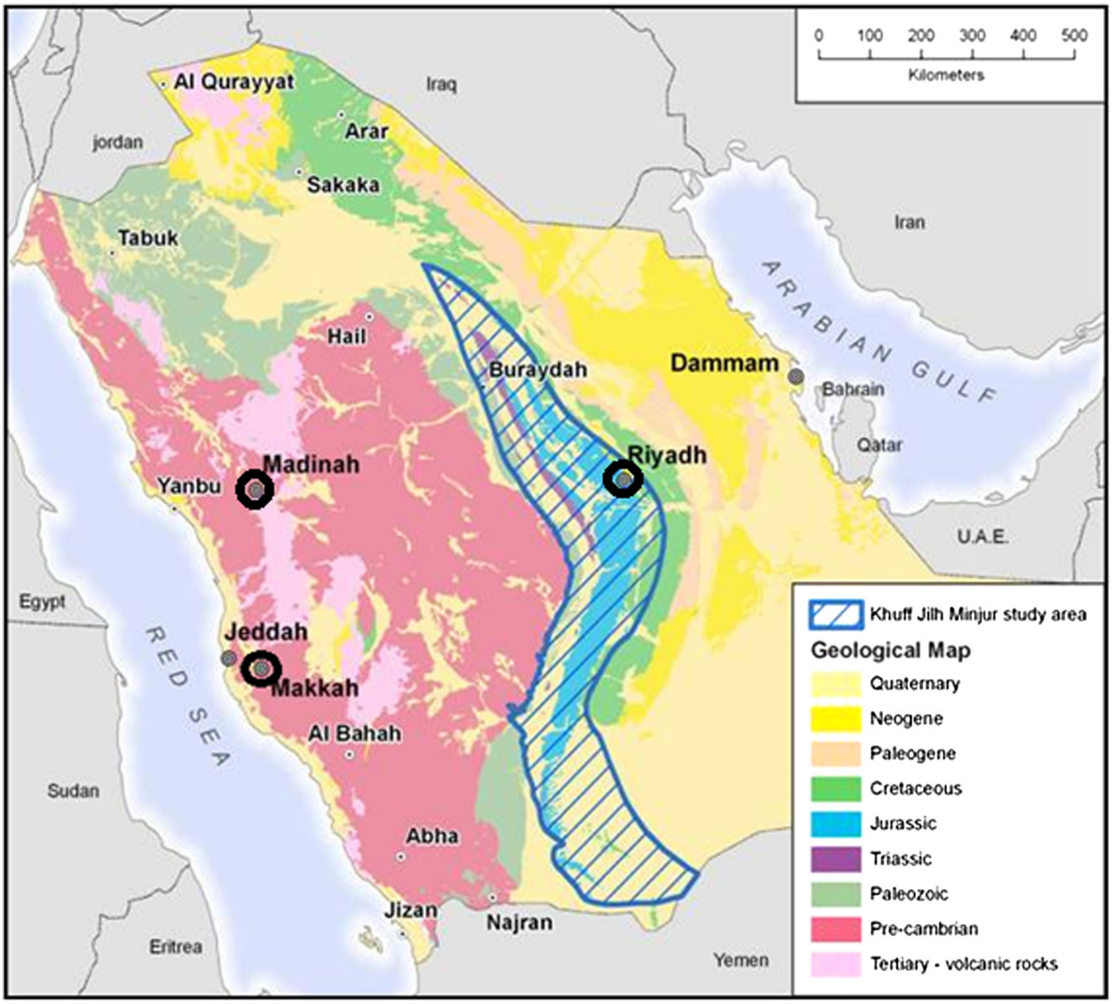


Fig. 1 Geological map of Saudi Arabia showing the locations of sampling Zamzam waters in Makkah (Mecca) Alocarama, Madinah Almoawara, and Riyadh city (The original well is located in Mecca)

(Br$^-$), chloride (Cl$^-$), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), nitrate (NO_3^-), and nitrite (NO_2^-) were determined using ion chromatography system (ICS 5000, Thermo (USA)). The arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) were measured using ICP-Perkin Elmer Model 4300DV. Furthermore, carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) were determined by titration with sulfuric acid (H_2SO_4) (Matiti 2004).

Standards and chemicals

Dionex combined cation standard and anion standard solutions and PerkinElmer quality control multi-element standards were purchased and used as a stock standard for preparing working standards of ICS and ICP, respectively. All solutions were stored in precleaned high-density polyethylene (HDPE) bottles and refrigerated at 4 °C. The working standards were prepared by serial volume/volume dilution in polypropylene vials (Sarstedt, Germany). Micropipettes (Eppendorf, Sigma-Aldrich) with disposable tips were used for pipetting all solutions. High-purity water (18.2 MΩ) was prepared using a Millipore ion-exchange system fed with deionized water (US filter).

Ion balance errors

The accuracy of chemical analysis was confirmed by calculating ion balance errors; moreover, blanks and standard solutions were frequently run to check for probable errors in the analytical processes. The error level in the data was calculated by the following method (Appelo and Postma 1996):

$$\text{Error of ion balance} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100. \tag{1}$$

An error of up to ±3% is tolerable, while every water sample with a calculated error outside this range has to be

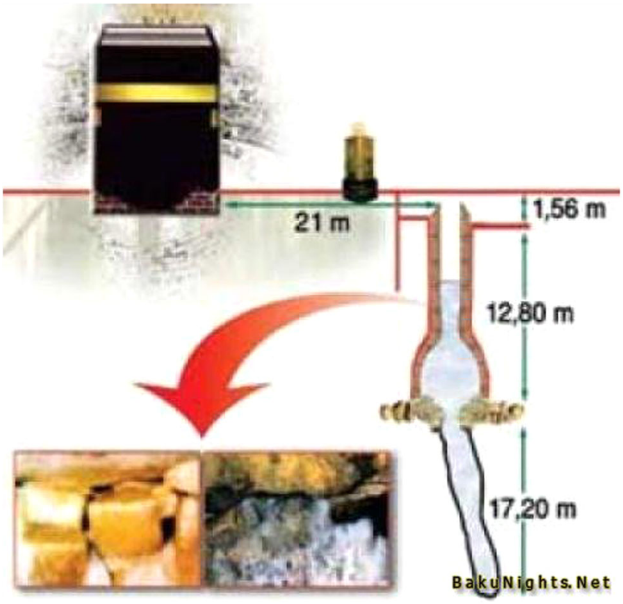


Fig. 2 Depth and location of Zamzam well near to Ka'ba Amosharafa (ZSRC 2011)

re-measured. Approximately 95% of the measured water samples were fall within this range. This means that the resultant data qualities are sufficient for chemical modeling and/or for drawing simple conclusions about water quality.

Water quality indices computing

The water quality index (WQI) calculations include three sequential steps as in Yidana and Yidana (2010), Al-hadithi (2012) and Aly et al. (2015). In this study, minor modification was performed when water contains coliform group and/or *E. coli*. The water is classified directly without calculation to be unsuitable for drinking (Al-Omran et al. 2015).

The first step is '*assigning weight*': each of the 13 parameters, with exception coliform group and/or *E. coli*, has been assigned a weight (wi), according to its relative importance in the overall drinking water quality as shown in Supplementary Table 2. The most significant parameters gave a weight of 5 and the least significant gave a weight of 1. The coliform group and *E. coli* gave no weight; however, the water quality changed directly to class V (water unsuitable for drinking). In this study, the maximum weight of 5 referred to As, Cd, Pb, NO_3, NO_2, and total counts; due to its adverse effect on water quality assessment (Ramakrishnalah et al. 2009), the less harmful elements, i.e., Fe, Zn, and Mn have been given a weight of 1.

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

$$\mathrm{Wi} = \frac{\mathrm{wi}}{\sum_{i=1}^{n} \mathrm{wi}}, \tag{2}$$

where Wi is the relative weight, wi is the weight of each parameter, and n is the parameters number. The calculated relative weight (Wi) values of each parameter are given in Supplementary Table 2.

The third step is '*quality rating scale calculation*': the quality rating scale (qi) for each parameter is calculated as follows:

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

where qi is the quality rating, Ci is the concentration of each chemical parameter in each water sample in mg L^{-1}, except pH, and Si is the WHO (2011) standard for each chemical parameter (Supplementary Table 2). In this study the WHO standard is adopted since the limits of this standard are the same as the local limits of KSA standard. Finally, Wi and qi are used to calculate the SI*i* for each chemical parameter, and then the WQI is calculated from the following equation:

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

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

where SI*i* is the sub index of each parameter; qi is the rating of each parameter, and n is the parameter number. The calculated WQI values are categorized into five classes (Supplementary Table 3).

Hydrochemical characteristics

The hydrochemical characterization of the groundwater samples was evaluated by means of major ions, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, and SO_4^{2-}. The chemical analysis data of the water samples were plotted on the Piper, Schoeller, and Durov diagrams using Geochemistry Software AquaChem 2014.2 for the identification of water types.

Geochemical modeling

Interactions between water and the surrounding rocks and soil are considered to be the main processes controlling the observed chemical characteristics of the water. The deviation of water from equilibrium with respect to dissolved minerals is quantitatively described by the saturation index (SI). The SI of a mineral is obtained from the following formula:

$$\mathrm{SI} = \log \mathrm{IAP}/k_t, \qquad (6)$$

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

The hydro-geochemical equilibrium model, Phreeqc model (Parkhurst and Appelo 1999), was used to calculate the SI of the groundwater with respect to the main mineral phases.

Results and discussion

Long-term Zamzam water salinity and rainfall monitoring

In this study, the Zamzam water salinity is monitored for long-term using our data for the years 2009, 2013 and 2015, and the salinity recorded by Salama (2005), Khalid et al. (2014), American Bedu (2010), and Custodian of the two Holy Mosques Institute for Hajj Research. Furthermore, the long-term water salinity is linked to the rainfall data gathered from WMO (2013) and Dawod et al. (2012) to investigate the impact of rainfall on Zamzam well water salinity (Fig. 3). It was noticed that there is direct relationship between water salinity and rainfall. In world dry period, between 1901 and 1950, the well water salinity increased dramatically to reach 4500 mg L^{-1}; however, it decreased in the wet period (1950–1965) to reach an average of 1800 mg L^{-1}. Since the average rainfall in Mekkah Almokaramah increased from 59 mm in the period of 1966–1989 to 109 mm in the period of 1990–2015 (Dawod et al. 2012) (Fig. 3), the water salinity decreased dramatically to reach 500 mg L^{-1} in the year 2015. Periodic monitoring seasonally and for long-term of Zamzam well hydrochemistry is recommended for more understanding of the well water chemistry and salinity behavior with rainfall (Aly et al. 2016).

Water quality assessment for drinking purpose

Microbial assessment

The results of this study showed that all studied Zamzam waters were free of *E. coli* contamination; moreover, the total colony counts (CFU) fall within the permissible limits for all samples. The USEPA (2009) allow microbial load of 500 CFU/mL; on the other hand, no cell of *E. coli* permit. Three water samples (6%) were found unsuitable due to total coliform contamination. The total coliform groups in the three samples were 689.6, 1986.3, and 1102 (CFU/100 mL); nevertheless, the remaining (94%) have no total coliforms. The samples collected from the main sources were found free of this contamination; consequently, this contamination is caused by an external source as a result of

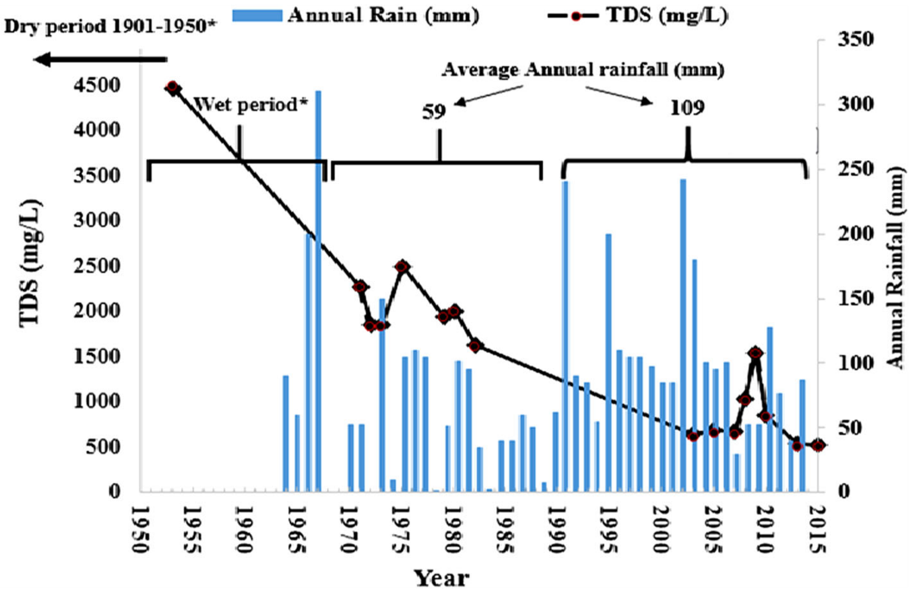


Fig. 3 Relationship between rainfall of Mekkah and Zamzam water salinity (TDS values of years 1953, 1972, 1973, and 1980 were cited by Salama (2005). TDS values of years 1971, 1975, 1982, 2008 were cited by Khalid et al. (2014). TDS values of years 2010 Posted on 2010 by American Bedu. TDS of years 1979 and 2005 cited by Custodian of the two Holy Mosques Institute for Hajj Research. Rainfall data were cited by Dawod et al. (2012). *Asterisk* world wet and dry periods were recorded by WMO (2013))

unacceptable human behavior (Al-Omran et al. 2015; Al-Barakah et al. 2016) (Supplementary Table 1).

Chemical assessment

The groundwater's maximum (max), minimum (min), and standard deviation (SD) of the measured parameters was conducted to find out the parameters which differs from the drinking water standards derived by WHO (2011). It was found that the maximum values of most chemical parameters in the studied water were within the permissible limits of the used standard (Al-Omran et al. 2012; Aly et al. 2013). Only one water sample, (the 2% of the water samples) contains nitrate concentration (52.8 mg L^{-1}) which slightly exceeds the limits given by the literature (WHO 2011; USEPA 2009). Although this study suggests that the Zamzam water salinity was within acceptable limit, most groundwaters in Saudi Arabia are characterized by high salinity (Al-Omran et al. 2012; Aly et al. 2013). The studied groundwater's EC ranged between 0.77 and 0.83 dS m^{-1} (SD = ±0.14); however, the pH lies in between 7.81 and 8.45 (SD = ±0.14). The max, min, and (SD) values of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, CO_3^{2-}, HCO_3^{-}, Cl^{-}, and SO_4^{2-} were 2.82–3.78 (±0.19), 1.90–2.64 (±0.14), 2.92–3.98 (±0.21), 0.39–0.70 (±0.04), 0.00–1.60 (±0.04), 2.20–4.10 (±0.35), 2.86–3.86 (±0.13), and 2.35–2.94 (±0.07) meq L^{-1}, respectively. Furthermore, the max and min concentrations, and (SD) of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb, PO_4^{3-}, NO_3^{-}, NO_2^{-}, Br^{-}, F^{-}, NH_4^{+}, and Li^{+} were 0.092–7.450 (±1.121), 0.028–0.632 (±0.131), 58.476–72.097 (±3.314), 0.009–0.414 (±0.046), 0.729–2.149 (±0.375), 1.687–9.717 (±1.083), 0.000–17.900 (±3.390), 0.006–7.728 (±1.621), 0.040–0.113 (±0.012), 0.000–0.385 (±0.078), 0.000–0.107 (±0.25), 30.00–52.79 (±3.52), 0.00–3.03 (±0.471), 0.230–0.685 (±0.057), 0.780–1.590 (±0.100), 0.000–2.489 (±0.624), and 0.010–0.243 (±0.069) µg L^{-1}, respectively. The average Li^{+} concentration found in water was 0.184 mg L^{-1}. The Li^{+} is considered a valuable elements when presence in drinking water since it reduced the incidence rates of suicide, homicide, and rape (Schrauzer and Shrestha 1990; Ohgami et al. 2009; Al-Barakah et al. 2016). F^{-} was also found in high concentrations in studied water samples and set within the recommended level of WHO (2011) standard. The mean value of F^{-} in the water is 0.9 mg L^{-1}.

Drinking water quality index

The computed WQI values for the studied Zamzam waters reveal that 94% of the water samples were excellent for drinking (class I), and their WQIs were ranged between 28 and 41 with an average of 31 (Fig. 4), Only 6% were considered unsuitable for drinking "class (V)" due to microbial contamination by total coliforms (Fig. 4) (Al-Omran et al. 2015; Deshpande and Aher 2012).

Hydrochemical aspects

The chemical data of the Zamzam groundwater samples were plotted on a Piper (1944) and Schoeller (1955), diagrams (Figs. 5, 6). The piper diagrams provide a convenient method to classify water types collected from different groundwater resources, based on the ionic composition of different water samples (Aly 2015; Semerjian 2011; Al-Omran et al. 2012; Baba et al. 2008). The main water types have been identified on the basis of the major ion concentrations such as in Aly and Benaabidate (2010) and Aly et al. (2013). The piper diagram reveals that the main water types of the groundwater are Ca^{2+}–Mg^{2+}/SO_4^{2-}–Cl^{-}. The water type showed that the geology in the Mecca Almokarama may comprise anhydrite and gypsum. The Schoeller diagram reveals that there is a prevalence of

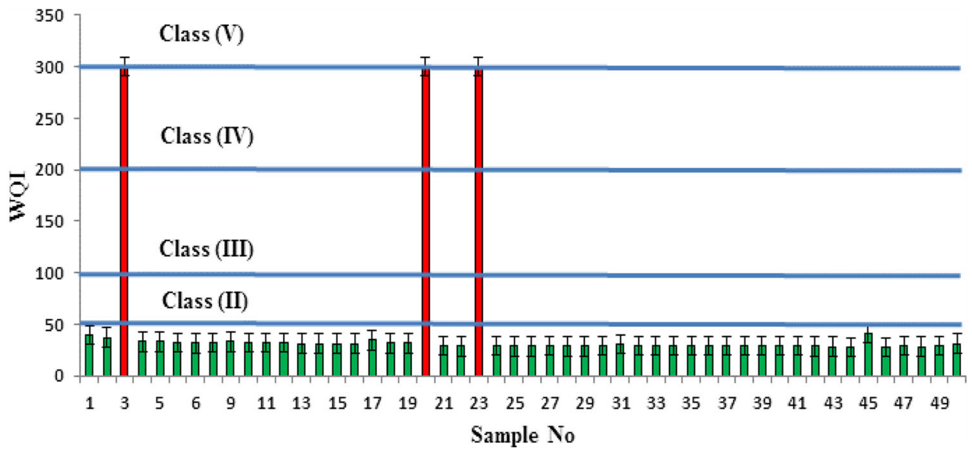


Fig. 4 Values of WQI of studied samples

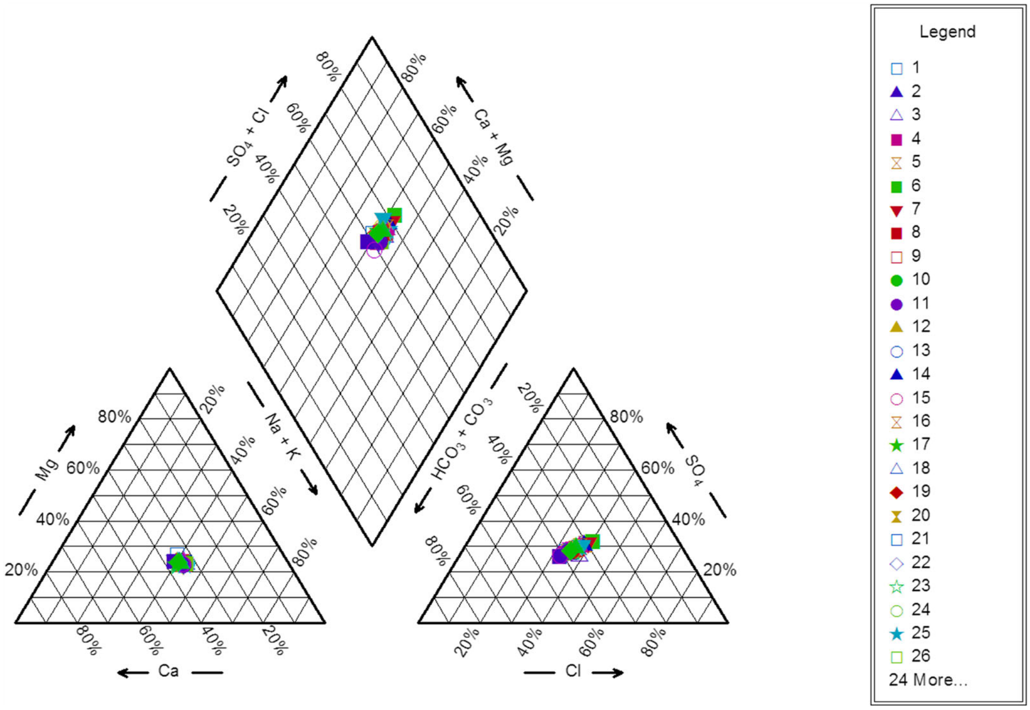


Fig. 5 Piper—tri-linear diagram

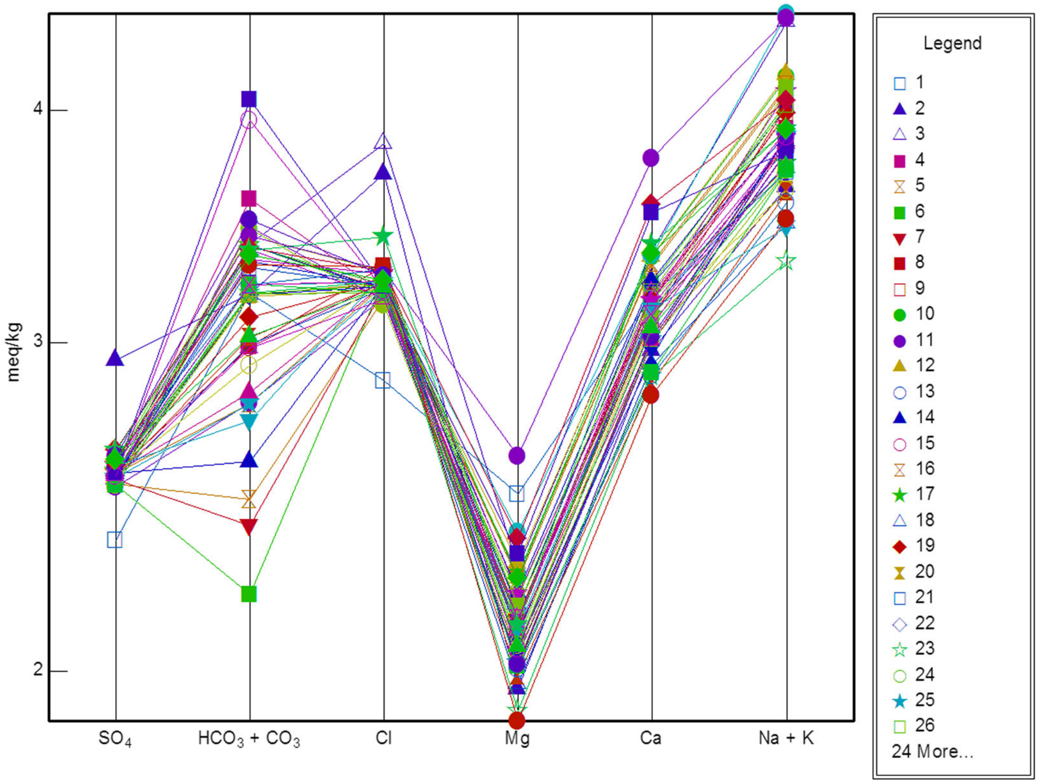


Fig. 6 Schoeller diagram indicating ionic concentrations of groundwater in the study area

Ca^{2+} and Na^{+} which influences the affinities to the HCO_3^{-}, Cl^{-}, and SO_4^{2-} (Fig. 6).

The major ions of the studied groundwater were plotted on Durov's diagram (Fig. 7). Durov's diagram helps the interpretation of the evolutionary trends and the hydrochemical processes occurring in the groundwater system and can indicate mixing of different water types, ion exchange, and reverse ion exchange processes. The result shows that all water samples fall in field 5. The samples belonging to field 5 suggest no clear facies and dominant type of water can be noted; furthermore, it demonstrates that mixing of two or more facies might be going on in groundwater system.

Gibbs's diagrams, representing the ratios of $Na^{+} + K^{+}$: $(Na^{+} + Ca^{2+} + Mg^{2+})$ and Cl^{-}: $(Cl^{-} + HCO_3^{-})$ as a function of TDS, are widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance, and evaporation-dominance (Gibbs 1970). The Chemical data of groundwater samples were plotted in Gibbs's diagrams (Fig. 8). The distribution of samples suggests that the chemical weathering of rock-forming minerals is influencing the groundwater quality. The rock domain suggests that rock–water interaction is the major source of dissolved ions over the control of the groundwater chemistry. The rock–water interaction process includes the chemical weathering of rocks, dissolution–precipitation of secondary carbonates, and ion exchange between water and clay minerals (Subba Rao 2006; Kumar et al. 2014).

Salinity and alkalinity hazard class *Irrigation*

According to US Salinity Laboratory diagram (Richards 1954) in Fig. 9, the salinity and alkalinity hazard class of water samples is C2–S1. The result shows that all groundwaters possess medium salinity hazards with low sodium hazards. This means that this water is suitable for irrigation to almost all crops with no restriction (Lauchli and Epstein 1990).

Geochemical modeling

The saturation index (SI) is the parameter generally used for groundwater. Water is in equilibrium with a mineral

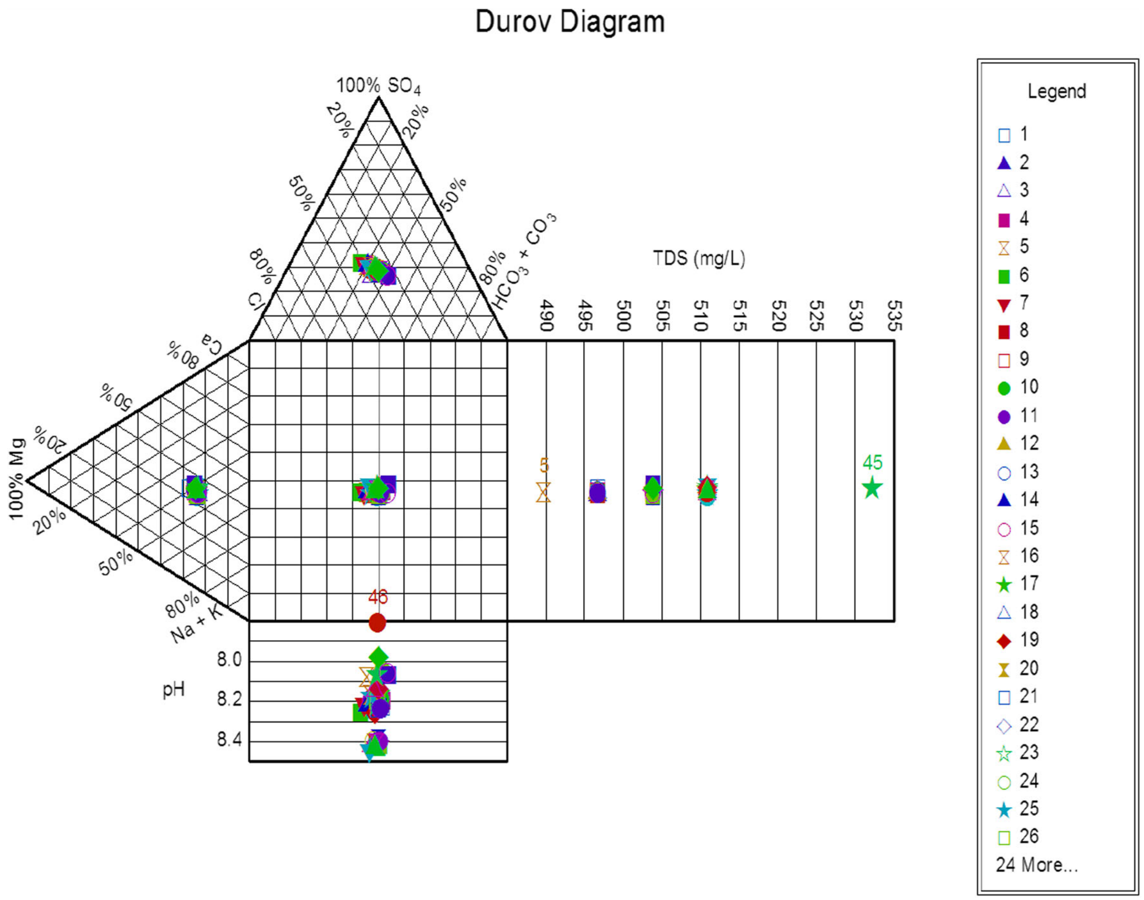


Fig. 7 Durov's diagram for Zamzam groundwater samples: All water fall in field 5 which represents the results of mixing of two or more different facies

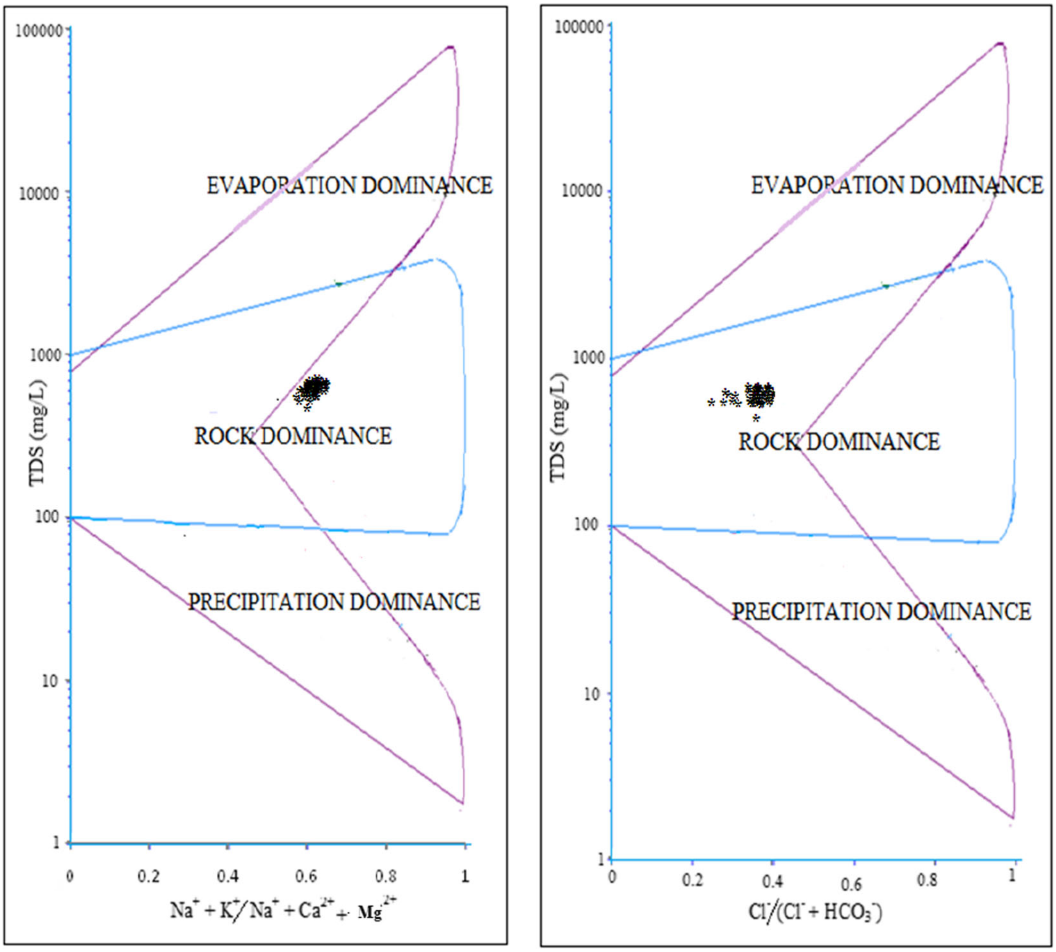


Fig. 8 Diagram depicting the mechanism controlling groundwater quality

when the SI $=$ zero. It is under-saturated if the SI $<$ zero and it is over-saturated when the SI $>$ zero. Nonetheless, to overcome the measurement inaccuracies and changes in the water composition when it makes its way towards the surface, it is proposed to consider a wider range of SI, such as $-1 < \text{SI} < +1$ (Aly 2015).

Figure 10a, b shows the mineral saturation indices (SI) of water calculated by PHREEQC model. The minerals considered by the model were; halite (NaCl), gypsum ($CaSO_4{:}2H_2O$), fluorite (CaF_2), dolomite ($CaMg(CO_3)_2$), Calcite ($CaCO_3$), Aragonite ($CaCO_3$), and anhydrite ($CaSO_4$). The SI indicated that all investigated waters are undersaturated regarding halite, gypsum, fluorite, and anhydrite. However, they are saturated regarding dolomite, calcite, and aragonite (Fig. 8a, b). Consequently, the halite, gypsum, fluorite, and anhydrite minerals tend to dissolve (Alexakis 2011; Aly 2015). Thus, there is opportunity for more Na^+, Ca^{2+}, Cl^-, F, and SO_4^{2-} concentration increase in all investigated samples because of the dissolution of these undersaturated minerals.

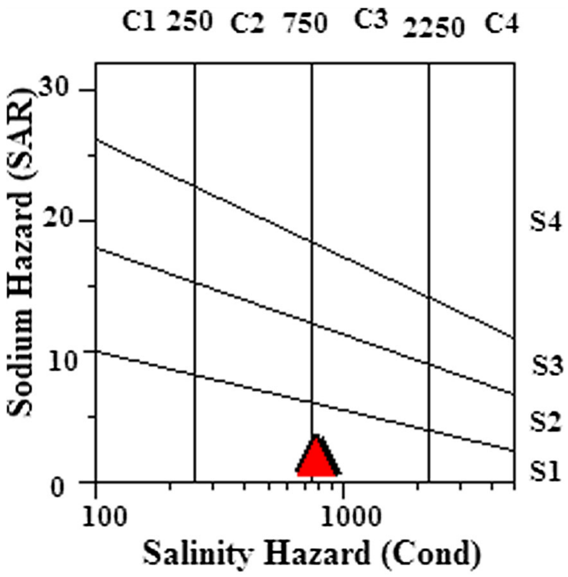
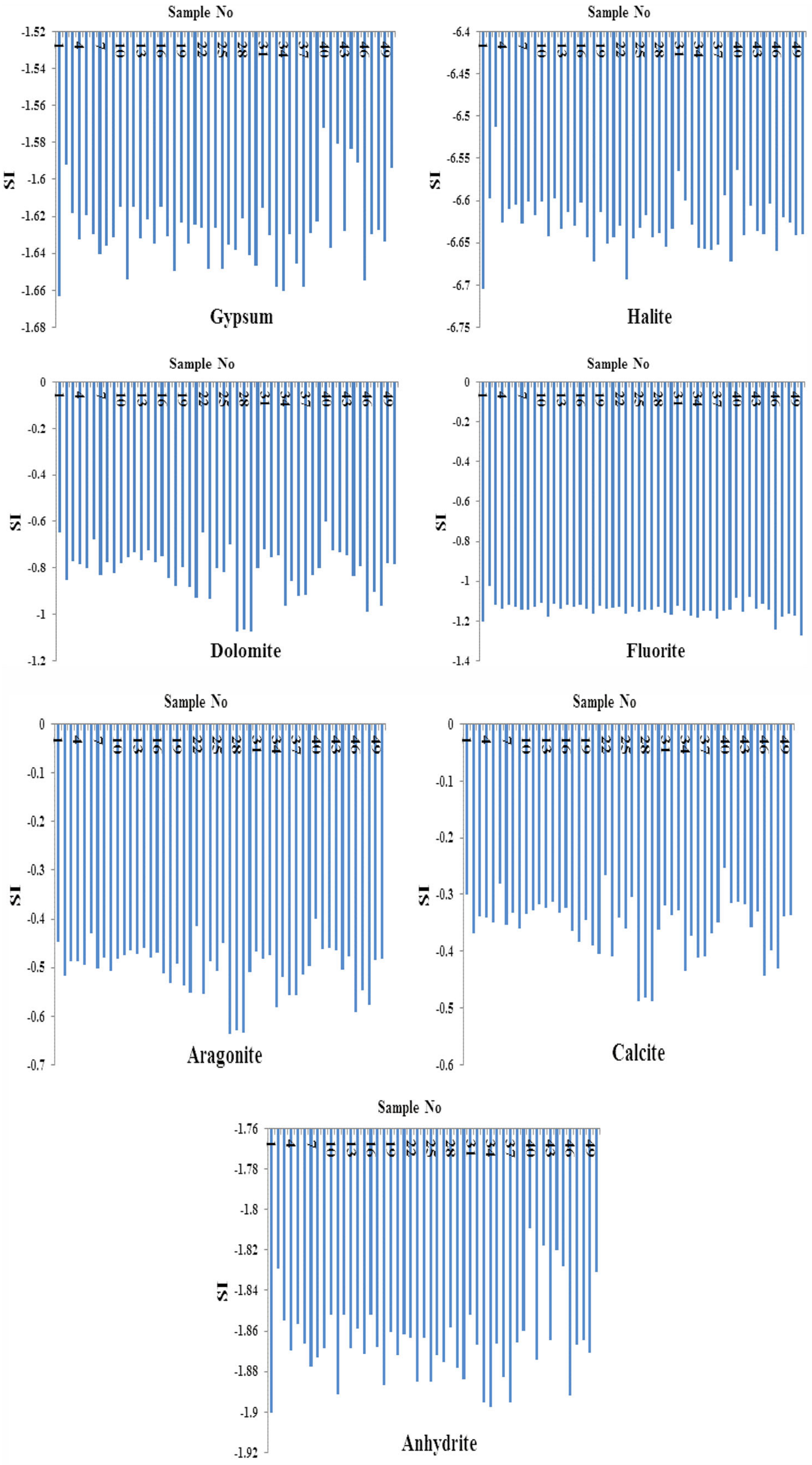


Fig. 9 Salinity classification of Zamzam groundwater if used for irrigation

Fig. 10 The mineral saturation indices (SI) of gypsum, halite, dolomite, fluorite, aragonite, calcite, and anhydrite



Conclusions

In this study, a direct relationship between Zamzam groundwater salinity and rainfall is recorded. The distribution of chemical and microbial constituents of the waters were determined and compared with WHO drinking water quality standard. Furthermore, the water quality index (WQI), a mathematical method used to facilitate water quality explanation, was also calculated. The results revealed that the water lies within acceptable limits with respect to dissolved salts, soluble cations and anions, Pb, Cd, As, Zn, Cu, Ni, Co, Fe, Mn, Cr, PO_4^{3-}, NO_2^-, Br^-, F^-, NH_4^+, and Li^+. The nitrate contents of only a small proportion (2%) of the water samples were slightly exceeded the corresponding permissible limits. The computed WQI values reveal that 94% of the water samples were excellent for drinking (class I), and its WQIs were ranged between 28 and 41 with an average of 31. The remaining water samples were considered unsuitable for drinking "class (V)" due to microbial contamination by total coliforms. The chemical data of the water samples were plotted on Piper, Schoeller, Durov, and Gibbs diagrams. The results concluded that the main water types of the studied well are the following: Ca^{2+}–Mg^{2+}/SO_4^{2-}–Cl^-. The Schoeller diagram reveals that there is a prevalence of Ca^{2+} and Na^+ which influences the affinities to the HCO_3^-, Cl^-, and SO_4^{2-}. The Durov's diagram demonstrates that there are mixing processes of two or more different facies that might be occurring in groundwater system. The distribution of samples in Gibbs's diagrams suggests that the chemical weathering of rock-forming minerals is influencing the groundwater quality. The SI indicated that all investigated waters are undersaturated with respect to halite, gypsum, fluorite, and anhydrite. However, they are saturated with respect to dolomite, calcite, and aragonite. Consequently, the undersaturated minerals tend to dissolve and there is an opportunity for more Na^+, Ca^{2+}, Cl^-, F, and SO_4^{2-}concentration increase in the groundwater.

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