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Assessment of groundwater quality and hydrochemical characteristics in Farashband plain, Iran

Farshid Aref[1] · Reza Roosta[2]

Abstract Groundwater in Farashband plain, Southern Iran, is the main source of water for domestic and agricultural uses. This study was carried out to assess the overall water quality and identify major variables affecting the groundwater quality in Farashband plain. The hydrochemical study was undertaken by randomly collecting 84 groundwater samples from observation wells located in 13 different stations covering the entire plain in order to assess the quality of the groundwater through analysis of major ions. The water samples were analyzed for various physicochemical attributes. Groundwater is slightly alkaline and largely varies in chemical composition; e.g., electrical conductivity (EC) ranges from 2314 to 12,678 μS/cm. All the samples have total dissolved solid values above the desirable limit and belong to a very hard type. The abundance of the major ions is as follows: $Na^+ > Ca^{2+} > Ma^{2+} > K^+$ and $Cl^- > SO_4^{2-} > HCO_3^-$. Interpretation of analytical data shows three major hydrochemical facies (Ca–Cl, Na–Cl, and mixed Ca–Mg–Cl) in the study area. Salinity, total dissolved solids, total hardness, and sodium percentage (Na%) indicate that most of the groundwater samples are not suitable for irrigation as well as for domestic purposes and far from drinking water standard. A comparison of groundwater quality in relation to drinking water standards showed that most of the water samples are not suitable for drinking purposes. Based on the US salinity diagram, most of samples belong to high salinity and low to very high sodium type.

✉ Farshid Aref
  farshidaref@yahoo.com; f.aref@iauf.ac.ir

[1] Department of Soil Science, Faculty of Agriculture, Firouzabad Branch, Islamic Azad University, Firouzabad, Iran

[2] Department of Irrigation and Drainage, Faculty of Agriculture, Firouzabad Branch, Islamic Azad University, Firouzabad, Iran

Introduction

Groundwater has become the main source of water supply for domestic, industrial, and agricultural parts of many countries. Without a well-functioning water supply, it is difficult to imagine productive human activity, be it agriculture or livestock. Due to the ever-increasing demand for potable and irrigation water and inadequacy of available surface water, the importance of groundwater is increasing exponentially every day. Further, about 80% of the diseases and deaths in the developing countries are related to water contamination (UNESCO 2007). It is estimated that approximately one third of the world's population uses groundwater for drinking (Nickson et al. 2005). Iran, like any other developing country of the world, is facing increasing environmental problems. The vast population and ever-increasing industrial activities in Iran make its water resources more vulnerable to water quality deterioration. Groundwater is one of the important sources of water used for domestic and industrial purpose. In Iran, sedimentary aquifers are the important source of groundwater.

Groundwater is the major source of drinking water in Farashband plain, Iran. In the recent past, water demand of the plain has been raised abruptly by increasing population and industrial activities, and it has led to heavy exploitation of the available water resources. In the meantime, the unplanned disposal of the anthropogenic wastes has resulted in an excessive accumulation of pollutant into the land surface and the subsequent leaching of the pollutants has caused the significant degradation of water quality of surface and shallow groundwater of the plain. As a result, there is increasing

dependence to the deep groundwater resource as an alternative, safe, and reliable water source; however, knowledge on groundwater quality is limited, and there is a lack of comprehensive study on groundwater quality. Despite the region's tremendous potential for economic growth, its future is threatened by deteriorating environmental and economic conditions that are not being sufficiently addressed by the present governmental policies and actions.

The global goal of ensuring that human beings have access to acceptable quality water and sufficient quantity faces a number of challenges for the years to come. Urbanization, population mobility, population growth, natural hazards, and lately the anticipated climate change are expected to make matters worse in many parts of the globe (Nalbantis and Tsakiris 2009; Tsakiris et al. 2009). The World Health Organization has estimated that over 1 billion people lack access to safe drinking water and about 4000 children die every day from waterborne disease (Bacha et al. 2010). Water-related diseases are responsible for 80% of all illnesses/deaths in developing countries and kill more than 5 million people every year (UNESCO 2007). The groundwater resources are at higher risk, as its remediation is very difficult. The major anthropogenic activities for continuous groundwater quality deterioration are urbanization, industrialization, and agriculture runoff. Also the problem of drinking water contamination, water conservation, and water quality management has assumed a very important role for sustainable development of countries, such as Iran. Changes in groundwater quality are due to rock–water interaction and oxidation–reduction reactions during the percolation of water through the aquifers. In addition to these processes, water-borne pathogens and toxic and nontoxic pollutants are the major water quality degradation parameters, which are transported from recharge area to discharge area through aquifers by groundwater motion (Chatterjee et al. 2010). Unfortunately, the quality of the largest groundwater reservoir of the Middle East has been deteriorated (Yesilnacar and Gulluoglu 2007).

Water quality plays an important role in promoting agricultural production and standard of human health. The overexploitation of groundwater has detrimentally affected groundwater in terms of the quality and quantity (Janardhana Raju et al. 2009). The suitability of groundwater for drinking purposes is generally assessed by comparing its quality with drinking water standards established by national and international bodies. The water quality parameters beyond the prescribed limits in the standards can render the water nonpotable and may cause adverse health effects (Shankar et al. 2008; Vijay et al. 2011). Water quality analysis is one of the most important aspects in groundwater studies. The hydrochemical study reveals quality of water that is suitable for drinking, agriculture, and industrial purposes. Chemical analysis forms the basis of interpretation of the quality of water in relation to source, geology, climate, and use. Because water is an excellent solvent, it is important to know the geochemistry of dissolved constituents and methods of reporting analytical data (Nagaraju et al. 2014). Excessive amounts of dissolved ions in irrigation water affect plants and agricultural soil physically and chemically, thus reducing the productivity. The physical effects of these ions are to lower the osmotic pressure in the plant structural cells, thus preventing water from reaching the branches and leaves. The chemical effects disrupt plant metabolism (Yesilnacar and Gulluoglu 2008).

In regions of intense agricultural activities, the degradation results from the addition of salts by dissolution during the irrigation process, from salts added as fertilizers or soil amendments, and from the concentration of salts by evapotranspiration. Because irrigation is the primary use of water in arid and semi- arid regions, irrigation return flow can be the major cause of groundwater pollution in such regions (Kumar 2010). The present study investigates the quality of groundwater for drinking as well as irrigation purpose in rural areas of Farashband plain. The data have been analyzed with reference to WHO standard. An attempt has also been made to discuss the major ion chemistry and hydrochemical facies and classify the groundwater on the basis of different classification schemes.

Materials and methods

Study area

Farashband plain in Fars province, situated in the southern part of Iran, is a highly productive agricultural area (Fig. 1). The climate of the study area is categorized as semi-arid, which is dry and hot throughout the year. However, transitional zones between Mediterranean and monsoon climates predominate in winter and early spring. Mean temperature ranges between 30 and 40 °C during summer and between 10 and 20 °C during winter. Annual average rainfall varies between 200 and 250 mm. The plain is underlain by Quaternary alluvial sediments consisting of clay, silt, sand, and gravel of various grades. Different wells have been drilled into the alluvial aquifer, supplying water mainly for irrigation, and show groundwater levels from approximately 60 to 150 m in depth. The aquifer is mainly recharged by precipitation and irrigation water. The most important economic activity of this area is agriculture, and the major crops are palm date, wheat, barley, watermelon, sweet melon, tomato, vegetables, etc. The irrigation system is mostly feed by the groundwater as well as the canal system in this area.

Physicochemical analysis

Groundwater samples were collected from 84 representative wells from 13 different regions in 2015. The
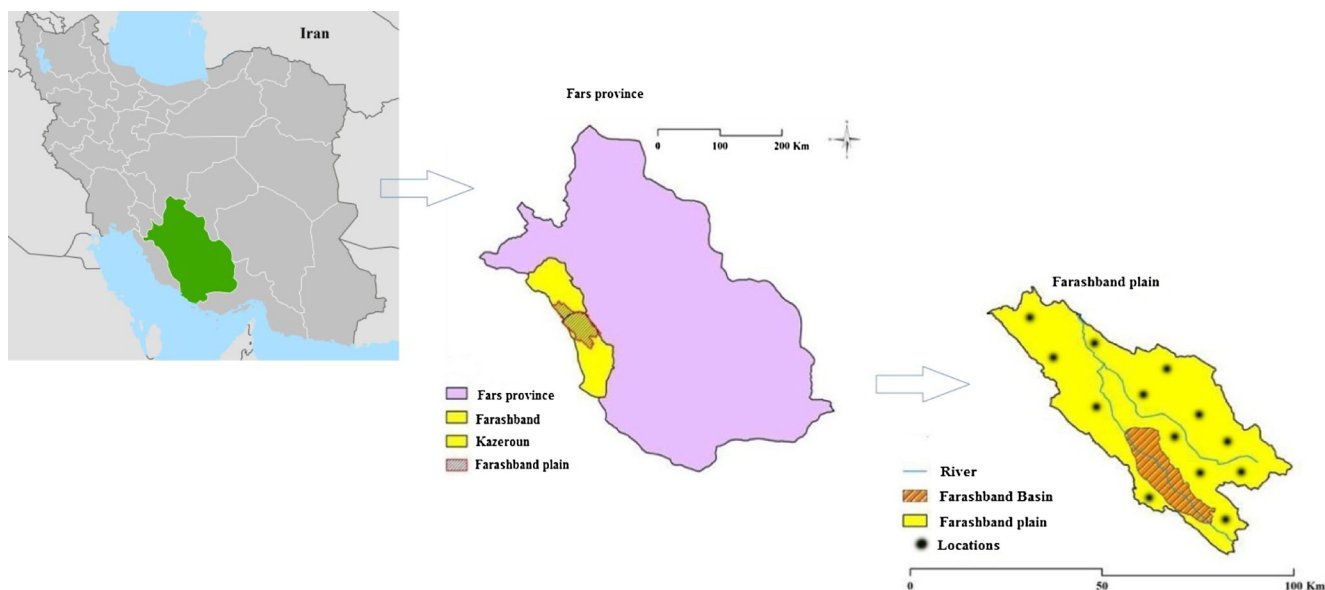
Fig. 1 Location map of the study area

samples were collected in new 1-l HDPE bottles pre-washed with dilute hydrochloric acid and rinsed three to four times with the water sample before filling it to capacity and then labeled accordingly. The samples were stored at a temperature below 4 °C prior to analysis in the laboratory. For collection, preservation, and analysis of the samples, the standard methods were followed (APHA 1995). Sampling was carried out without adding any preservatives in the rinsed bottles directly for avoiding any contamination and brought to the laboratory. Only highly pure (AnalR Grade) chemicals and double-distilled water were used for preparing the solutions for analysis. The samples were analyzed in the laboratory to determine the concentration of major ions including Ca, Mg, Na, K, HCO3, Cl, and SO4 in addition to total dissolved solid (TDS), total hardness (TH), electrical conductivity (EC), and pH. EC and hydrogen ion concentration (pH) were measured using Eutech digital portable meters in the field at the time of sampling. The pH meter was calibrated beforehand using 4.01, 7, and 10.01 buffer solution, and the EC meter was calibrated using 84- and 1413-µS conductivity solution. All solutions and instruments were procured from Eutech Instruments. Groundwater samples collected were transported to the laboratory on the same day. Calcium (Ca^{2+}), magnesium (Mg^{2+}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and chloride (Cl^-) were analyzed by volumetric titration methods; sodium (Na^+) and potassium (K^+) were measured using the flame photometer; and sulfate (SO_4^{2-}) was determined by spectrophotometric technique as per the methods described by the American Public Health Association (APHA 1995).

The accuracy of the results was checked by calculating the ionic balance errors, and it was generally within ±5%.

Results and discussion

In water resources management, water quality is as significant as the quantity of water. Understanding the quality of groundwater is important because it is the main factor which decides its suitability for domestic, agricultural, and industrial purposes. The range of chemical parameters in groundwater of Farashband plain and their comparison with WHO standard are presented in Tables 1 and 2. According to the analytical data, parameter values range widely except for the pH (it is expressed by coefficient of variation).

Hydrogeochemical facies and water types

The term "hydrogeochemical facies" is used to describe the occurrence modes of groundwater in an aquifer that differs in their chemical composition. The facies are a function of lithology, solution kinetics, and flow patterns of the aquifer (Raju et al. 2011). Hydrochemical diagrams are aimed at facilitating interpretation of evolutionary trends, particularly in groundwater systems, when they are interpreted in conjunction with distribution maps and hydrochemical sections. The classification for cation and anion facies, in terms of major ion percentage and water types, is according to the domain in which they occur on the diagram segment (Alam et al. 2012). Piper's trilinear diagram method is used to classify the groundwater, based on basic geochemical characters of the constituent ionic

Table 1 Chemical analysis of groundwater samples collected from locations in Farashband plain

S. no.	Locations	pH	EC (μS/cm)	TDS (mg/l)	TH	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$ mg/l	SO$_4^{2-}$	Cl$^-$	HCO$_3^-$
1	Barcheshmeh	7.4	2314	1516	766	179	78	202	4.7	549	290	270
2	Boloutabad	7.6	5314	3840	2300	631	176	253	12.5	1519	860	183
3	Chahshouli	7.5	5102	3470	2625	426	380	89	10.6	2107	346	183
4	Dehno	7.6	3433	2339	1063	225	122	377	8.9	519	815	241
5	Farashband	7.5	6108	3930	1281	296	307	557	14.9	1431	1064	244
6	Ghanbarabad	7.3	7788	4780	3000	476	441	438	16.8	898	1967	244
7	Ghebleh Farashband	7.4	5106	3287	2125	426	258	250	10.4	1919	620	214
8	Gonbad	7.7	6224	6224	813	210	70	1989	29.3	788	2960	259
9	Guraki	7.8	4941	3255	1500	406	119	513	13.3	1031	975	214
10	Hoseinabad	7.5	2324	1534	656	190	67	217	5.1	463	384	236
11	Konarmalek	7.4	7317	4689	1338	281	176	1147	17.0	1322	1905	229
12	Pahnapahn	7.4	12,678	9471	2313	571	216	2215	38.5	1239	4077	275
13	Tolegeli	7.4	10,087	6760	1588	351	173	1873	31.6	1107	3080	249

concentrations. The chemical data of the groundwater samples collected from the study area are plotted in Piper's diagram (Fig. 2). The plot shows that the main hydrochemical species in the study area are Ca–Cl (46% of the locations), Na–Cl (31% of the locations), and mixed Ca–Mg–Cl (23% of the locations), respectively, according to their order of dominance. From the plot, it is observed that alkalis (Na$^+$ and K$^+$) exceed the alkaline earths (Ca^{2+} and Mg^{2+}) and strong acids (Cl$^-$ and SO$_4^{2-}$) significantly exceed the weak acids (HCO$_3^-$ and CO$_3^{2-}$). Sodium and potassium exchange by calcium and magne-

Types of water
1. CaHCO₃ Type
2. NaCl Type
3. Mixed CaNaHCO₃
4. Mixed CaMgCl
5. CaCl Type
6. NaHCO₃ Type

Legend
☐ Barcheshmeh
◇ Boloutabad
○ Chahshouli
● Dehno
☆ Farashband
◆ Ghanbarabad
■ Ghebleh...
▲ Gonbad
● Guraki
◇ Hoseinabad
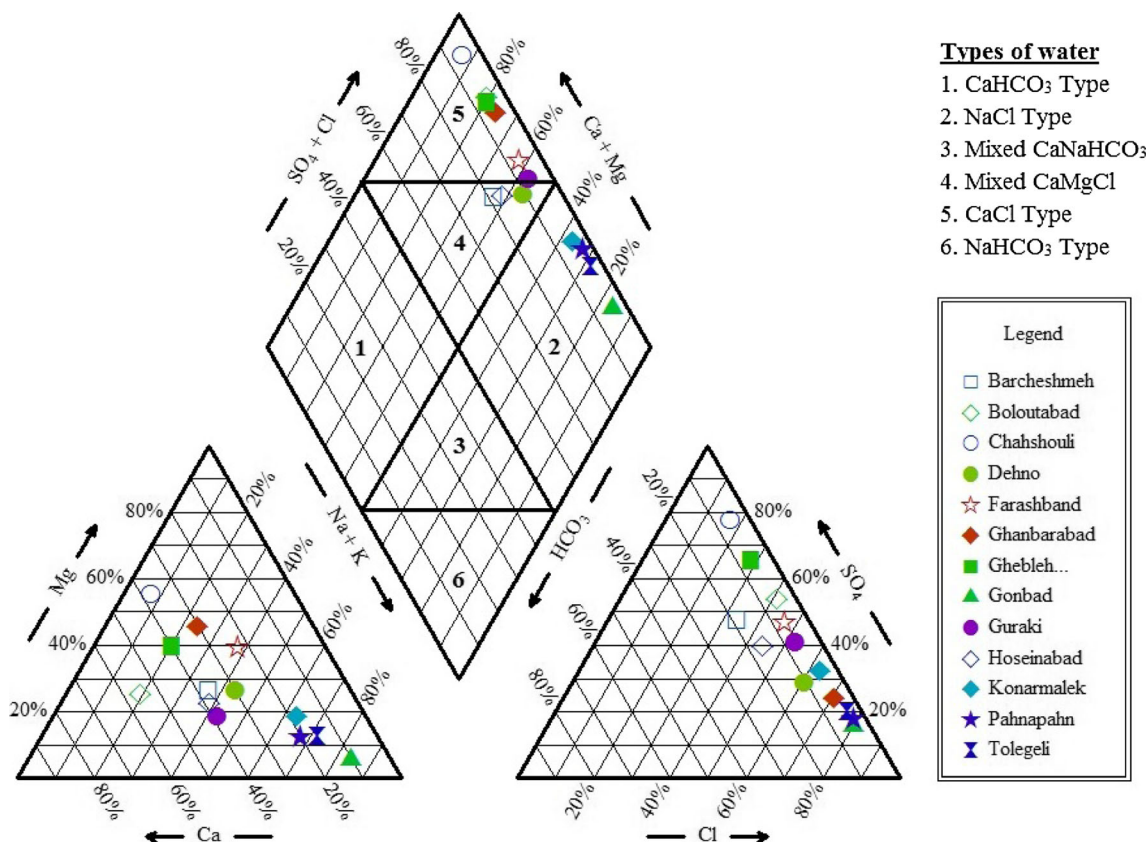◆ Konarmalek
★ Pahnapahn
✴ Tolegeli

Fig. 2 Distribution of the water samples on Piper's diagram

Table 2 Range of chemical parameters in groundwater of Farashband plain

S. no.	Locations	Na%	RSC	PI	Na%	SAR	Gibbs ratio I	Gibbs ratio II	Kelly's ratio	MH
1	Barcheshmeh	36.7	−10.9	45.1	36.7	3.18	0.649	0.500	0.57	41.9
2	Boloutabad	19.7	−43.0	22.3	19.7	2.29	0.890	0.264	0.24	31.5
3	Chahshouli	7.3	−49.5	9.9	7.3	0.75	0.765	0.163	0.07	59.5
4	Dehno	43.9	−17.3	48.8	43.9	5.02	0.853	0.596	0.77	47.1
5	Farashband	38.1	−36.0	40.8	38.1	5.41	0.882	0.625	0.61	63.1
6	Ghanbarabad	24.5	−56.0	26.6	24.5	3.48	0.933	0.451	0.32	60.4
7	Ghebleh Farashband	20.7	−39.0	23.9	20.7	2.36	0.833	0.344	0.26	50.0
8	Gonbad	84.3	−12.0	86.2	84.3	30.34	0.952	0.893	5.32	35.4
9	Guraki	43.0	−26.5	46.2	43.0	5.76	0.887	0.528	0.74	32.5
10	Hoseinabad	39.0	−11.1	46.7	39.0	3.45	0.737	0.502	0.63	36.7
11	Konarmalek	63.8	−24.8	66.1	63.8	13.22	0.935	0.782	1.75	50.9
12	Pahnapahn	67.8	−41.8	69.0	67.8	20.03	0.962	0.773	2.08	38.4
13	Tolegeli	72.1	−27.7	73.7	72.1	20.44	0.955	0.825	2.56	44.9

Values of ions in milligram per liter (excluding physical data)

EC conductivity (μS/cm at 25 °C), *TDS* total dissolved solids (mg/l), *TH* total hardness (as $CaCO_3$) (mg/l)

sium adsorbed on the clay mineral surfaces may be responsible for the high sodium and potassium concentrations (Singh et al. 2012).

Suitability of groundwater for drinking and general domestic use

The range of hydrochemical parameters of groundwater of the Farashband plain and their comparison with World Health Organization (WHO 1997) are summarized in Table 3, to evaluate the suitability of groundwater for drinking and domestic and public health uses. It is observed that most of the hydrochemical parameters of the groundwater samples in the study area exceed the desirable limits of the WHO, although a

number of samples are within the maximum permissible limits.

The pH values of the groundwater in the Farashband plain vary between 7.3 and 7.8, with an average of 7.5, which indicates the alkaline nature of groundwater of the study area (Tables 1, 2, and 3). The pH value of all the collected samples are within the permissible limit of 6.5 to 8.5 prescribed for drinking water by WHO (1997). Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters, the optimum pH required often being in the range 6.5–8.5 (WHO 2008).

EC ranges from 2314 to 12,678 μS/cm at 25 °C, with an average of 6056 μS/cm (Table 1). EC was above the maximum permissible limit (1500 μS/cm) in all the groundwater

Table 3 Groundwater quality parameters for irrigation purposes

Parameters	Min		Max		Mean	St. error	SD deviation	Variance	WHO standard	Percent compliance	Match
	Rate	Location	Rate	Location							
pH	7.3	Ghanbarabad	7.8	Guraki	7.5	0.04	0.14	0.02	6.5–8.5	100	Yes
EC	2314	Barcheshmeh	12,678	Pahnapahn	6056	813.10	2931.69	8,594,802.92	1500	0	No
TDS	1516	Barcheshmeh	9471	Pahnapahn	4238	616.16	2221.62	4,935,584.74	1000	0	No
TH	656	Hoseinabad	3000	Ghanbarabad	1644	210.84	760.19	577,898.40	500	0	No
Ca^{2+}	179	Barcheshmeh	631	Boloutabad	359	40.43	145.78	21,253.24	200	30.1	No
Mg^{2+}	67	Hoseinabad	441	Ghanbarabad	199	32.96	118.86	14,127.23	50	0	No
Na^+	89	Chahshouli	2215	Pahnapahn	778	210.88	760.36	578,147.27	200	23.1	No
K^+	4.7	Barcheshmeh	38.5	Pahnapahn	16	2.89	10.42	108.66	12	53.4	No
SO_4^{2-}	463	Hoseinabad	2107	Chahshouli	1145	143.25	516.52	266,788.93	250	0	No
Cl^-	290	Barcheshmeh	4077	Pahnapahn	1488	337.88	1218.24	1,484,113.74	250	0	No
HCO_3^-	183	Boloutabad, Chahshouli	275	Pahnapahn	234	8.05	29.02	842.24	600	100	Yes

sampling stations as per WHO standards (Table 3). The higher EC may cause a gastrointestinal irritation in human beings. The large variation in EC is mainly attributed to geochemical processes like ion exchange, reverse exchange, evaporation, silicate weathering, rock–water interaction, sulfate reduction, and oxidation processes and anthropogenic activities like application of agrochemicals prevailing in this plain.

Higher concentration of calcium can cause abdominal ailments and is undesirable for domestic uses causing encrustations and scaling. The Ca^{2+} concentrations range from 179 to 631 mg/l with an average value of 359 mg/l (Table 1). About 70% of the groundwater sampling stations exceed the maximum permissible limit of 200 mg/l for calcium, but all the stations are above highest desirable limit of 75 mg/l as suggested by WHO (Table 3). Low concentrations of calcium versus sodium in groundwater samples indicate the absence of readily soluble calcium minerals, whereby calcium present in groundwater samples has been exchanged by sodium due to base exchange reaction (Sharma and Rao 1997).

The Mg^{2+} concentration in the study area ranges from 67 to 441 mg/l with a mean value of 199 mg/l (Table 1). Comparison of Mg^{2+} concentrations in water samples with the WHO standards showed that all the stations exceed the permissible limit of 50 mg/l as set by WHO (Table 3). The principal sources of Mg^{2+} in the natural waters are magnesium-bearing minerals in rocks, and secondary sources are animal, domestic, and industrial wastes. Magnesium salts are cathartic and diuretics, and its high dose causes laxative effect (Marghade et al. 2011).

In the study area, the Na^+ concentration in groundwater ranges from 89 to 2215 mg/l with a mean value of 778 mg/l (Table 1). About 77% of the groundwater sampling stations exceed the permissible limit of 200 mg/l as per WHO standard (Table 3). High concentrations of Na^+ in the groundwater are attributed to cation exchange among minerals. Excess sodium causes high pressure, nervous disorder, etc. In general case, the Na^+ is the dominant ion among the cations and is present in most of the natural waters. This is because of the silicate weathering and/or dissolution of soil salts stored by the influences of evaporation, anthropogenic activities, agricultural activities, and poor drainage conditions (Krishna Kumar et al. 2015). The higher contribution of Na^+ than that of the contribution of Ca^{2+} to the total cations is expected due to the influence of ion exchange.

K^+ is a naturally occurring element, but its concentration remains quite lower compared with Ca, Mg, and Na. The K^+ concentration varies from 4.7 to 38.5 mg/l with an average value of 16 mg/l (Table 1). Nearly 53% of the groundwater sampling stations are within the permissible limit of 12 mg/l suggested by WHO (Table 3).

Chloride in drinking water originates from natural sources, sewage and industrial effluents, urban runoff containing deicing salt, and saline intrusion (WHO 2004). Chloride ion concentration varied from 290 to 4077 mg/l with a mean value of 1488 mg/l (Table 1). The chloride ion concentration in groundwater of the study area exceeds the permissible limit of 250 mg/l in 15 locations (Table 3). The threshold level for chloride in drinking water is 250 mg/l (WHO 1997). However, no adverse health effects on human have been reported from intake of water containing an even higher content of chloride. Chloride is the most dominant anion in most samples, followed by SO_4^{2-} and HCO_3^-. High chloride concentrations may be attributed to leaching by irrigation water of the readily soluble salts (e.g., NaCl) precipitated in soil due to high evaporation rates.

The chloride ion can be toxic to plants having low salt tolerance when taken up by their roots and absorbed through their leaves (Singh et al. 2012). The chlorinity index of the groundwater sources was computed using measured chloride ion concentrations. Water samples in the study area were classified (Mills 2003; Singh et al. 2006) based on the chlorinity index as shown in Table 4. Based on this index, about 38% of the groundwater sampling stations can be considered unsuitable for any crops and the remaining 62% are suitable for low- to high-tolerant crops.

Sulfate occurs naturally in water as a result of leaching from gypsum and other common minerals. The sulfate content changes significantly with time during infiltration of rainfall and groundwater. The concentration of sulfate is likely to react with human organs if the value exceeds the maximum allowable limit of 400 mg/l and causes a laxative effect on human system with the excess magnesium in groundwater. However, the sulfate concentrations vary greatly between 463 and 2107 mg/l with an average value of 1145 mg/l and found beyond the maximum allowable limit in all sampling locations as per WHO specification (Tables 1 and 2). These variations in concentration may indicate the breaking of organic substance from top soil/water, leachable sulfate present in fertilizer, and other human influences (Srinivasamoorthy et al. 2008). Sulfate ion concentrations are probably derived from the weathering of sulfate and gypsum-bearing sedimentary rocks (Jeevanandam et al. 2007).

Hardness in water is caused by dissolved calcium and, to a lesser extent, magnesium. It is usually expressed as the equivalent quantity of calcium carbonate (WHO 2008). The principal natural sources of hardness in groundwater are dissolved polyvalent metallic ions from sedimentary rocks, seepage, and runoff from soils. Calcium and magnesium, the two principal ions, are present in many sedimentary rocks, the most common being limestone and chalk. There does not appear to be any convincing evidence that water hardness causes adverse health effects in humans (Yesilnacar and Gulluoglu 2008). Hard water causes scales in the boilers, pipes, and other domestic appliances, while soft water is more corrosive and contains more metal contaminants from the water pipes (Dudeja et al. 2011). TH as $CaCO_3$ in the study area ranges from 656 to

Table 4 Classification of groundwater quality based on Cl concentration

Class	Chloride concentration (mg/l)	Suitability for irrigation	Location numbers	Percentage of locations
Class I	<350	Suitable for all crops	1, 3	15.4
Class II	350–700	Suitable for high-, medium-, and low-salt-tolerant crops	7, 10	15.4
Class III	700–900	Suitable for high- and medium-salt-tolerant crops	2, 4	15.4
Class IV	900–1300	Suitable for high-salt-tolerant crops	5, 9	15.4
Class V	>1300	Not suitable for any crops	6, 8, 11, 12, 13	38.4

Source: Mills (2003) and Singh et al. (2006)

3000 mg/l with an average value of 1644 mg/l (Table 1), which is beyond the safe limit of 500 mg/l as suggested by WHO (1997). Depending on the interaction of other factors, such as pH and alkalinity, water with a hardness above approximately 200 mg/l may cause scale deposition in the treatment works, distribution system, and pipework and tanks within buildings. It will also result in excessive soap consumption and subsequent "scum" formation (WHO 2004). The classification of groundwater (Table 5) based on TH (Sawyer and McCartly 1967) shows that all the groundwater samples fall in the very hard category. There is some suggestive evidence that long-term consumption of extremely hard water might lead to an increased incidence of urolithiasis, anencephaly, prenatal mortality, some types of cancer, and cardiovascular disorders (Durvey et al. 1991). The hardness of water may be removed by a water-softening unit containing exchange resins. This will result in the exchange of calcium and magnesium by sodium, so it may be a concern to people on a low-sodium diet for medical reasons (Self 2010).

To ascertain the suitability of groundwater of any purposes, it is essential to classify the groundwater depending upon their hydrochemical properties based on their TDS values (Davis and DeWiest 1966; Freeze and Cherry 1979), which are represented in Tables 6 and 7. The groundwater of the area is brackish water for all of the sampling locations based on Freeze and Cherry (1979). The study shows that none of the samples is desirable or permissible for drinking. Only 13% of the sample is between 1000 to 3000 mg/l of TDS, which can be useful for irrigation, but 87% of the samples are unfit for

drinking and irrigation. The TDS in the water sampling stations of the study area ranged from 1516 to 9471 mg/l with a mean value of 4238 mg/l (Table 1). Higher concentration of TDS is observed in the northern part of the plain. This is because all these parts of the plain have semi-arid climatic condition and also consist of hard rock and low groundwater table. The higher the groundwater table and topography, the lower the concentration of TDS. This clearly supports the role of direction and amount of groundwater flow for variation in groundwater quality. Higher content of TDS can be attributed to the contribution of salts from the thick mantle of soil and the weathered media of the rock and further due to higher residence time of groundwater in contact with the aquifer body (Ahmad Dar et al. 2011). As the host rocks belong to calcite and dolomite suits, there can be some oxidation and reduction processes in groundwater and surface water, thereby also causing enrichment in the total dissolved solids.

Suitability for irrigation use

The suitability of groundwater for irrigation is contingent on the effects of the mineral constituents in the water on both the plants and soil (Richard 1954). The important hydrochemical parameters of groundwater used to determine its suitability for irrigation are EC, salinity, percent sodium (Na%), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), permeability index (PI), chloroalkaline indices (CAI), and magnesium ratio.

Table 5 Classification of groundwater quality based on hardness

TH (mg/l)	Classification	Locations	Number of locations	Percentage of locations
<75	Soft	–	–	–
75–150	Moderate hard	–	–	–
150–300	Hard	–	–	–
>300	Very hard	All locations	13	100

Source: Sawyer and McCartly (1967) and Alam et al. (2012)

Table 6 Groundwater quality classification based on TDS

TDS (mg/l)	Classification	Locations	Number of locations	Percentage of locations
<500	Desirable for drinking	–	–	–
500–1000	Permissible for drinking	–	–	–
1000–3000	Useful for irrigation	Barcheshmeh, Hoseinabad	2	13
>3000	Unfit for drinking and irrigation	All locations except Barcheshmeh and Hoseinabad	13	87

According to Davis and DeWiest (1966) and Alam et al. (2012)

Salinity and alkali hazard

Salts may harm plant's growth physically by limiting the uptake of water through modification in the osmotic processes or chemically by metabolic reactions such as those caused by toxic constituents (Todd 1980). Electrical conductivity is a good measure of salinity hazard to crops as it reflects the TDS in groundwater. Four out of 13 sampling locations fall into doubtful, and the rest fall into unsuitable (Table 8), so all the sampling regions exceed the permissible limit for irrigation purposes (Wilcox 1955). Excess salinity reduces the osmotic activity of plants and thus interferes with the absorption of water and nutrients from the soil (Saleh et al. 1999; Subramani et al. 2005). Minerals of the bed rock are subjected to weathering and subsequently affected by leaching, which contribute dissolved salts to groundwater, resulting in an increase in TDS, EC, and hence water salinity (Pathak et al. 2008; Rao et al. 2006).

The SAR vs EC values for groundwater samples of the study area were plotted in the USSL graphical diagram of irrigation water (Fig. 3). Based on USSL diagram (USSL 1954), the water quality shows that the majority of the samples fall in the C_4S_1 (very high salinity with low sodium) category and a few samples fall in the C_4S_2 (very high salinity with medium sodium) and C_4S_4 (very high salinity with very high sodium) categories. These groundwater samples show very high salinity hazard with low to very high alkali hazards. Based on the USSL diagram, the groundwater samples are unsatisfactory for irrigation use in almost all soil types.

Sodium concentration is an important factor in classifying the water for irrigation purposes because sodium concentration can reduce the soil permeability and soil structure (Domenico and Schwartz 1990; Krishna Kumar et al. 2009; Todd 1980). The high soluble salt content in the water (high EC) leads to formation of saline soil, and high sodium content (SAR) leads to formation of an alkaline soil. SAR is an important parameter for determining the suitability of groundwater for irrigation because it is a measure of alkali/sodium hazard to crops. SAR is defined by Karanth (1987)

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)\big/2}}$$

where the concentrations are reported in milliequivalents per liter. The SAR values range from 0.75 to 20.44 with an average value of 8.90 (Tables 2 and 9). Groundwater sampling locations of the study area fall in the low-sodium class (S_1) except four locations, which one of them is in good class (S_2), one is doubtful (S_3), and two are unsuitable (S_4) for irrigation purposes. If the SAR value is greater than 6 to 9, the irrigation water will cause permeability problems on shrinking and swelling types of clayey soils (Saleh et al. 1999). The rating of water samples in relation to salinity and sodium hazard reflects that the high sodium ion concentration in the water at some of the stations may produce harmful levels of exchangeable sodium in the soil. The rating of water samples in relation to salinity and sodium hazard reflects that the high sodium ion concentration in the water at some of the stations may produce harmful levels of exchangeable sodium in the soil.

Table 7 Groundwater quality classification based on TDS

TDS (mg/l)	Classification	Locations	Number of locations	Percentage of locations
<1000	Fresh water type	–	–	–
1000–10,000	Brackish water type	All locations	15	100
10,000–100,000	Saline water type	–	–	–
>100,000	Brine water type	–	–	–

According to Freeze and Cherry (1979)

Table 8 Quality of irrigation water based on electrical conductivity

EC (μS/cm)	Classification	Location numbers	Number of locations	Percentage of locations
<250	Excellent	–	–	–
250–750	Good	–	–	–
750–2250	Permissible	–	–	–
2250–5000	Doubtful	1, 4, 9, 10	4	27
>5000	Unsuitable	2, 3, 5, 6, 7, 8, 11, 12, 13	11	73

The sodium percentage (Na%) is calculated using the formula given in the following:

$$Na\% = \frac{(Na + K) \times 100}{(Ca + Mg + Na + K)}$$

where all the concentrations are expressed in milliequivalents per liter. The Na% indicates that the groundwater is excellent to doubtful for irrigation (Table 10) except one sampling station (Raghunath 1987). EC and Na concentrations are important in classifying irrigation water. According to Wilcox (1955), the water quality diagram for irrigation and domestic purposes shows that two locations are falling under doubtful to unsuitable and the others are unsuitable (Fig. 4). When the concentration of sodium is high in irrigation water, sodium ions tend to be absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. This exchange process of Na^+ in water for Ca^{2+} and Mg^{2+} in soil reduces the permeability and eventually results in soil with poor internal drainage. Hence, air and water circulation is restricted during wet conditions and such soils are usually hard when dry (Saleh et al. 1999; Subramani et al. 2005).

Residual sodium carbonate

The quantity of bicarbonate and carbonate in excess of alkaline sediments (Ca and Mg) also influences the suitability of water for irrigation purposes. When the sum of carbonates and bicarbonates is in excess of calcium and magnesium, there may be possibility of complete precipitation of Ca and Mg (Raghunath 1987). To quantify the effects of carbonate and bicarbonate, RSC has been computed by the following equation:

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

All ionic concentration is in milliequivalents per liter. A high value of RSC in water leads to an increase in absorption of sodium in soil (Eaton 1950). Waters having RSC values greater than 5 meq/l are considered harmful to the growth of plants, while waters with RSC values above 2.5 meq/l are not considered suitable for irrigation purpose. In all of the analyzed water samples, RSC values are below 2.5 meq/l. This indicates that water is suitable for irrigation uses (Table 2).

Permeability index

The permeability index (PI) also indicates whether groundwater is suitable for irrigation. PI is calculated by considering the ions (in meq/l), which influence permeability and account for the presence of total salt concentration and sodium and carbonate content. It is calculated by the following formula:
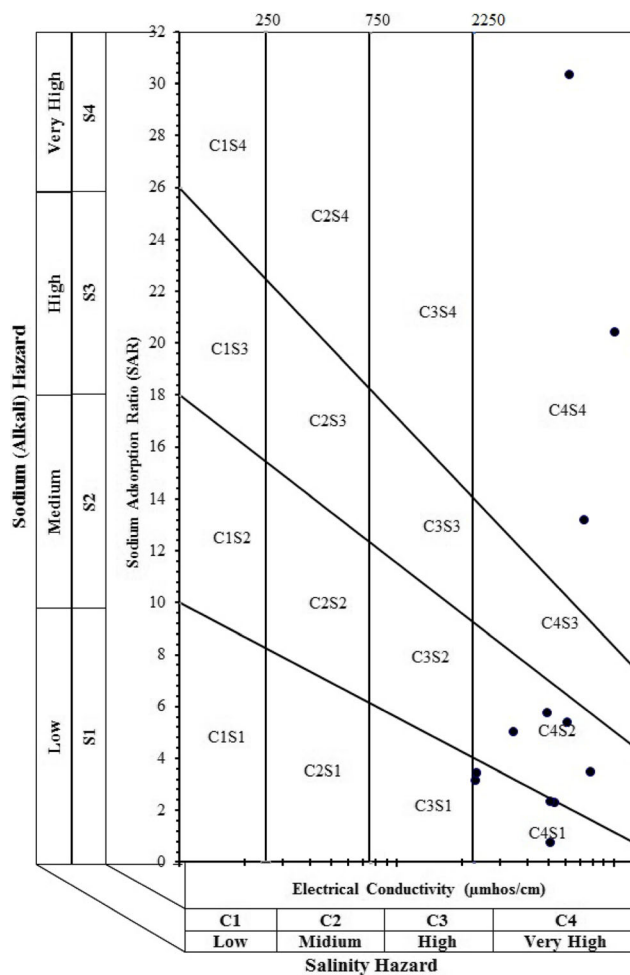
$$PI = \frac{Na + \sqrt{HCO3}}{Ca + Mg + Na} \times 100$$

Fig. 3 USSL diagram for irrigation water quality classification (USSL 1954)

Table 9 Quality of irrigation water based on SAR

SAR	Alkalinity hazard	Classification	Location numbers	Number of locations	Percentage of locations
<10	S_1	Excellent	1, 2, 3, 4, 5, 6, 7, 9, 10	9	69.2
10–18	S_2	Good	11	1	7.7
18–26	S_3	Doubtful	12, 13	2	15.4
>26	S_4	Unsuitable	8	1	7.7

where all the ions are expressed in milliequivalents per liter. Water can be classified as class I, class II, and class III orders with regard to PI. Class I and class II waters are categorized as good for irrigation with 75% or more of maximum permeability. Class III waters are unsuitable with 25% of maximum permeability (Doneen 1964). From Table 2, it can be demarcated that the PI values vary from 9.9 to 86.2 with an average value of 46.6. Majority of the groundwater sampling locations (77%) fall into the class II category of Donnen's chart and are categorized as suitable for irrigation (Table 11).

Kelly's ratio

Kelley's ratio (KR) is used to find whether the groundwater is suitable for irrigation or not. Sodium measured against calcium and magnesium was considered by Kelly (1951) for calculating KR. Kelly's ratio is calculated by the following equation:

$$\text{Kelly's ratio} = Na \big/ (Ca + Mg)$$

where all the concentrations are expressed in milliequivalents per liter. Groundwater having KR more than one is generally considered as unfit for irrigation. Kelly's ratio for the study area varies from 0.07 to 5.32 with a mean value of 1.23 (Table 2). In the study area, 69% of the groundwater sampling stations have KR value <1, indicating the good quality of the water for irrigation uses, but the remaining is unsuitable for irrigation as the KI values are more than one.

Magnesium hazard

Generally, alkaline earths are in equilibrium state in groundwater. If soils have more alkaline earths, they reduce a crop yield. The magnesium hazard of irrigation water is proposed

by Szabolcs and Darab (1964) with the formulae given in the following:

$$MH = \frac{Mg}{Ca + Mg} \times 100$$

where all the ionic concentrations are expressed in milliequivalents per liter. The magnesium hazard values exceeding 50 are considered harmful and unsuitable for irrigation use. In the analyzed groundwater samples, it is found between 31.5 and 63.1 with a mean value of 45.6 (Table 2). The analyzed water samples indicate that about 31% of the groundwater sampling stations are exceeding the magnesium ratio of 50, while 69% have magnesium hazard less than 50 and hence are suitable for irrigation.

Processes controlling the hydrochemical variation of the groundwater

Gibbs ratio

Gibbs (1970) has proposed a chemical diagram of mechanisms controlling chemistry of groundwater to understand the relationship of the chemical components of waters with their respective aquifer lithologies. Three types of distinct fields are recognized in the Gibbs diagram such as precipitation dominance, evaporation dominance, and rock dominance. The Gibbs ratios are calculated with the formulae given in the following:

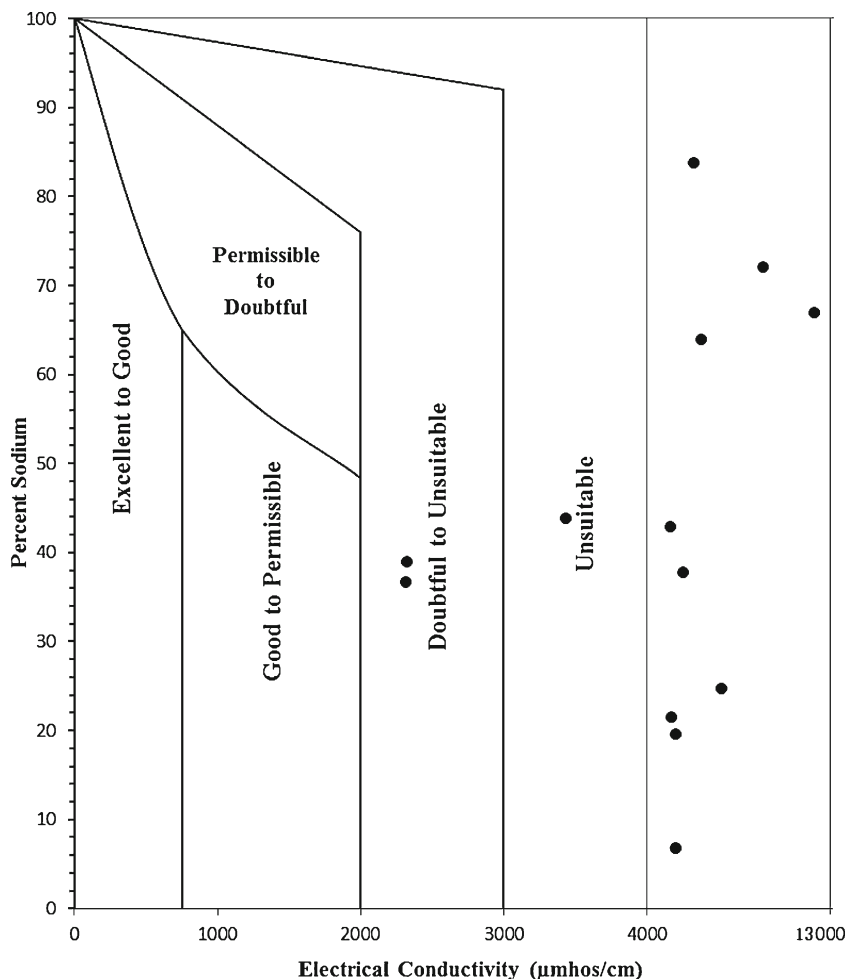$$\text{Gibbs ratio I (for Anion)} = Cl^- \big/ (Cl^- + HCO_3^-)$$

Gibbs ratio II (for Cation)

$$= (Na^+ + K^+) \big/ (Na^+ + K^+ + Ca^{2+})$$

Table 10 Quality of irrigation water based on Na%

Na%	Classification	Location numbers	Number of locations	Percentage of locations
<20	Excellent	3	1	7.7
20–40	Good	1, 2, 5, 6, 7, 10	6	46.2
40–60	Permissible	4, 9	2	15.4
60–80	Doubtful	11, 12, 13	3	23
>80	Unsuitable	8	1	7.7

Fig. 4 Sodium percentage vs EC value plot for water quality classification (Wilcox 1955)

where the concentrations are reported in milliequivalents per liter. Gibbs ratio I for anion and ratio II for cation of groundwater samples of the study area were plotted separately against the respective values of total dissolved solids. This gives a characteristic boomerang-shaped plot, depicting the major factors operating behind the water chemistry. Gibbs ratios I and II of groundwater samples range from 0.65 to 0.96 with an average of 0.86 and from 0.16 to 0.89 with an average of 0.56, respectively (Table 2). The chemistry of groundwater samples indicates that all samples have evaporation or crystallization dominance, as per Gibbs ratio I. According to Gibbs ratio II, 54% of the groundwater sampling stations also are evaporation/crystallization dominant (Fig. 5). Based on Gibbs ratios, the water–rock interaction might be related to the dissolution of evaporite minerals, or the evaporation of water, which means that the water samples are collected from the discharge zone of the aquifer system.

Correlation coefficient analysis

Correlation coefficient is a commonly used measure to establish the relationship between two variables. It is simply a measure to exhibit how well one variable predicts the other. The correlation matrices for EC, TDS, TH, and major ions were prepared and illustrate (Table 12) that EC and TDS show high positive correlation with Na^+, K^+, and Cl^-. In particular, Na^+ and Cl^- show a strong correlation with TDS and among themselves, indicating that such ions are derived from the same source of saline water. A high positive correlation between TH and Ca^{2+} ($r = 0.86$), Mg^{2+} ($r = 0.83$), and SO_4^{2-}

Table 11 Classification of groundwater quality based on permeability index (PI)

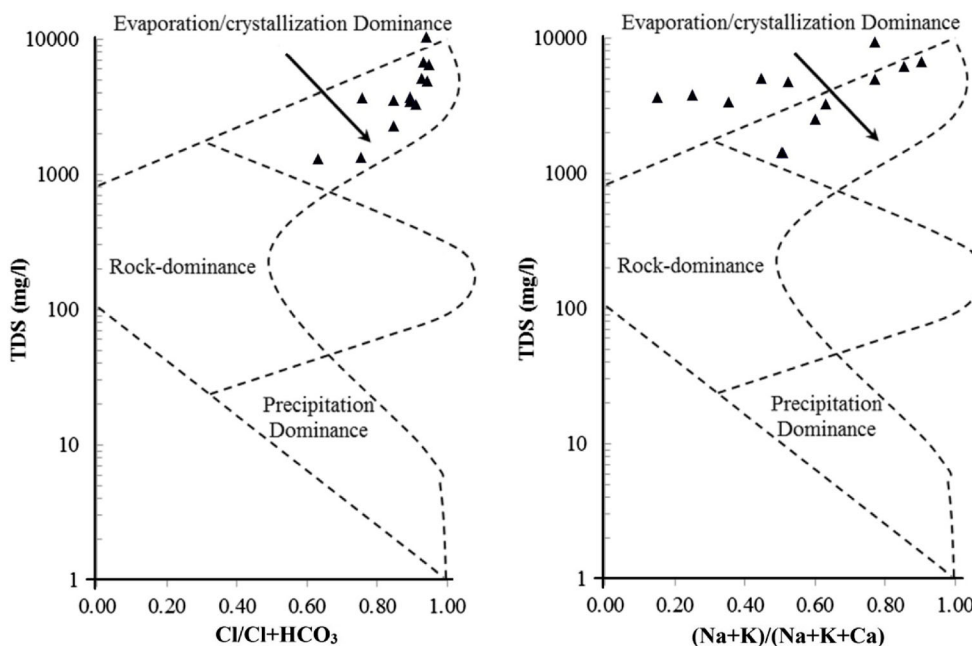| PI	Standard for irrigation	Class	Location numbers	Percentage of locations
<25	Unsuitable	III	2, 3, 7	23
25–75	Good	II	1, 4, 5, 6, 8, 9, 10, 11, 12, 13	77
>75	Permeability	I	–	–

Fig. 5 Mechanism controlling chemistry of groundwater based on Gibbs ratios

($r = 0.64$) indicates that the hardness in the groundwater is related to these constituents. pH shows a weak negative correlation with other parameters. K^+–Na^+, SO_4^{2-}–Ca^{2+}, SO_4^{2-}–Mg^{2+}, Cl^-–K^+, HCO_3^-–Na^+, and HCO_3^-–SO_4^{2-} are also the more significant correlation pairs. From the correlation analysis can be found information about the source of major ions; the close relationship between Ca–Mg–SO_4 can reflect the source of Ca, Mg, and SO_4 and maybe related to sulfate minerals (gypsum), and the relationships between Na–K–Cl are implications for dissolution of chloride minerals; then, the relationships between Na–K–HCO_3 are implications for the weathering of silicate minerals.

Conclusions

The hydrogeochemical analysis reveals that the groundwater of the study area is very hard and slightly alkaline in nature. All the groundwaters of the study exceeded the permissible limits of TH and TDS. The groundwater of the area is brackish water for all of the sampling locations based on Freeze and Cherry (1979). The study showed that only 13% of the samples are between 1000 and 3000 mg/l of TDS, which can be useful for irrigation, but the rest of the sampling locations are unfit for drinking and irrigation purposes. According to Gibbs ratios, the water–rock interaction is related to the evaporation

Table 12   Correlation coefficient matrix of water quality parameters

pH		EC	TDS	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	Cl^-	HCO_3^-
pH	1										
EC	−0.343	1									
TDS	−0.183	0.959**	1								
TH	−0.360	0.478	0.358	1							
Ca^{2+}	−0.108	0.531	0.456	0.860**	1						
Mg^{2+}	−0.490	0.336	0.183	0.830**	0.514	1					
Na^+	−0.032	0.790**	0.892**	−0.078	0.057	−0.205	1				
K^+	−0.090	0.912**	0.979**	0.202	0.316	0.044	0.952**	1			
SO_4^{2-}	−0.140	0.266	0.195	0.638*	0.589*	0.606*	−0.109	0.070	1		
Cl^-	−0.164	0.897**	0.956**	0.158	0.249	0.008	0.956**	0.977**	−0.075	1	
HCO_3^-	−0.286	0.308	0.367	−0.418	−0.424	−0.292	0.571*	0.447	−0.637*	0.550	1

***Correlation is significant at the 0.01 level (two tailed); correlation is significant at the 0.05 level (two tailed)

of rocks and minerals in the aquifer. The concentrations of Mg^{2+}, SO_4^{2-}, and Cl^- ions in all the groundwaters are not within the permissible limit for drinking purpose. Groundwater in most of the study area exceeded the permissible limit of Ca^{2+}, Na^+, and K^+. The concentration of bicarbonate is within the permissible limit for drinking. Based on the RSC criteria, all the groundwater sampling stations can be considered safe for irrigation use. Gibbs chemical diagram indicates that majority of the groundwater samples show evaporation or crystallization dominance. The alkalis (Na^+ and K^+) exceed the alkaline earth ($Ca^{2+} + Mg^{2+}$), and strong acids (Cl^- and SO_4^{2-}) exceed the weak acids (HCO_3^- and CO_3^{2-}). This leads to a CaCl, NaCl, and mixed CaMgCl types of groundwater. Due to very high salinity hazard, all the study area is beyond the maximum allowable limit for irrigation.

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