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RESEARCH PAPER

Assessment of Hydrochemical Characteristics and Groundwater Suitability for Drinking and Irrigation Purposes in Garmsar Plain, Iran

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Abstract

Groundwater is an important water supply for irrigation and drinking purposes in semi-arid regions. In the Garmsar Plain, Iran, groundwater has severely deteriorated during recent years due to human activities and environmental changes. Hence, the main purpose of the current research is to investigate the chemical processes that control hydrochemistry and assess the groundwater quality to determine its suitability for irrigation and drinking uses and potential human health risks. Analysis results of the groundwater samples revealed that the most common water type is the sodium chloride type (82%) in the Garmsar Plain, followed by the mixed Ca-Mg-Cl type (18%). The main processes that contribute to groundwater chemistry are the dissolution along the flow path, evaporation, rock water interaction, ion exchange, and the mixing processes. According to the Irrigation Water Quality Index (IWQI), 51% of samples represent a severe restriction category and the remaining 49% constitute a high restriction class which reveals moderate to high salt tolerance, indicating that salt plants under some irrigation conditions can be cultivated in the Garmsar Plain. Besides, calculation of other indicators such as Sodium Absorption Ratio (SAR), Soluble Sodium Percentage (SSP), Permeability Index (PI), Kelly's Ratio (KR), and Magnesium Adsorption Ratio (MAR) shows that the samples in the Garmsar Plain are mainly not suitable for irrigation. Based on human health considerations, 33%, 31%, 46%, 44%, 95%, and 77% of the groundwater samples are classified as poor water because of their high concentrations of Ca2+, Mg2+, Na+, HCO3-, Cl-, and SO42-, respectively. Drinking this water may cause a risk to human health, therefore water treatment strategies are required for sustainable groundwater quality protection in the Garmsar Plain before using it for irrigation and drinking purposes.

Keywords: Garmsar plain, Groundwater quality, Water type, Irrigation Water Quality Index, Health risk assessment, Iran.

Introduction

Groundwater is a vital and an invisible natural resource that accounts for more than 90% of available fresh water at the global scale (Ghalib, 2017). It comprises the main water source for agriculture and the food industry (Wang et al., 2022). Intense pumping and irrigation in many areas have severely changed groundwater quantity and quality. Groundwater quality can be affected by both geogenic processes and anthropogenic activities. When groundwater flows from recharge to discharge areas through the aquifer, its characteristics change due to contacting the aquifer rocks and sediments, artificial recharge, mixing, and other processes, which make these waters unsafe for drinking and even irrigation purposes. Understanding the significant factors influencing the hydrochemistry of groundwater is crucial to protect and maintain this

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valuable water resource. Many researchers have investigated the quality of groundwater using hydrochemical parameters all around the world. Karroum et al. (2017) used chemical analyses to evaluate controlling processes involved in groundwater chemistry and identify the processes responsible for the groundwater quality in Bahira Plain of Morocco. Their research indicated three potential processes affecting groundwater geochemistry, including evaporation, water-rock interaction, and mixing of various waters. Hydrogeochemistry was also applied by Snousy et al. (2021) to assess health risk in Assiut Province, Egypt. Based on human health considerations, they found some groundwater samples are categorized as poor water because of their high contents of hydrochemical parameters, which have a serious effect on the human body. Using water quality indices, Iqbal et al. (2021) determined the groundwater's suitability for irrigation and drinking in the Khanewal District of Punjab, Pakistan. According to their results, half of the groundwater samples were not safe to drink and around 32% of them were unsuitable for irrigation purposes. Mohammed et al. (2022) used multivariate statistical and hydrochemical approaches for evaluation of groundwater quality in north Bahri city-Sudan. Gibbs plot of their research suggested that the dissolution of the minerals is the main factor influencing the water quality. The statistical analysis revealed the effect of the physical and human-induced activities as the main factors influencing groundwater chemistry. These factors are rock-water interaction, agricultural practice, and organic contamination from septic tanks. Their study indicated that the integrated approach was effective in calibrating water quality assessment methodologies.

It should be noted that the over-exploitation of the groundwater resources, in addition to drought, unavoidably resulted in soil and water quality degradation, particularly in semi-arid regions like Garmsar in Semnan province of Iran, where the extraction of groundwater for irrigation and drinking purposes is a fundamental element of socio-economic development. Garmsar agriculture consumes most of the water available, and water degradation is a key problem that has become particularly important in the last decade. In addition, the irrigation of low-quality water disrupts plants' growth process through toxicity and changes in nutrient supply (Ali et al., 2018; Amiri et al., 2021). Hence, investigating the irrigational suitability of groundwater is essential to identify high-risk areas and to understand the subsequent adverse effects on sustainable groundwater management (Sefiani et al., 2019). The groundwater suitability for irrigation purposes can be evaluated by determining a number of qualitative indicators and components such as electrical conductivity (EC), sodium percentage (Na %), sodium absorption ratio (SAR), soluble sodium percentage (SSP), permeability index (PI), magnesium absorption ratio (MAR), residual sodium carbonate (RSC), and Kelly's ratio (KR) (Kumar et al., 2007). These indices have been proved efficient in the agricultural water quality assessment in many studies (e.g., Chaudhary and Satheeshkumar, 2018; Sefiani et al., 2019; Shah et al., 2019; Haldar et al., 2020; Zhou et al., 2021; Amiri et al., 2021).

In recent years, in addition to water quality evaluation, health risk assessment has received a great deal of attention (He et al., 2019; Jiang et al., 2020; He and Li, 2020). The primary purpose of a health risk assessment is to estimate possible negative health effects due to exposure to contaminated water (Shukla and Saxena, 2020; 2021). A particular combined assessment of drinking water quality and human health risks would assist make the evaluation even more meaningful (Wu et al., 2020b).

Groundwater in the study area (Gamsar Plain) is the primary source of consumption for agriculture, drinking, domestic water, and industry. Thus, the objective of this research is to determine the groundwater hydrogeochemistry in this region, identify the hydrochemical processes involved in its quality and to evaluate groundwater suitability as agricultural and drinking water, and to assess the probable risk of human health from exposure to the selected physico-chemical parameters.

Materials and methods

Study area

The Garmsar Plain shown in Fig. 1 is located in the south of the Alborz Mountains in northern Iran and east of Semnan Province, occupying approximately 5500 km^2. The Garmsar Plain covers an area of around 2322 km^2 and is composed of alluvial sediments. According to Amberge method, the study area is included in the arid climate zone. Based on measurements from 1975 to 2020 at Garmsar Station operated by the Iran Meteorological Organization, the average annual precipitation is 150.7 mm and the mean annual temperature is 13.7°C. The annual evaporation is between 800 and 3000 mm, which is many times the average annual precipitation. Minimum and maximum rainfall occur in August and March, respectively.

From the geological point of view, Garmsar Plain is limited from the east to alluvial terraces and from the northeast to Kahrizak conglomerate and Upper Red Formation. North and northwest of this plain are covered by the Lower Red Formation containing gypsum, salt, and clay units; and the southern, southwestern and southeastern margins of the plain are surrounded by Quaternary deposits. The main aquifer of the plain is formed in the Garmsar alluvial fan, as a result of the accumulation of sedimentary deposits of Hableh Rud river on impermeable marl and shale bedrocks. Hableh Rud River is the main source of recharging the aquifer. The Garmsar Plain alluvial aquifer is of unconfined type covering 785 square kilometers with an average alluvial thickness of about 140 meters. The average thickness of the saturated layer is about 35 meters. The geological map of the Garmsar Plain is depicted in Fig. 1.

Data and Chemical Analysis

In Garmsar Plain, 39 representative groundwater sample data were collected for water quality indicators from October and November 2019 from wells to study the hydrochemical characteristics and suitability for agriculture and drinking purposes.

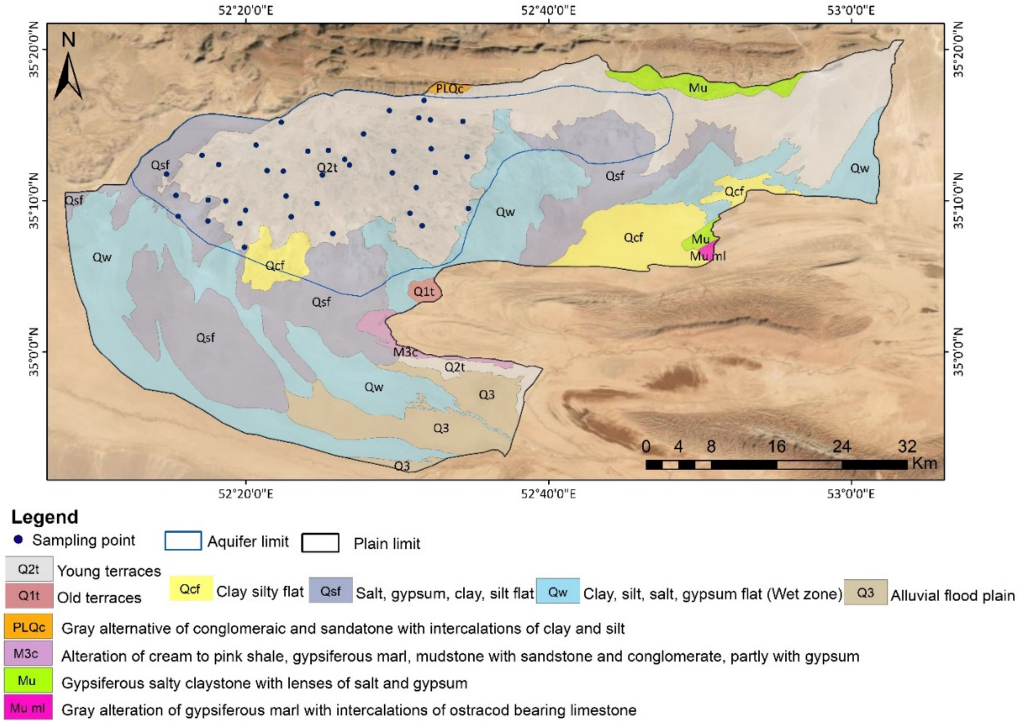


Figure 1. Geological map of the Garmsar Plain and location of the sampling points

The groundwater samples were analyzed for water quality indicators including water temperature, pH, electrical conductivity, total dissolved solids, sodium, magnesium, calcium, bicarbonate, sulfate, and chloride, according to the standard methods proposed by American Public Health Association (APHA, 2012).

To reveal the quality of the water analysis, the charge balance error (CBE) was determined, as follows:

$$\text{CBE} = \frac{[\sum \text{cations} - \sum \text{anions}]}{[\sum \text{cations} + \sum \text{anions}]} \times 100 \tag{1}$$

Where the concentrations of anions and cations are expressed in milliequivalent per liter (meq/L). For all water samples, the CBE values had been within ±5 %, reflecting the reliable analytical data (Appelo and Postma, 2005).

Health Risk Assessment

Contaminated groundwater causes serious impacts on human health. Even though the major ions in drinking water are essential nutrients for the human body, if these ions exceed certain limits, they may pose serious health hazards (Sarfraz, 2019). For instance, high levels of total dissolved solids (TDS), calcium, and total hardness are associated with the frequent occurrence of renal stones (Mohamed et al., 2015). Concentrations of major chemicals and substances in drinking water in many countries, such as Pakistan, Ghana, Bangladesh, and Zimbabwe are reported to exceed the World Health Organization (WHO) guideline values (GVs) (Laluraj and Gopinath 2006, Memon et al., 2011; WHO, 2022). This study also discussed the health risk assessment of groundwater intake for major cations and anions (calcium, magnesium, sodium, bicarbonate, chloride, and sulfate).

Results and Discussion

Groundwater Chemistry

Table 1 provides a statistical summary of physicochemical parameters and their standard limits for drinking water. The pH value ranges between 7 and 8, indicating that the Garmsar groundwater is slightly alkaline. Although the pH does not directly affect human health, but is usually associated with other chemical constituents in water (Mostafa et al., 2017). TDS values in Garmsar Plain vary from 1461 to 7090 mg/L.

Table 1. Statistical summary of the physico-chemical parameters of Garmsar groundwater

Parameter	Unit	Min	Max	Mean	Median	SD	WHO (2022)
PH		7	8	7.5	7.4	0.16	6.5-8.5
EC	µS/cm	2200	10630	4218.7	3660	1932.4	1000
TDS	mg/L	1461	7090	2810.7	2450	1287.7	600-1000
TH	mg/L $CaCO_3$	385	2760	907.5	760	493.5	100-300
Ca^{2+}	mg/L	90.2	633.3	206.4	181.4	111.9	75
Mg^{2+}	mg/L	35.9	286.9	94.1	76.6	55.2	50
Na^{+}	mg/L	260.3	1661.1	635.2	539.4	332.4	200
HCO_3^{-}	mg/L	54.9	372.2	199.4	195.3	74.8	250
Cl^{-}	mg/L	438.9	3284	1043.4	859.7	858.3	200-300
SO_4^{2-}	mg/L	307.4	1724.3	619.6	513.4	338.9	250
SAR		4.6	18.2	9.2	9.1	3.3	
Na%	%	46.7	79.5	59.7	59.8	8.5	
MH		31.3	58.3	43	42.2	6.1	

According to the WHO guidelines for drinking water quality, water containing TDS of approximately 1000 mg/L and above is not recommended to drink. All samples are beyond this limit of TDS. High TDS concentrations may also be unpleasant to consumers (WHO, 2022). TDS values of more than 500 indicate carbonate weathering or brine water (Hounslow, 2018). Lithology and agricultural activities account for the high salinity of the water in the Garmsar Plain.

The quality of groundwater depends on the content of major cations and anions. The dominance of the cations in descending order is $Na^+ > Ca^{2+} > Mg^{2+}$ and the anion is $Cl^- > SO_4^{2-} > HCO_3^-$. The Na concentrations in the Garmsar Plain vary from 260 to 1661 mg/L with a mean value of 635.2. Sodium concentration should not be more than 200 mg/L in drinking water. The main sources of Na in water are weathering of Na-rich minerals in the provenance (e.g., sodium plagioclase and halite), or human activities such as industrial wastes and municipal sewage, as well as natural ion exchange processes (Freeze and Cherry, 1979; Hounslow, 2018). Calcium and magnesium concentrations vary from 90 to 633 and 36 to 287 mg/L in the Garmsar Plain with a mean value of 206.4 and 94.1 mg/L (Table 1), respectively. The concentrations of calcium and magnesium in groundwater are primarily due to the dissolution of carbonate minerals (calcite, dolomite, etc.), and the carbonate cement within the formations (Magesh et al., 2013; Ghalib, 2017). They are vital to human health, but they may have harmful effects on the human body at high levels. High concentrations of Ca^{2+} and Mg^{2+} could be due to the occurrence of calcic and ferromagnesian rocks based on the geology of the area, although, in the Garmsar Plain, according to the mean value, Na^+ is significantly higher than Ca^{2+} and Mg^{2+}. Chloride concentration in the Garmsar Plain varies between 439 and 3284 mg/L with a mean value of 1043.4 mg/L. The Na^+/Cl^- ratio in the samples is almost close to 1, indicating that halite dissolution is happening. Moreover, elevated Cl^- concentrations in groundwater may also be a result of infiltration of irrigated water. Sulfate concentrations in the Garmsar Plain range from 307 to 1724 mg/L with a mean value of 619.6 mg/L. Considering the possible sources of sulfate in the groundwater, the dissolution of evaporites and gypsum-bearing carbonate sedimentary rocks seems to be the main source. Finally, bicarbonate values are observed at 55 to 372 mg/L, with a mean value of 199.4 mg/L. Higher concentrations of Cl^- and SO_4^{2-} compared to HCO_3^- indicate that the dominant chemical processes are not associated with carbonate rocks.

Hydrogeochemical Facies

The graphical methods were created to investigate changes in groundwater quality at a glance (Fijani et al., 2017; Appelo and Postma, 2005). The Piper Trilinear Plot (Piper, 1944) was prepared to characterize hydrochemical facies and different water types (Fig. 2). Fig. 2 clearly shows that chloride is superior to other anions. The anionic triangle indicates that 92% of the samples are in chloride type and 5% and 3% are in no dominant and sulfate type, respectively. The cationic triangle shows that 82% of samples fall under the Na+K field and the rest (18%) fall under no dominant field. Two distinct hydrogeochemical facies were identified in the Garmsar Plain. The samples mostly belong to the sodium chloride type (82%) followed by the mixed Ca-Mg-Cl type (18%). The main hydrochemical facies of the samples are listed in Table 2.

Table 2. Hydrochemical facies of Garmsar groundwater

Anionic triangle		Cationic triangle		Diamond field	
Percent	**Type**	**Percent**	**Type**	**Percent**	**Type**
92	Cl-	82	Na+K	82	Sodium chloride
5	No dominant	18	No dominant	18	Mixed Ca-Mg-Cl
3	SO_4^{2-}	-	-	-	-

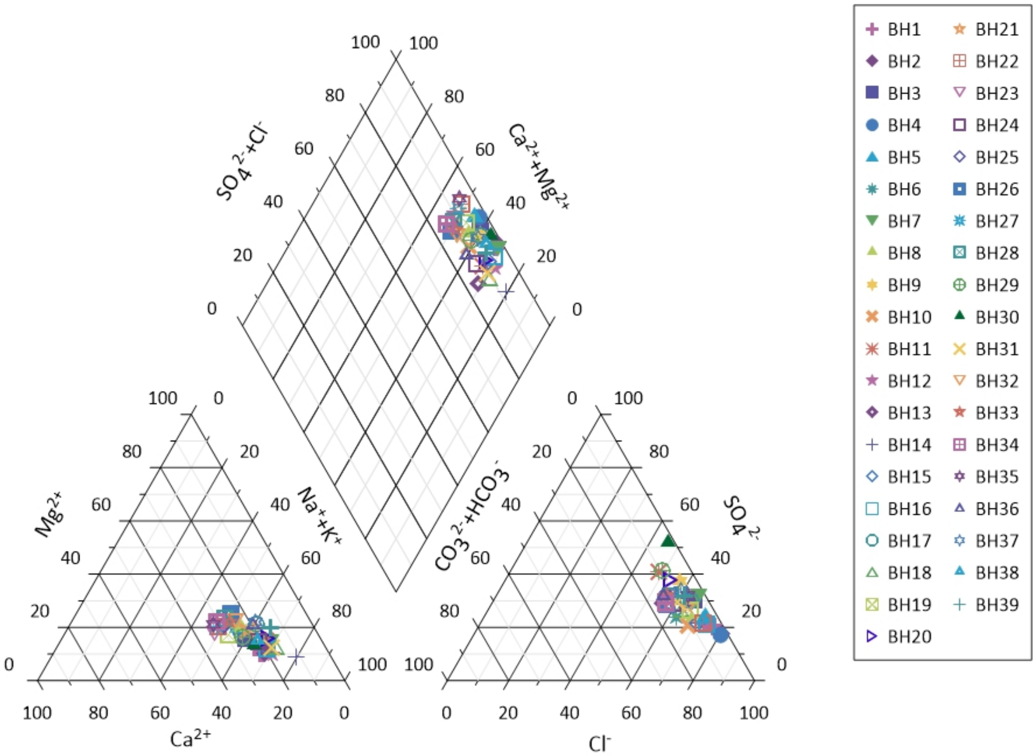


Figure 2. Piper diagram of Garmsar groundwater samples

The expanded Durov Diagram (Fig. 3) was also used to plot the major cations and anions in Garmsar groundwater samples. This diagram helps to understand evolutionary trends and hydrogeochemical processes. As it is shown in Fig. 3, most samples are in Mg-Na rich cation field and Cl-SO_4 rich anion field. The square part of the diagram illustrates that all the samples participate in the ion exchange process.

The Pie Diagram Map shown in Fig. 4 provides the evolution and distribution of groundwater chemistry in Garmsar Plain. In this diagram, the circle has a relative size to the quantity of the total dissolved solids. Consequently, waters with similar chemical constituents are rapidly identified. According to Fig. 4, the quality of groundwater decreases generally in the direction of the hydraulic gradient due to the increase in residence time. However, as shown in Fig. 4, groundwater in the northwestern part of the plain is affected by salt water from the dissolution of the evaporite formations.

Hydrochemical Processes

The elemental concentrations in groundwater depend on the chemistry of precipitation, bedrock composition, water-rock interaction, climatic conditions, as well as the residence time of groundwater in the aquifers (Drever, 1997). Following Gibbs, (1970), two scatter plots are applied to identify the connection between groundwater chemistry and its controlling mechanisms (Fig. 5). In these diagrams, weight ratios of $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ to TDS (in mg/l) are plotted separately. Groundwater chemistry has a low $Na^+/(Na^+ + Ca^{2+})$ ratio when carbonate minerals predominate. In other areas where silicates predominate $Na^+/(Na^+ + Ca^{2+})$ ratio can be high (Banks and Frengstad, 2006). As illustrated in Fig. 5, the main process that determines the composition of water is evaporation. Evaporation of surface water has emerged as the main process of changing elemental concentrations of groundwater near the surface (Richter and Kreitler, 1993). The elements of remaining water are concentrated by evaporation, causing evaporite deposits to settle and eventually leach into the saturated zone (Saberinasr et al., 2019).

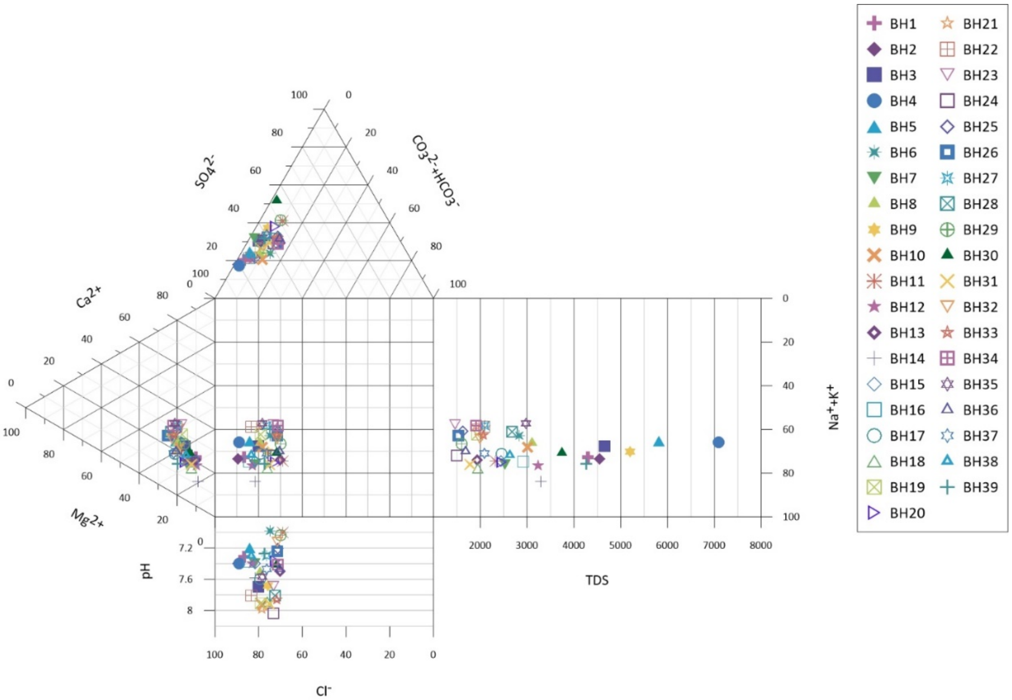


Figure 3. Chemical facies of Garmsar groundwater in Durov diagram

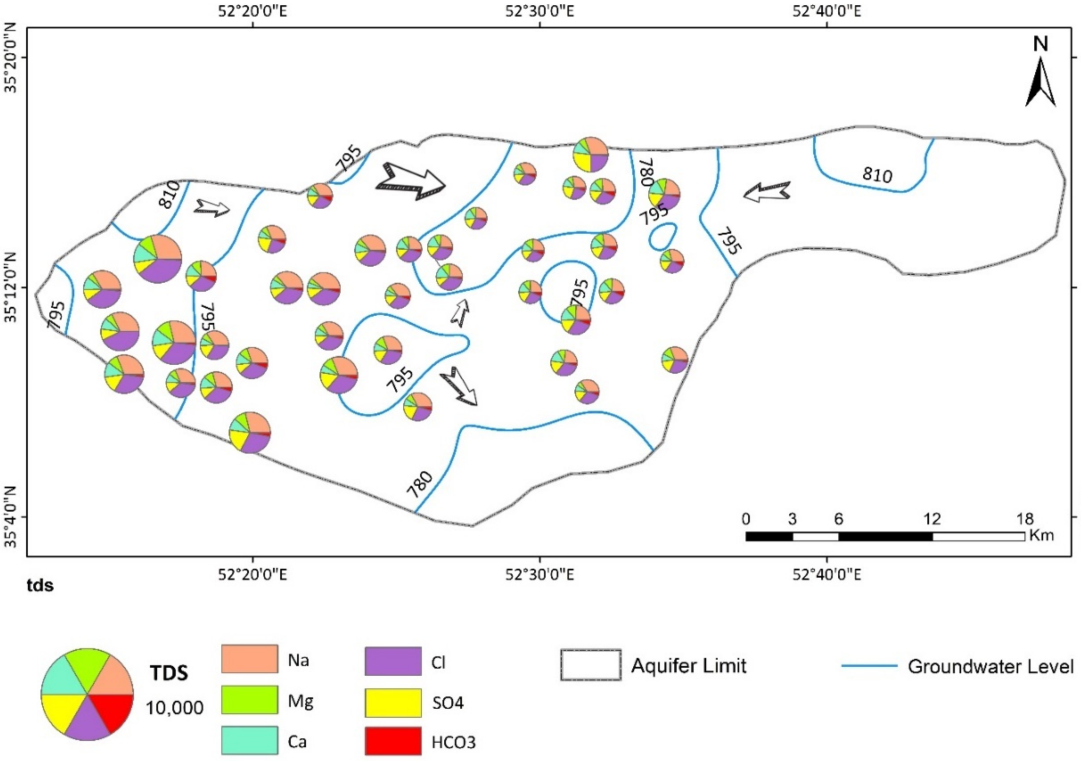
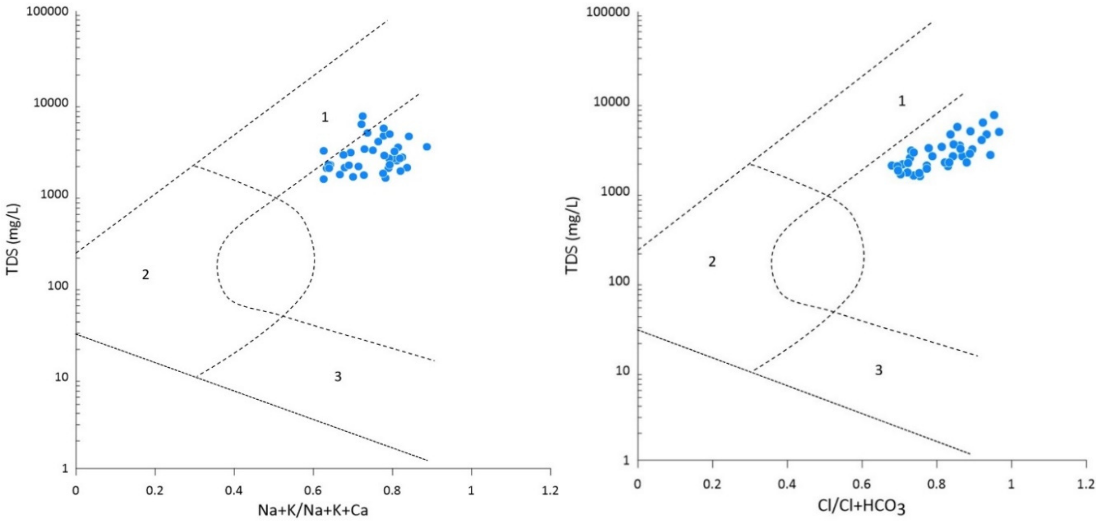


Figure 4. Pie diagram map of Garmsar groundwater samples

High evaporation and low rainfall enlarge this groundwater salinity source in arid lands such as the Garmsar Plain, stimulating the above processes and reducing the dilution effect on salt water as well. This is obviously reflected in the Gibbs Plot of Garmsar Plain, which shows the tendency of evaporation. Inference from the Gibbs diagrams indicates that the evaporation process has had a profound effect on the major ion chemistry of groundwater. Evaporation increases the salt content by increasing the levels of sodium and chloride, and therefore the increase in these ions originates from the weathering of sulfate minerals with high magnesium and sodium. If there is no potential source of evaporation, it is assumed to be another source of evaporation, such as the mixing of high saline water (Marandi and Shand, 2018).

Hydrochemical facies of groundwater can be categorized by major ions using the Chadha diagram (Chadha, 1999). The results of the chemical analysis were plotted on this chart to investigate the groundwater classification and recognize the hydrochemical process shown in Fig. 6. Most of the groundwater samples in the Garmsar Plain (Fig. 6) are classified into a subfield in which alkaline-earth elements are more than alkali elements and also heavy acidic anions exceeding slightly acidic anions, creating Ca–Mg–Cl water type, such types of water have permanent hardness (Snousy et al., 2021). The remaining samples can be classified as Na–Cl water type (Fig. 6); which causes serious salinity problems in both irrigation and drinking uses (Chadha, 1999).



1. Evaporation dominance
2. Rock-weathering dominance
3. Precipitation

Figure 5. Gibbs Diagram for controlling factors of groundwater quality in the Garmsar Plain

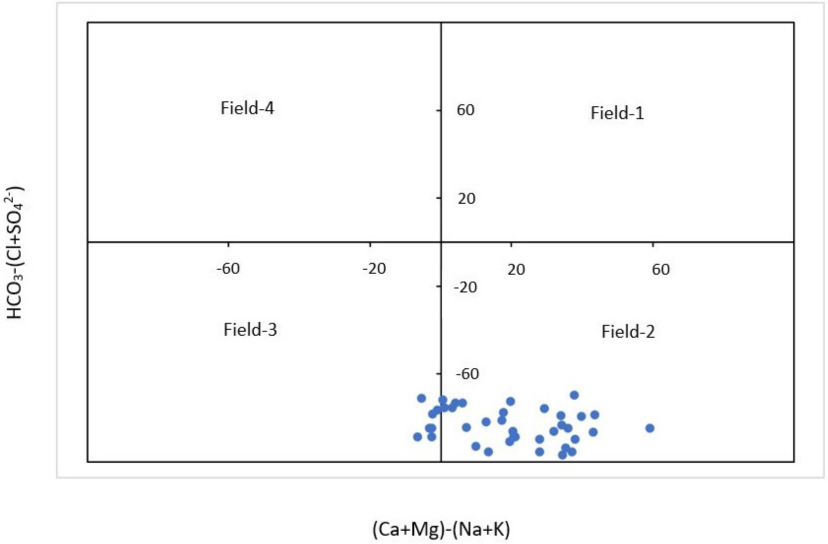


Figure 6. Chadha diagram classification of the groundwater Samples

Water Quality Assessment

In the Garmsar Plain, groundwater is the major water supply for a variety of purposes. Therefore, it is important to determine if it is suitable for use for drinking or irrigation purposes.

Total Hardness (TH)

Calcium and magnesium are one of the eight elements abundant in the Earth's crust. Therefore, surface water may dissolve Ca^{2+} and Mg^{2+} salts as it penetrates the crust, increasing its concentration in groundwater. Dissolved calcium and magnesium are believed to be primarily responsible for the hardness of groundwater, further limiting its use in household, agricultural, and industrial applications (Adimalla and Qian, 2019; Liu et al., 2019). High levels of total hardness are harmless to human health; however, both extreme degrees of very soft (<75 mg/L as $CaCO_3$) and very hard (>300 mg/L as $CaCO_3$) are not favorable (Sappa et al., 2014; WHO, 2022). Total hardness of water is defined as the sum of the calcium and magnesium concentrations in desired water sample which is expressed as calcium carbonate concentration. The TH content in Garmsar groundwater varies from 385 to 2760 mg/L, averaging 907.5 mg/L (Table 3). According to Sawyer and McCartly (1967), all Garmsar samples fall into a very hard category.

Table 3. Classification of Garmsar water samples according to different parameters

Parameter	Method	Range	Water Classification	Number of Samples	Percentage
TH	Sawyer and McCarthley	<75	Soft	-	-
		75-150	Moderately hard	-	-
		150-300	Hard	-	-
		>300	Very hard	39	100
SAR	Richard	<10	Excellent	23	59
		10-18	Good	15	38
		18-26	Doubtful	1	3
		>26	Unsuitable	-	-
Na%	Wilcox	<20	Excellent	-	-
		20-40	Good	-	-
		40-60	Permissible	20	51
		60-80	Doubtful	19	49
		>80	Unsuitable	-	-
PI	Doneen	>75% (Class Ⅰ)	Very good water quality	5	13
		25%-75% (Class Ⅱ)	Good water quality	34	87
		<25% (Class Ⅲ)	Bad water quality	-	-
KR	Kelley	<1	Suitable	7	18
		>1	Unsuitable	32	82
MAR	Ragunath	<50	Suitable	33	85
		>50	Unsuitable	6	15
RSC	Eaton	<1.25	Safe	39	100
		1.25-2.5	Marginal	-	-
		>2.5	Unsuitable	-	-

Sodium absorption ratio (SAR)

Sodium adsorption ratio is an important measure of the suitability of water for use in irrigation, as the higher the SAR value, the higher the sodium concentration, which can destroy the soil structure and reduce irrigation performance (Sappa et al., 2014; Srinivas et al., 2017; El Bilali and Taleb, 2020). The SAR parameter evaluates the sodium hazard based on the relationship between Na^+ ion and divalent cations (Kalra and Maynard, 1991; Singh, 2018), and is calculated as follows:

$$SAR = \frac{Na^+}{\sqrt{1/2(Ca^{2+}+Mg^{2+})}} \tag{2}$$

SAR values in the Garmsar Plain range from 4.6 to 18.2. According to the Richards classification, 59 % of Garmsar samples are classified as the excellent category, 38 % are good, and only 3 % fall under the doubtful category. As shown in Table 3, according to SAR, none of the Garmsar samples are favorable for irrigation.

Soluble Sodium Percentage (SSP)

Soluble Sodium Percentage or the Percentage of Sodium (Na%) is important for evaluating irrigation water. High concentrations of sodium in irrigational water retards the plant growth by reducing soil permeability (Raju, 2007; Ghalib, 2017). According to Wilcox (1955), irrigation water based on Na% is classified into five categories including excellent, good, acceptable, doubtful, and unsuitable classes, which have SSP under 20 percent, 20 to 40 percent, 40 to 60 percent, 60 to 80 percent, and above 80 percent, respectively (Khodapanah et al., 2009). This indicator can be determined as follows (Wilcox, 1955):

$$\%Na = \frac{(Na^+ + K^+)}{(Ca^{2+}+Mg^{2+}+Na^+ + K^+)} \times 100 \tag{3}$$

Where the ion concentration is expressed in meq/L. A Na%-based groundwater quality assessment (Wilcox, 1995) shows that about 51% of the samples have acceptable categories, about 49% of them have suspicious categories, and values of Na% vary from 46.5% to 79.5% (Table 3). Long-term irrigation with such water can lead to soil deterioration due to the accumulation of Na (Darwisha et al., 2011).

Permeability Index (PI)

After long-term use of mineral-rich irrigation water, the soil permeability is considerably influenced by sodium, calcium, magnesium, and bicarbonate contents in the water, which can indirectly affect crop production (Thockchom and Kshetrimayum, 2019). Doneen (1964) developed criteria to use different water qualities in order to assess the potential of changes in soil permeability based on PI. The permeability index can be applied to classify the groundwater into class I (excellent), Ⅱ (good), and Ⅲ (unsuitable) with PI above 75 %, 25 to 75 %, and under 25 %, respectively (Ragunath, 1987). The permeability index is determined by Equation 4:

$$PI = \frac{(Na^+ + \sqrt{HCO_3^-})}{(Ca^{2+}+Mg^{2+}+Na^+)} \times 100 \tag{4}$$

The PI of the samples in the Garmsar Plain ranges between 50.3 and 83.3. Thus, most groundwater samples are classified as class Ⅱ and only 5 samples are classified as class I, showing very good water quality. However, there are no class Ⅲ samples that are not suitable for irrigation.

Kelly's Ratio (KR)

The Kelly Ratio is an important parameter to determine the Na^+ content against Ca^{2+} and Mg^{2+}

for evaluating the quality of irrigation water (Eq. 5) (Kelley, 1963):

$$KR = \frac{Na^{+}}{(Ca^{2+}+Mg^{2+})} \tag{5}$$

Where the ion concentration is expressed in meq/L. A KR of <1 shows suitable irrigational water. A KR amount greater than 1 indicates unsuitable water quality for irrigation due to elevated sodium levels and effects on soil permeability (Naseem et al., 2010). KR values in the Garmsar Plain range from 0.9 to 3.9, revealing that 18% of the samples are of good quality and 82% of them are not suitable for irrigation (Table 3).

Magnesium Adsorption Ratio (MAR)

Irrigation water with a high magnesium content make the soil more alkaline and therefore adversely affects crop yields (Kumar et al., 2007). Paliwal (1972) introduced the magnesium adsorption ratio (MAR) or magnesium hazard (MH) index. The index is used to qualify the groundwater for irrigation by measuring the excess amount of magnesium over calcium and magnesium as follows (Ragunath, 1987):

$$MH = \frac{Mg^{2+}}{(Ca^{2+}+Mg^{2+})} \times 100 \tag{6}$$

The acceptable MAR limit for irrigational water is 50 (Kalaivanan et al., 2018). In the Garmsar Plain, the MR values range from 31.2 to 58.3 meq/L (Table 3). 85 % of MAR in Garmsar groundwater samples are considered safe for irrigation and 15 % of samples are considered unsafe, indicating a negative impact on crop yields.

Residual Sodium Carbonate (RSC)

If the concentration of bicarbonate and carbonate in the water is higher than that of Ca^{2+} and Mg^{2+}, then calcium and magnesium will precipitate (Mirza et al., 2017). This may result in increasing sodium in the water in the as sodium carbonate through precipitating Ca^{2+} and Mg^{2+}, and leaving sodium as dominant cation. This excess of sodium ion can be determined by RSC (Eq. 7), which explains the risk of soil alkalinity. High concentration of bicarbonate in the soil prepares a condition known as black alkali soil, which also has a high pH value (Thockchom and Kshetrimayum, 2019). If a value of RSC is more than 2.5 meq/L, then Na^{+} adsorption occurs. In the Garmsar Plain, the RSC value of the samples ranges from -52.5 to -4.6, indicating that the samples are good for irrigation (Naseem et al. 2010).

$$RSC = (CO_3^{-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+}) \tag{7}$$

Index of Base Exchange (IBE)

It is important to determine the changes in chemical compounds of groundwater during its subsurface movement (Johnson, 1979). Ion exchange is a key process, which affects the groundwater chemistry and adjusts the transport of contaminant chemicals in both soil and aquifer (Ahamed et al., 2015). IBE is evaluated by means of the chloro-alkaline indices, CAI-1 and CAI-2, proposed by Schoeller (1977) to interpret the ion exchange process between groundwater and the host rocks during the stay or movement. The chloro-alkaline indices are calculated using Equations 8 and 9, as follows:

$$\text{Chloro alkaline index 1} = \frac{[Cl^{-}-(Na^{+}+K^{+})]}{Cl} \tag{8}$$

$$\text{Chloro alkaline index 2} = \frac{[Cl^{-}-(Na^{+}+K^{+})]}{(SO_4^{2-}+HCO_3^{-}+CO_3^{2-}+NO_3^{-})} \tag{9}$$

Where the concentrations are stated in meq/L. If sodium and potassium from the groundwater exchange with magnesium and calcium in the soil, then the direct exchange process is occurred and therefore, the index is positive. On the other hand, if this exchange happens conversely, therefore the exchange process is indirect and the index will be negative (Thockchom and Kshetrimayum, 2019). In the Garmsar Plain, the CAI 1 values range between -0.3 and 0.3, while CAI 2 values lie between -0.3 and 1. It is also found that 59 % of the groundwater samples show positive value implying the reverse ion exchange and 41 % of samples have negative value showing normal ion exchange.

Potential Salinity (PS)

Potential salinity is determined by measuring the concentration of Cl^- and SO_4^{2-} and is used to measure the suitability of groundwater for irrigation (Ahamed et al., 2015; Ezugwu et al., 2019), and is expressed as:

$$PS = Cl^- + \left(\frac{SO_4^{2-}}{2}\right) \tag{10}$$

The higher the PS values, the higher is the resultant chloride ion concentration. Samples with less than 10 PS value are suitable for irrigational water. The PS values in the Garmsar Plain are high and fluctuate between 15.8 and 102.6 meq/L, indicating unsuitable for irrigation purposes.

Irrigation Water Quality Index (IWQI)

Water quality indices are used as indicators for determining the fitness of water for different uses. Various water quality indicators have been created and used worldwide (Adimalla and Taloor, 2020; Pak et al., 2021; Dimri et al., 2021; Uddin et al., 2021). The water quality index can convert large amount of unprocessed data into a single value, representing the overall water quality. The IWQI was primarily developed by (Meireles et al., 2010), as an indicator of groundwater quality for irrigation purposes (Adimalla and Qian, 2019). Five parameters are taken into account to evaluate IWQI including SAR, EC, HCO_3^-, Na^+, and Cl^-. The concentration units should be in meq/L. IWQI is determined by Equation 11:

$$IWQI = \sum_1^n q_i \times w_i \tag{11}$$

Where *n* refers to the number of parameters considered, in this case there are 5 parameters (Table 4); q_i is the water quality measurements for each parameter and w_i is the relative weight of each parameter shown in Table 5 according to Meireles et al. (2010). The value of q_i for each of the parameters was calculated by Equation 12:

$$q_i = q_{imax} - \frac{\lfloor (x_{ij} - x_{inf}) q_{iamp} \rfloor}{x_{iamp}} \tag{12}$$

Where q_{imax} is the maximum value of q_i in each class, x_{ij} is the observed value of each parameter, x_{inf} represents the minimum value of the observed parameter in the class, q_{iamp} refers to the amplitude of the class, and x_{iamp} corresponds to the amplitude of the class to which the parameter belongs (Meireles et al., 2010). The IWQI is a dimensionless irrigation water index in the range 0-100. The higher the IWQI, the better the water quality for irrigation. IWQI is classified into five categories, as shown in Table 6 (Abbasnia et al., 2018).

Table 4. Quality parameters of irrigation water and their proposed limits

q_i	Electrical Conductivity (µS/cm)	Sodium Adsorption Ratio $(meq/L)^{1/2}$	Sodium (meq/L)	Chloride (meq/L)	Bicarbonate (meq/L)
85 to 100	200 to 750	<3	2 to 3	<4	1 to 1.5
60 to 85	750 to 1500	3 to 6	3 to 6	4 to 7	1.5 to 4.5
35 to 60	1500 to 3000	6 to 12	6 to 9	7 to 10	4.5 to 8.5
0 to 35	<200 or >3000	>12	<2 or >9	>10	<1 or >8.5

Table 5. IWQI Parameters weights

Parameter	W_i
Electrical Conductivity	0.211
Sodium	0.204
Bicarbonate	0.202
Chloride	0.194
Sodium Adsorption Ratio	0.189
Total	1.000

Table 6. Suitability of Garmsar groundwater for irrigation purposes based on IWQI

IWQI values and types of restriction	Percentage	Plants Type	Soil
85-100 (No restriction)	-	No toxicity	Groundwater can be used for all soil types
70-85 (Low restriction)	-	Avoid the use of salt-sensitive plants	Groundwater can be used for medium to high permeability light soil texture
55-70 (Moderate restriction)	-	Plants with moderate salt tolerance	Groundwater can be used for moderate to highly permeable soils, taking into account the moderate soil leaching process
40-55 (High restriction)	48.7	Plants with moderate to high salt tolerance	Groundwater can be used for permeable soil with the lack of compact layers, considering the high frequency of irrigation schedule for irrigation water with electrical conductivity greater than 2000 µS/cm and SAR value of more than 7
0-40 (Severe restriction)	51.3	Only plants with high salt tolerance	Under normal conditions, groundwater cannot be used to irrigate the soil

Health Effects of Water Quality Indices

Health risk assessment for human is the process of estimating the potential adverse effects on human health that may be exposed to chemicals in environmental media such as drinking water (Snousy et al., 2021). However, over-exposure to common non-toxic chemicals that are often found even in natural water may also raise significant risks to human health. The results in this study indicated that some of the hydrochemical parameters in the groundwater of Garmsar Plain exceed permissible limits. Therefore, in this section, the adverse effects of these parameters on human health were investigated.

PH generally does not directly affect human health through the consumption of drinking water. Indirect health effect is caused by increased ingestion of metals resulting from toxic colloidal stabilization and the amounts of pipes corrosion (optimal pH must lie between 6.5 and 9.5 in water distribution system). Exposure to pH levels above 11 leads to eye irritation and deterioration of skin condition (WHO, 2022). In the Garmsar Plain, the pH of all groundwater samples falls within the ranges of acceptable levels (Table 7).

Similar to pH, TDS and EC have little direct impact on human health. Water with less than 1000 mg/L TDS concentration of is acceptable to consumers, but increased values of TDS in the water cause bitterness and saltiness, which discolors the water and makes it unpleasant for consumers (WHO, 2022). EC also increases with the ion concentration in the water (Hem, 1985;

Hounslow, 2018). Table 7 shows that the EC of all groundwater samples is above the permissible limit. In general, high levels of TDS and EC in drinking water are harmful to patients with kidney deficiency and heart disease (Craun and McGabe, 1975; Snousy et al., 2021; WHO, 2022).

Although Calcium and magnesium are among essential chemicals, exceeding the permissible limit can cause hardness of water, resulting digestive system problems and cleaning issues (Khan et al., 1999; Sarfraz, 2019). Magnesium plays an important role in the cell functions that activate enzymes, but increased intake of Mg^{2+} may lead to a laxative agent and diarrhea and hypermagnesemia in people with renal dysfunction (WHO, 2022). Furthermore, exposure to hard water is a risk factor for exacerbating the etiology of atopic eczema (Thomas and Sach, 2000). Table 7 shows that 33 and 31 % of groundwater samples have high Ca^{2+} and Mg^{2+} content compared to WHO guideline values. Moreover, approximately 27 % of groundwater samples have exceeded the maximum permissible TH limit (500 mg/L) that is not potable in the study area (WHO, 2022).

Sodium ion is an essential element to maintain a proper health, helping to balance the water in the human body, but intake of water with elevated concentration of sodium raises blood pressure and causes severe health problems such as high blood pressure and vomiting (Narsimha and Sudarshan, 2017b; Adimalla, 2018; WHO, 2022). Table 7 indicates that more than 46 % of groundwater samples have high concentrations of Na.

Table 7 reveals that the HCO_3^- concentration of 44 % of the groundwater sample exceeds the desirable limit and none is more than the permissible limits to water consumers. HCO_3^- can increase the pH and affects corrosion rates due to importing alkalinity to water.

Chloride ions are one of the natural components of groundwater, and it derives mainly from the geological formations as well as industrial wastes and municipal effluents (Subba Rao et al., 2017). Below permissible limits, chloride helps keep the kidneys and nervous system healthy (Cantor et al., 1987). However, high content may give a salty taste to drinking water along with creating problems in the digestive system and even react with sodium ions in the human body to cause a heart attack (Khan et al., 2000). Table 7 shows that about 95 % of groundwater samples have Cl^- content higher than WHO permissible limits.

Sulfate is also a common component of groundwater. Ingestion of water containing high concentration of sulfate along with calcium and magnesium ions can cause a laxative effect on the human body (WHO, 2022).

Table 7. Comparison of physicochemical analysis with WHO (2022) limits in the Garmsar Plain

	WHO Limit				**Groundwater**	
					% Sample	
Parameter	**Desirable Limit (DL)**	**Permissible Limit (PL)**	**Min**	**Max**	**DL**	**PL**
pH	6.5-8.5	-	7	8	100	-
EC	500	1500	2200	10630	-	100
TDS	500	1500	1461	7090	3	97.4
Ca^{2+}	75	200	90.2	633.3	67	33
Mg^{2+}	50	100	35.9	286.9	56	31
Na+	200	600	260.3	1661.1	54	46
HCO_3^-	200	500	54.9	372.2	44	-
Cl^-	250	500	438.9	3284	5	95
SO_4^{2-}	200	400	307.4	1724.3	23	77

A number of waterborne diseases like diarrhea, respiratory illness, gastrointestinal disorder, weight abatement and dehydration are linked to elevated concentrations of SO_4^{2-} in drinking water (Mazloomi et al., 2009). In addition, if the sulfate concentration exceeds 200 mg/L (WHO desirable limit for sulfate), the drinking water will become bitter as well as unwanted metals intake due to corrosion of the water pipe network (USEPA, 1999a; b). Sulfate content of more than 400 mg/L is not acceptable in drinking water (WHO, 2022). Table 7 reveals that 76.9 % of groundwater samples have SO_4^{2-} concentration higher than water consumers' permissible limits.

Conclusions

The hydrochemical processes controlling groundwater quality of the Garmsar Plain, as well as the assessment of its suitability for agricultural and domestic purposes have been considered in this study. Hydrochemical analysis data revealed that the concentration of $Na^+ > Ca^{2+} > Mg^{2+}$ and $HCO_3^- > Cl^- > SO_4^{2-}$, respectively. In addition, dissolution of the aquifer matrix strongly affects the groundwater quality, interaction of water with rocks, and penetration of irrigation water. Water is classified to the types of sodium chloride (82%) and the mixed Ca-Mg-Cl (18%) based on Piper diagram, indicating the geology of the Garmsar Plain. According to the expanded Durov and Gibbs diagrams, the ion exchange and the evaporation are respectively the main processes controlling the chemical compounds of groundwater.

As a result of evaluating the suitability of Garmsar irrigation water samples using quality indicators such as SAR, Na (%), PI, KR, MAR, and RSC, it is shown that groundwater in this plain is suitable for irrigation only from the viewpoint of RSC. Hence, only the moderate to high salt tolerance plants under special irrigation condition can be cultivated. Moreover, the IWQI showed that the groundwater samples could not be used for irrigation purpose, reflecting the negative impact on crop yields.

Based on human health risk assessments, water quality in most regions of the Garmsar Plain exceeds the World Health Organization (WHO) guideline values; so that 33, 31, 46, 44, 95, and 77 % of groundwater samples in the Garmsar Plain have higher concentrations than the permissible drinking water quality limits for calcium, magnesium, sodium, bicarbonate, chloride, and sulfate, respectively. If the major ions in the drinking water exceed certain limits, they may pose significant health hazards such as hypertension, heart attack, diarrhea, vomiting, and digestive problems, along with discoloring the water, bitter or salty taste, and an unpleasant odor. Therefore, water treatment strategies are highly recommended to decrease the health hazards. The findings of the current study are expected to improve water quality management in the Garmsar Plain. This research, thus, recommends the need for regular monitoring of groundwater quality parameters and adopting appropriate measures to overcome degradation of groundwater quality in the study area.

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Consent to Participate

The authors declare that they are aware and consent with their participation on this paper.

Consent to Publish

The authors declare that they are consent with the publication of this paper.

Availability of data

The datasets analyzed during the current study are available from the Semnan Regional Water Authority, owned by Ministry of Energy, but restrictions apply to the availability of these data and so are not publicly available. Data are however available from the authors upon reasonable request and permission of owner.

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