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Salinity, Chemistry, and Quality of Groundwater in Robat-Khorramabad Plain, West of Iran

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Abstract

Groundwater salinization in semiarid regions is a limiting factor of use with strategic importance. In this study, the sources of salinity, chemistry, and quality of groundwater in Robat (Khorramabad plain, Iran) were identified through the geochemical methods. Using data analysis, the concentration of cations and anions were recognized with the order of Ca^{2+}>Na^{+} >Mg^{2+}>K^{+} and HCO_3^{-}> Cl^{-}> SO_4^{2+}> NO_3^{-}> F^{-}, respectively. The high concentration of Na^{+}, Cl^{-}, and EC in some places is attributed to the gypsum and salty formations. In the study area, the salinization processes are identified by natural and artificial activities. The salinization mechanisms are identified by the natural dissolution of gypsum and salt from Gachsaran formation and man-made sources including boreholes drilled through Gachsaran Formation, salt mining, and agricultural activity. Also, the high concentration of nitrate is related to agricultural fertilizers and karstification effects. It is seen that the atmospheric NO_3^{-}. HCO_3^{-}, Ca^{2+}, and Mg^{2+} concentration exceeded the standard limit in a few samples probably due to the calcareous formation. Besides, hydrochemical facies of the groundwater are Ca- HCO_3 and Na-K-HCO_3. Due to the presence of calcareous and salt bearing formations, 46%, 26%, and 20% of all samples show a higher concentration of Ca^{2+}, Na+, and Mg^{2+}, respectively, which exceed the

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permissible limits. Sulfate and fluoride concentrations are less than the permissible limits. However, due to the presence of calcareous formation, salt bearing formation, and use of agricultural fertilizers, 100%, 26%, and 20% of all samples show a higher concentration of HCO_3^-, Cl^-, and NO_3^- than the permissible limits.

Keywords: Groundwater Resource; Gachsaran Formation; Chemical Analysis; Hydrogeology

Introduction

Groundwater resource assessments and sustainability considerations are of great importance in the arid and semi-arid regions, where water is of critical economic and social significance. The continuous growth of the population in Iran has led to a rapid depletion of groundwater supplies in some areas [1]. However, groundwater chemistry depends on several factors such as general geology, degree of chemical weathering of various rock types, quality of recharge water, and the inputs from the sources other than water-rock interaction. Such factors and their interactions lead to a complex groundwater quality [2]. The relations between groundwater composition and water-rock interaction have been investigated in different areas. Researchers [3][4] have used a weathering algorithm to assess the contributions made by chemical weathering and anthropogenic inputs to the groundwater composition. Background information on the petrology and mineralogy of the area let us choose the most realistic water-mineral interactions [4]. Moreover, salinity plays a significant role in water resource developments and

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management worldwide [5]. The largest source of Cl^- in the Earth's crust is the mineral halite in evaporate deposits formed over geologic time by the evaporation of seawater [5][6]. Increasing the concentration of these ions in groundwater and surface water can adversely affect environmentally-sensitive areas. Moreover, it has some natural sources including rock-water interactions, saline seeps, and minor atmospheric contributions [5][7]. Several studies worldwide focusing on the quality and salinity of groundwater have identified the effective processes in the origin of dissolved salt [1][5][8][9]. The present study aims to investigate the main processes controlling groundwater hydrochemistry in Robat-Khorramabad plain, in the west of Iran. Affected by the salinity increase in the study area, groundwater quality degradation introduces some problems for drinking and farming. The study area, as an active agricultural zone in Lorestan province, west of Iran, is of great importance. In the present study, the sources of groundwater salinity in Robat plain were identified using geochemical methods. Also, the chemical quality of groundwater is related to the lithology of the area.

Geographic and Geologic Setting

The study area, located in the northern of Khorramabad, lies between latitudes 33° 30´ to 33° 43´ N and longitudes 48° 15´ to 48° 22´ E. The area is a part of the Karkheh watershed with a semi-arid climate. Precipitation is the major source of groundwater recharge. The average annual rainfall of the area is 286.5 mm. Monthly distributions of precipitation show that the rainiest month of the region is February, while the lowest amount of annual precipitation occurs in September. The geographical location of the study area is shown in Figure 1. Zagros orogen flanks Turkish-Iranian plateau to the south whose climax reaches as a maximum of 4,548 m in Khuzestan province in NW Zagros. Geologically, the study area is located between folded Zagros and thrust or crushed Zagros. The N to NW of the area is in thrust Zagros, while S to SW of the area is placed in folded Zagros. Moreover, in the east and north of Khorramabad, the crushed Zagros zone includes two parts of the residual unit and allochthon unit [10]. Thus, the study area can be divided into two zones. This first one is the southern part of the area with normal tectonic in which sediments with uniform layering overlie each other in the order of their age. Here, except for intra-formational fault, there is no other specific tectonic event. In contrast, the northern part of the area is tectonically complicated and disturbed.

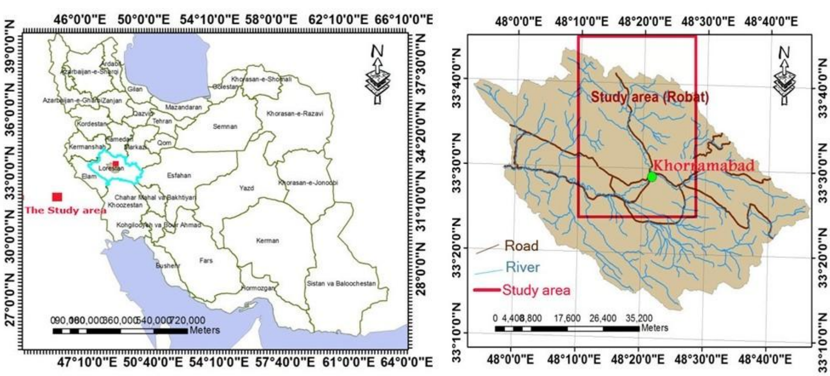

Figure 1. Location of the study area

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This complex tectonic is developed due to the activities of the folds and faults that lead to a constant variation of slope and strike of stratigraphy, differentiation of younger and older layers, faulting the rock units, causing the lithology disarray in this part of the study area (Figure 2). The emergence of some springs in the area is related to these faults [11].

Hydrogeology of the study area

In terms of aquifer and discharge rate, geological formations of the region are divided into three groups of calcareous formations, non-calcareous formations, and evaporative formations. The main lithologies in this group are marl, gypsum, anhydrite, and salt bearing formations. In this lithology unit, due to the result of fine-grained sediment development, the discharge is weak and the groundwater lacks the required quality and is usually saline. The study area is located in the Zagros Mountains, which consist of calcareous formation with a high potential of karstification. Meanwhile, fractures such as fault and joint play an important factor in the karstification and natural flow of groundwater. The outcrops of Asmari-Limestone, Kashkan-Sandstone, and Gachsaran-Salt Formation in Robat plain are the major source of material in the plain. The Kashkan-Sandstone and Gachsaran-Salt formation are the material source in the northeast of the study area. According to the well logs (Figure 3), generally, alluvium of Robat plain is heterogeneous and is composed of gravel, sand, silt, and silty marl.

According to the well log diagrams of the study area, to a certain depth of the aquifer, the study area is composed of granule, sand, gravel, and fine-grained sediments with salty marl. It is also seen that sediments exist at different depths. According to observation data, the water table in Robat plain is influenced by several factors including fault, river recharge, ~~k~~arstification, and agricultural returned water. The major fault in the area is Robat fault (Figure 2), which serves as a groundwater transmitter fault and underground channel and recharge in the plain. Due to the dominant trend of the fractures in the area, the flow direction is from the northeast and east in the plain. The waterways decline the quality of groundwater because they intrude saline water (agricultural return water, drainage water, etc.) into the aquifer. This is one of the major reasons for water salinity degradation in a particular trend. Another cause of groundwater salinity in the area might be the evaporate deposits in the alluvial deposits. Also, the water from the irrigation plays a role in the plain recharge and causes salinity of plain groundwater. According to the flow direction map of the study area (Figure 2), the aquifer flow direction is from the east. The faults in the region, along the border of the mountain and plain, cause the groundwater to be transmitted from the eastern heights to Robat aquifer. In this regard, the hidden fractures crossing the river play a significant role in water transport.

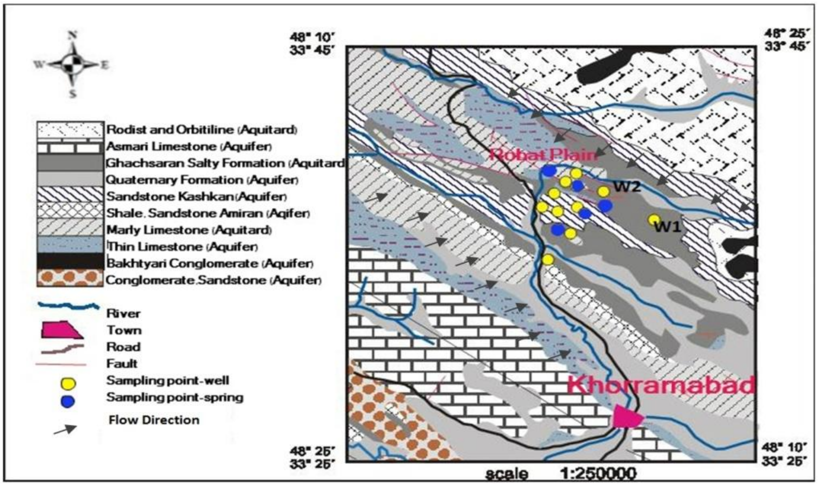

Figure 2. Geology map, flow direction and sampling of the study area

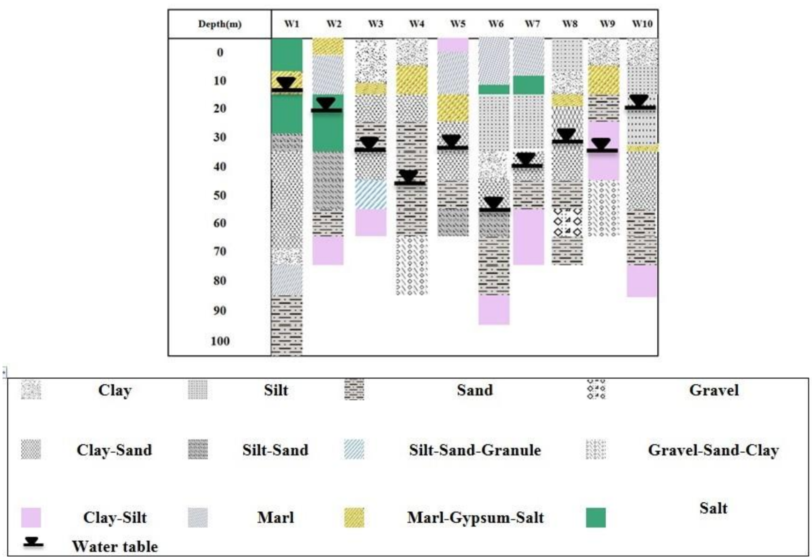

Figure 3. Well-logs of the study area

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Materials and Methods

Water sampling is a technique that is applied to analyze water from a variety of different sources [5]. In this research, groundwater samples were collected from 10 wells and 5 springs in Robat area. All samples were collected in 250-ml polyethylene bottles. Water samples were acidified with HNO_3 to prevent metal precipitation on the bottle walls. The samples were transported to the laboratory in iceboxes and refrigerated at 4℃ until they were analyzed. The samples were collected after 10 minutes of pumping the wells. Analytical techniques were performed following the suggestions of [12]. Immediately after sampling, pH and electrical conductivity (EC) were measured in the field with portable kits. Calcium, magnesium, chloride, bicarbonate (by titration) sodium and potassium (by flame photometry), sulfate and nitrate (by spectrophotometer), and fluoride (by ion chromatography) were measured. Total dissolved solids (TDS) were measured by evaporating 100 ml of water and weighting the residual (Table 1). ArcGIS-10 software [13] was applied to illustrate sampling locations. Besides, the geology map of Khorramabad at a scale of 1:250,000 was used as the base map. Piper and Schuler's diagram was drawn using the AqQA software [14] to identify hydrochemistry facies and water resource quality. Besides, the US Salinity Laboratory hazard diagram [15] and Wilcox diagram [16] were employed to classify and determine the suitability of groundwater for irrigation by correlating sodium absorption ratio/electric conductivity and percent sodium/electric conductivity, respectively.

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Table 1. Analytical result for physico-chemical parameters of groundwater samples of the study area

Sample	pH	EC	TH	TDS	SAR	Na^+	K^+
	±0.1	**±2%**					
	-	μ_m/cm	mg/l	mg/l	mg/l	mg/l	mg/l
S1	7.4	670	313.7	670	1.57	19.2	0.3
S2	7.3	1248	537.5	626	0.78	41.5	0.35
S3	8.1	570	266.8	283	0.28	10.5	0.15
S4	7.5	1110	2.41	560	2.41	96.5	0.35
S5	7.6	2287	161.4	1149	13.49	395	0.3
W1	6.4	568000	10063.4	283500	537.3	124000	3.5
W2	6.2	548000	9352.1	274000	554.2	123500	3
W3	6.8	550	200.6	390.5	18.50	114	0.8
W4	6.8	674	269.2	478.5	8.05	58.5	0.34
W5	6.4	932	185.9	661.72	2.83	16.4	0.3
W6	7.1	2010	319.6	1427.1	33.93	241	0.28
W7	6.5	690	392.3	489.9	5.24	43.9	0.19
W8	6.7	1006	211.05	149.8	1.17	7.1	0.3
W9	7.3	918	317.3	651.7	2.13	15.3	0.15
W10	7.9	731	441.1	519	2.23	20.1	0.29

Ca^{2+}	Mg^{2+}	Cl^-	F^-	SO_4^{2-}	HCO_3^-	NO_3^-
± 1ppm						
mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
106	12.1	102.8	0.48	16.8	207.5	2.8
128.5	53.2	92.1	0.67	144	371.4	52
71.4	21.8	17.73	0.59	20.3	274.7	20
65.2	34	138.3	0.3	51.2	409	3
48.9	9.7	292.5	0.6	50.6	860	3.3
2850	729	44000	1.4	50	271000	3.1
2620	295	40400	1.41	62	264938	2.8
69.1	6.8	114.8	0.63	33.3	356.4	2.7
102.3	3.3	25.4	0.56	10.5	741.5	3.3
55.2	11.7	18.9	0.38	15.9	218.6	2.8
58.8	42.1	98.1	0.42	53.4	179.5	13.9
114.3	26	95.5	0.4	14.3	280.1	9.3
54.9	18	37.2	0.67	48.4	324.5	3.2
66.1	37.1	146.8	0.33	23.7	306.7	2.6
138.1	23.4	109.3	0.3	63.5	291.4	4.8

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Discussion

The chemical compositions of the water samples were analyzed, and the minimum, maximum, and mean concentrations of physicochemical parameters of water quality such as pH, EC, TDS, and the major anions and cations were calculated (Table 2). Here, pH is considered as one of the important water quality parameters, since most of the aquatic organisms are adapted to an average pH range [1]. Water resources of wells W1, W2, and W5 have an acidic pH less than the standard, making it usable only for industrial proposes. Although pH has no direct effect on human health, its higher range accelerates the scale formations in the water heating apparatus. A low pH (< 4) and high pH (> 8.5) lead to sour and alkaline tastes of water, respectively. Electrical conductivity (EC) is regarded as the most important parameter to demarcate salinity hazards and the suitability of water for irrigation purposes [9]. In the present study, the EC varied from 550 to 568,000 µm/cm, indicating higher mineralization in the region. As the electrical conductivity is temperature dependent, its variability in a given water sample depends on the concentration and types of inorganic ions presence [17]. Comparing the experimental values with the standard values for drinking water and public health recommended by [18], EC values were found to exceed the prescribed limit of WHO (2006) through the Robat area [19]. In the study area, TDS values varied in a range from 149.8 to 283,500 mg/l, proving sufficient input of ionic material into groundwater samples. However, geological units, soil properties, and even lithology of the study area may also contribute to total dissolved solids content in groundwater. In the present study, total hardness values ranged from 2.41 to 10063.4 mg/l. Besides, 13% of the samples showed higher values of total hardness, exceeding the maximum permissible limit of 600 mg/l for drinking water.

Table 2. Summary statistics of chemical compositions of major ions (mg/ l) in the groundwater of the study area

Parameters	Minimum	Maximum	Sum	Mean	Std. Deviation	Variance	Skewness	Kurtosis	WHO
pH	6.20	8.10	106.00	7.066	.5790	.335	.197	-.985	6.5-8.5
EC	550.00	568000.0	1129396.0	75293.06	196015.60	3.842	2.407	4.364	300
TH	2.41	10063.40	23034.36	1535.62	3322.964	11042095.124	2.406	4.393	600
TDS	149.80	283500.0	565556.22	37703.74	97881.498	9.581	2.406	4.362	500
Na^+	7.10	124000.0	248579.00	16571.93	43514.41	1.894	2.405	4.349	200
K^+	.15	3.50	10.60	.7067	1.047	1.097	2.353	4.355	20
Ca^{2+}	48.90	2850.00	6548.80	436.58	934.594	873466.6	2.411	4.421	75
Mg^{2+}	3.30	729.00	1323.20	88.21	191.112	36523.893	3.163	10.295	50
Cl^-	17.73	44000.00	85689.43	5712.62	14829.60	2.199	2.415	4.432	250
F^-	.30	1.41	9.14	.6093	.3479	.121	1.754	2.469	2
SO_4^{2-}	10.50	144.00	657.90	43.860	33.343	1111.795	1.984	5.518	250
HCO_3^-	179.50	271000.0	540759.30	36050.62	94165.780	8.867	2.405	4.355	250
NO_3^-	2.60	52.00	129.60	8.6400	13.025	169.657	3.030	9.833	10

According to Table 3, there are positive correlations between Cl^- and Na^- (r = 0.999), Cl^- and Ca^{2+} (r = 1), and Cl^- and Mg^{2+} (r = 0.919). Table 3 shows that TDS has a significant correlation with all cations and Cl^- and HCO_3^- anions. Moreover, TDS had statistically positive correlation with EC (r = 1) and negative correlation with pH (r = -0.536). Based on Table 3, correlation coefficients between total hardness (TH) and Ca^{2+}, Mg^{2+}, Na^+, Cl^-, and HCO_3 were statistically significant (r = 1, 0.917, 0.999, 0.999, and 0.999, respectively). NO_3 did not have any correlation with the presented hydrochemical characteristics of groundwater samples (Table 3). A frequency distribution shows how often each value in a set of data occurs. A

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histogram is the most commonly used graph to show frequency distributions. In a normal distribution, the occurrence likelihood of points on one side of the mean is the same as the other side. However, it is of note that other distributions seem to be the same as a normal distribution. The skewed distribution is unsymmetrical because a natural limit prevents outcomes on one side. Hydrologic data are typically skewed, suggesting that data sets are not symmetrical around the mean or median, with extreme values extending out longer in one direction. When extreme values extend the right tail of the distribution (Figure 4), the data are called as skewed to the right, or positively skewed. On the other hand, when the tail extends to the left, the data are called negative skew [20]. The data of this case study were examined for normality using frequency histograms, normal probability plots, and the skewness test. Results of the case study data analysis (Figure 4) show the frequency histograms of the data series with the best-fitted distributions. As can be seen, pH has a normal distribution. Several other variables showed skewed distributions. As shown in Figure 4, variables including EC, Calcium, magnesium, chloride, bicarbonate sodium, potassium, sulfate, nitrate, fluoride, and TDS have right-skewed distributions. Cluster analysis is a method to place objects into more or less homogeneous groups to reveal the relation between them. Cluster analysis is mostly used when the clusters are formed sequentially by starting from the most similar pair of objects and forming higher clusters [21]. Hierarchical cluster analysis is

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comprised of agglomerative methods and divisive methods, which find clusters of observations within a data set. Four of the better-known algorithms for hierarchical clustering are average linkage, complete linkage, single linkage, and Ward's linkage [22]. Ward's method is the most popular hierarchical algorithm recommended as distance measures of clustering. The plot of the cluster with Ward's linkage is portrayed in Figure 5.

Table 3. Correlation between hydro chemical characteristics of groundwater samples

Parameters	pH	EC	TH	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	F^-	SO_4^{2-}	HCO_3	NO_3
pH	1												
EC	-.536	1											
TH	-.532	.999	1										
TDS	-.536	1.000	.999	1									
Na^+	-.537	1.000	.999	1.000	1								
K^+	-.556	.987	.987	.987	.986	1							
Ca^{2+}	-.530	.999	1.000	.999	.999	.988	1						
Mg^{2+}	-.442	.908	.917	.908	.901	.923	.919	1					
Cl^-	-.533	1.000	.999	1.000	.999	.989	1.000	.919	1				
F^-	-.525	.928	.928	.928	.928	.933	.926	.828	.927	1			
SO_4^{2-}	.127	.147	.161	.147	.148	.157	.154	.152	.145	.241	1		
HCO_3	-.537	1.000	.999	1.000	1.000	.987	.999	.905	.999	.928	.147	1	
NO_3	.260	-.177	-.154	-.177	-.178	-.187	-.165	-.110	-.178	-.019	.735	-.178	1

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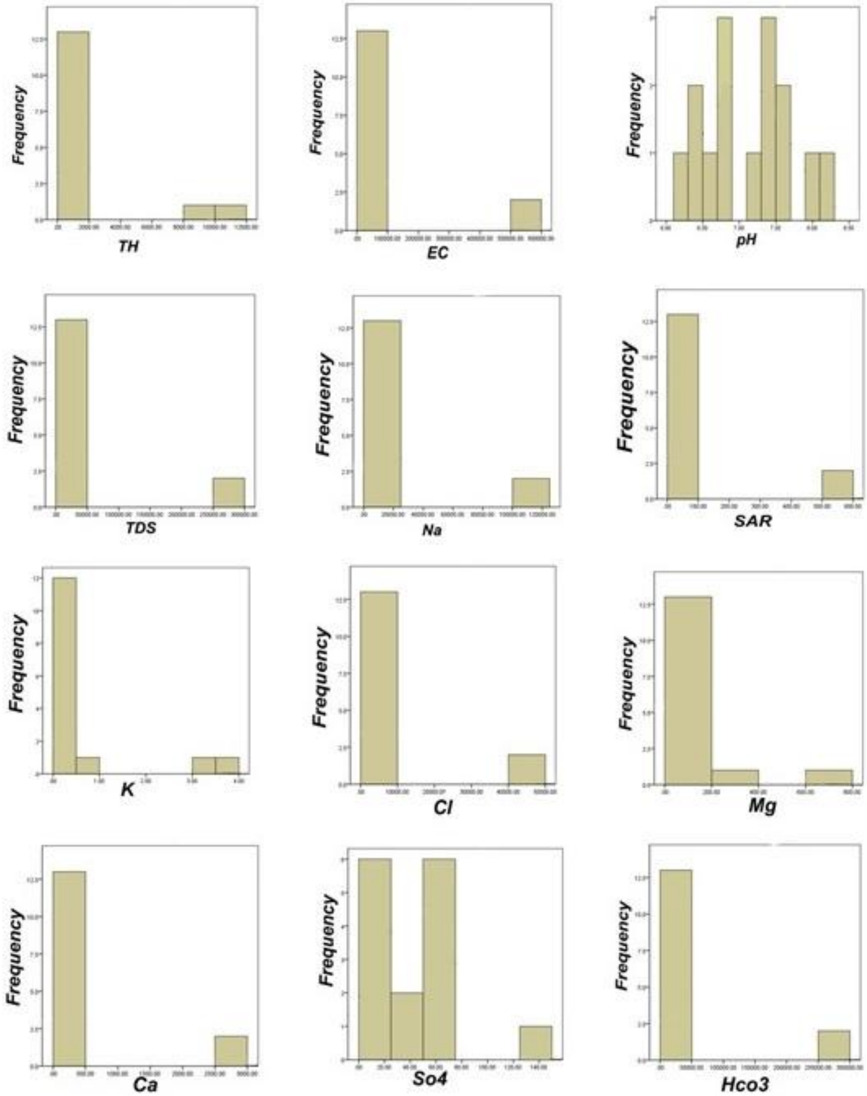

Figure 4. Frequency distributions showed by groundwater parameters variables

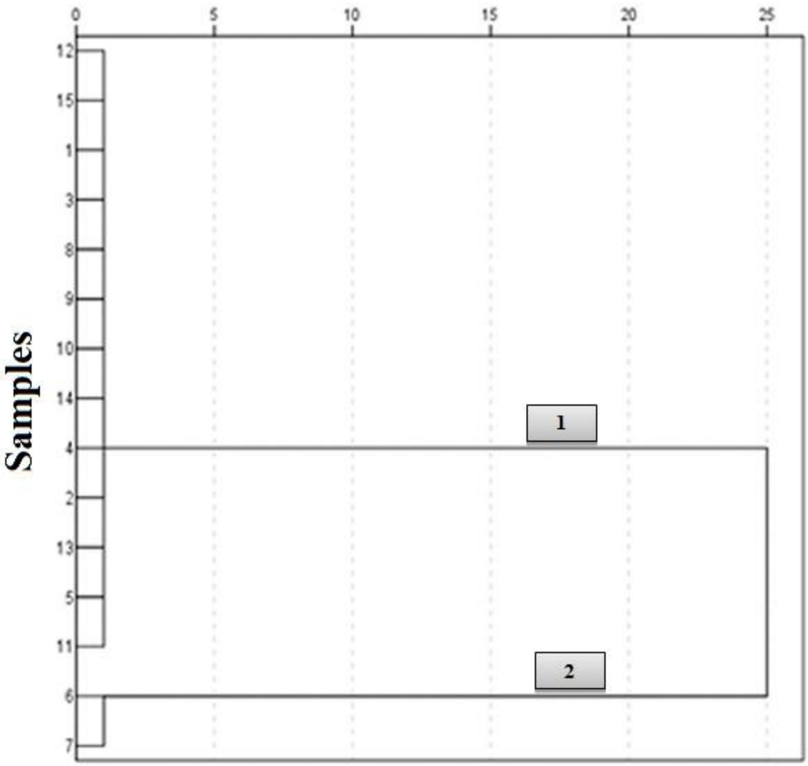

Figure **5. Dendogram for 15 samples from cluster analysis**

Cluster I is composed of wells No. 1 to 15, which make 87% of the water samples. This type of water with a mean EC of 730.8 µmhoscm-1 has a low salinity compared with clusters II. Unlike cluster I, Cluster II has a high salinity, dominated by Cl^- and Na^+ ions (Figure 5). Factor analysis is a multivariate statistical technique that can be applied to any kind of scientific data to establish the pattern of variation among variables or summarize information in a smaller set of factors or components for easy handling and interpretation [23]. A scree plot represents eigenvalue associated with a component or factor in descending order versus the number of the component or factor. A factor analysis was conducted on 14 different characteristics of groundwater. This scree plot shows that 3 of those factors explain most of the variability because the line starts to straighten after factor 3. The remaining factors are not so important such that they just explain a very small proportion of variability (Figure 6).

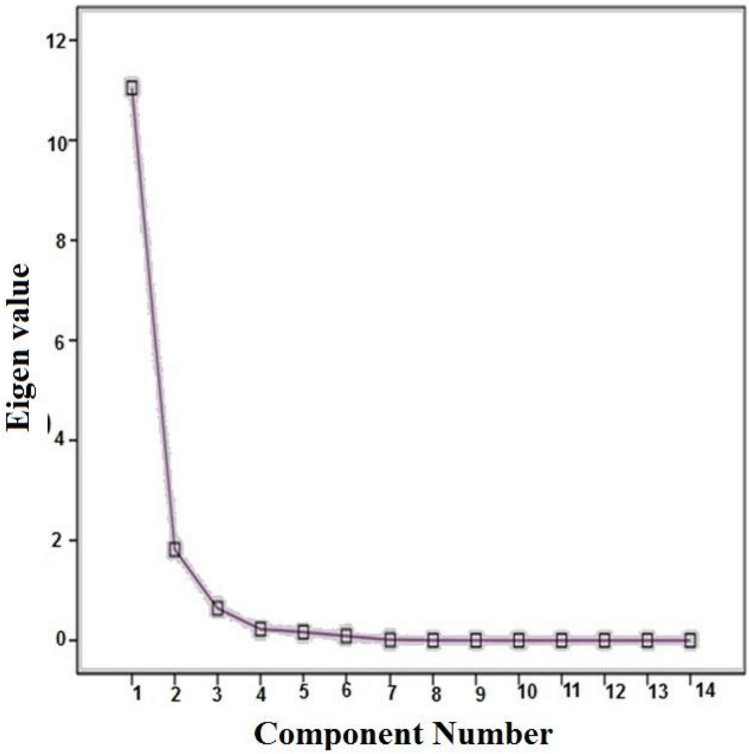

Figure 6. Scree plot of factor analysis of the study area

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1. Hydrochemical facies

In the area of Robat-Khorramabad, Piper trilinear diagram [24] was constructed using AqQA Scientific software to display the relative concentrations of different ions from individual water samples. Facies and types of samples in the study area are classified according to [25] and shown in Table 4. Hydrochemical facies reflected the effects of chemical reactions occurring between the minerals within the lithological framework and groundwater [26].

Table 4. Type and facies of samples in the study area [25]

Sample	Anions	Cations	Hydrochemistry facies
S1,W4,W5,W7	HCO_3> CL> SO_4	Ca> Na+ K> Mg	Ca- HCO_3
S2 , S3,W8	HCO_3> SO_4> CL	Ca> Mg> Na+ K	Ca- HCO_3
W9,W10	HCO3> CL > SO_4	Ca> Mg> Na+ K	Ca- HCO3
W1 , W2 , S4,S5 ,W3,W6	HCO_3> CL> SO_4	Ca> K> Ca> Mg	Na+ K- HCO_3

Trilinear diagrams suggest that Ca- HCO_3 facies are the major chemical facies in the area (Figure 7). So, it can be inferred that the water has a temporary hardness and the concentration of earth alkali cations is higher than the alkali cations. Moreover, unlike strong acidic anions, weak acidic anions have a higher concentration. Six samples have Na+ K- HCO_3 facies, in which the concentrations of alkali cations are higher than the earth alkali cations. Therefore, the water has a permanent hardness. The problem could be related to the placement of these resources around the gypsum and salt bearing formations. From a geochemical point of view, the evolution path of groundwater in the area is related to the dissolution of evaporate minerals such as gypsum and halite that lead to the salinity of groundwater.

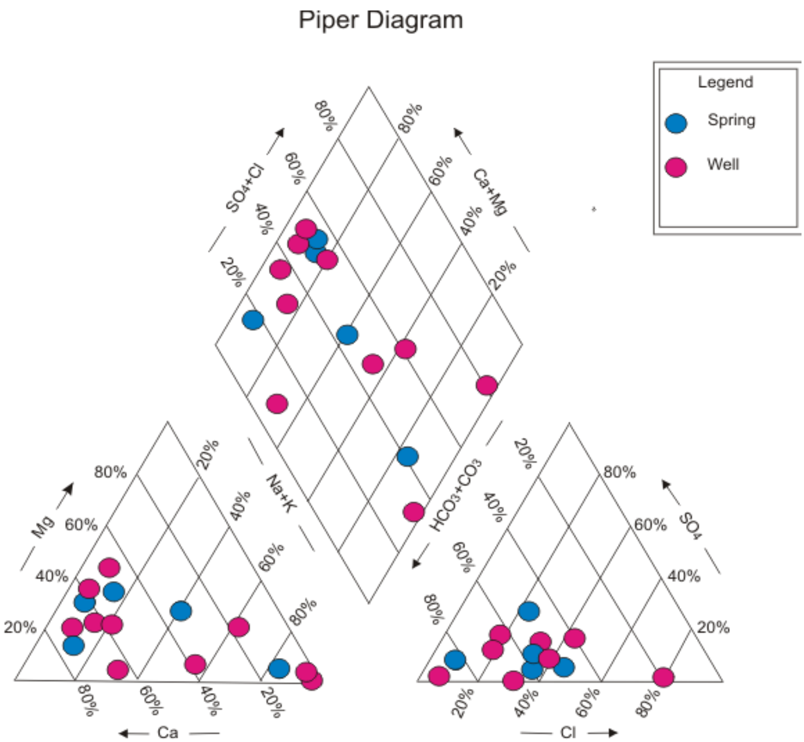

Figure 7. Piper diagram of the water samples in the study area

2. Quality of Groundwater

Groundwater always contains small amounts of soluble salts. The type and quality of these salts depend on the sources for groundwater recharge and the strata through which it flows [5]. The anions composition of the groundwater shows an order of HCO_3^-> Cl^-> SO_4^{2-}> NO_3^-> F^- [27]. A high ratio of HCO_3/ SO_4 indicates the higher dissolution of bicarbonate to sulfate. Affected by the high content of halite in evaporative formations, the chloride content varied from

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17.73 to 44,000 mg/l, which exceed the permissible limit. Moreover, the concentration of sulfate varied from 10.5 to 144 mg/l; less than the permissible limit for sulfate of 250 mg/l. The source of sulfate in the groundwater is gypsiferous bands associated with shale formation at higher depth. Nitrate (NO_3) is the most common contaminant of groundwater [28]. Determining NO_3 sources and other nitrogen (N) species has attracted much attention because it not only relates to health concerns regarding NO_3 ingestion but also the potential ecosystem effects of N loading [29]. Human activities, such as agricultural fertilizers and industrial effluents, affect the chemical composition of water [30]. The anthropogenic inputs must be considered to evaluate the contribution of chemical weathering to solutes in water. The application of fertilizer may accelerate the weathering and nitrification of N-fertilizer and thus mineral weathering by the acid nitric reaction [31][32]. The nitrification of $NH4^+$ from the fertilizers used in the study area produces nitrates mainly leaching the waters through soil during the rainy season. Moreover, dedolomitization is a major process that controls the chemical character of water. Dolomite and calcite play key roles in the dedolomitization process by the dissolution of gypsum fertilizers and nitrification of N-fertilizers [32]. In the study area, dissolution is controlled by the geochemical processes and the impact of gypsum fertilizers, which increase the concentration of calcium, magnesium, and sulfate ions and reduce the alkalinity through the dedolomitization and calcite deposition. Natural nitrate levels in groundwater are generally very low. $NO3^-$ concentrations in groundwater are controlled by karstification in the carbonate rocks. Natural nitrate sources are limited and exist in low concentrations in soil nitrate from the decay of sparse, natural vegetation, and nitrogen-bearing rock units [33]. The Asmari Formation is a mainly carbonate lithostratigraphic unit that outcrops in Zagros Basin and have a high karstification potential. These karst aquifers, which are the greatest water resources in Lorestan plain, are influenced by farming rapid transport of $NO3^-$ in many karst systems during high rainfall events and contribute to rapid contamination distribution of nitrate in wells and springs. The nitrate content varied from 0.3 to 1.41 mg/l and three samples exceed the permissible limit. Indeed, the chemical fertilizers used by farmers are considered as the main source of nitrate in the area. Fluoride values in the present study varied from 0.3 to 1.41 mg/l, which is less than the permissible limit of 2mg/l for fluoride. This difference can be attributed not only to the scarcity of fluoride bearing minerals in rocks but also to the degree of weathering and leachable fluoride in terrain. Diagrams such as Piper, Schoeller, US Salinity, and Wilcox have been used to assess the quality of the groundwater in the study area. A Schoeller diagram is a semi-logarithmic diagram of the concentrations of the main ionic constituents (SO_4^{2-}, HCO_3^-, Cl^-, Mg^{2+}, Ca^{2+}, and Na^+) in water. The semi-logarithmic diagram represents major ion analyses in meq/l [5]. The semi-logarithmic diagram of Schoeller is widely used to compare of groundwater quality. This diagram not only shows the exact value of ion but also shows the concentration differences between groundwater samples. Besides, this diagram is applied to classify drinking water. Schoeller plot (Figure 8) represents that the majority of water resources have a good to permissible quality for drinking. According to the classification, W1 and W2 water resources are not suitable enough for drinking. The main elements including sodium, calcium, magnesium, potassium, chloride, sulfate and boron lead to the salinity of soils. Sodium chloride is an important type of salt in the brine. The toxicity of salt for the plant is very high [34]. As salinity increases, the ratio of sodium ions to calcium increases as well because sodium salts are more soluble than

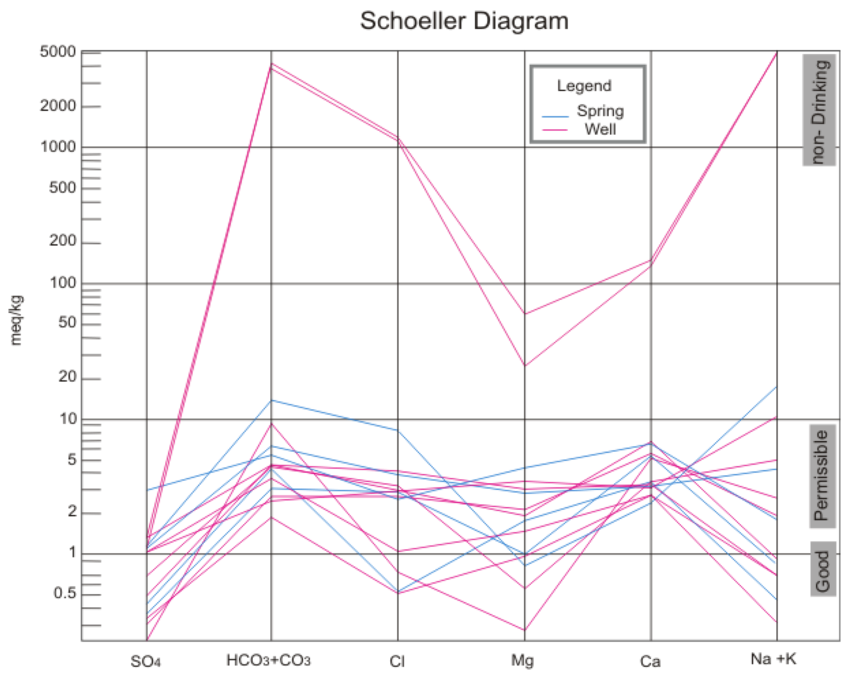

Figure 8. Schoeller diagram of the water samples in the study area

calcium salts. In contrast, in solution with low salinity, sulfate ion mainly reflects the effect of gypsum deposits [35]. To check the quality of groundwater resources in the area, Wilcox's diagram [36] was used. US salinity laboratory hazard diagram [15], constructed by correlating sodium absorption ratio and electrical conductivity, indicates that 5 groundwater samples of the study area fall in the category of C3-S1, proving their high salinity/low sodium. Also, 4 samples fall in the category of C2-S1, showing medium salinity/low sodium. As can be seen, there is just one sample that falls in all C2-S2/C2-S3/C3-S3 groups and 3 samples fall outside the diagram due to its high electrical conductivity and sodium adsorption ratio (Figure 9).

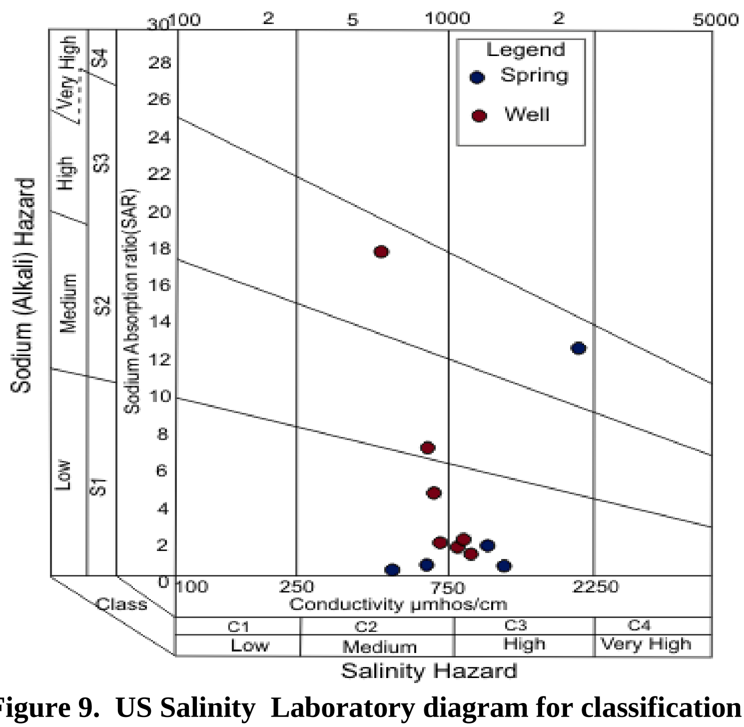

Figure 9. US Salinity Laboratory diagram for classification of irrigation waters [15]

Similarly, a perusal of Wilcox's diagram by correlating sodium percentage and electrical conductivity illustrates that 33.33 % of samples are from excellent to good quality for irrigation, 40% of samples are good to permissible, 13% doubtful to unsuitable, and 20% fall outside the diagram due to their high electrical conductivity and sodium percentage and thus are inappropriate for irrigation uses (Figure 10).

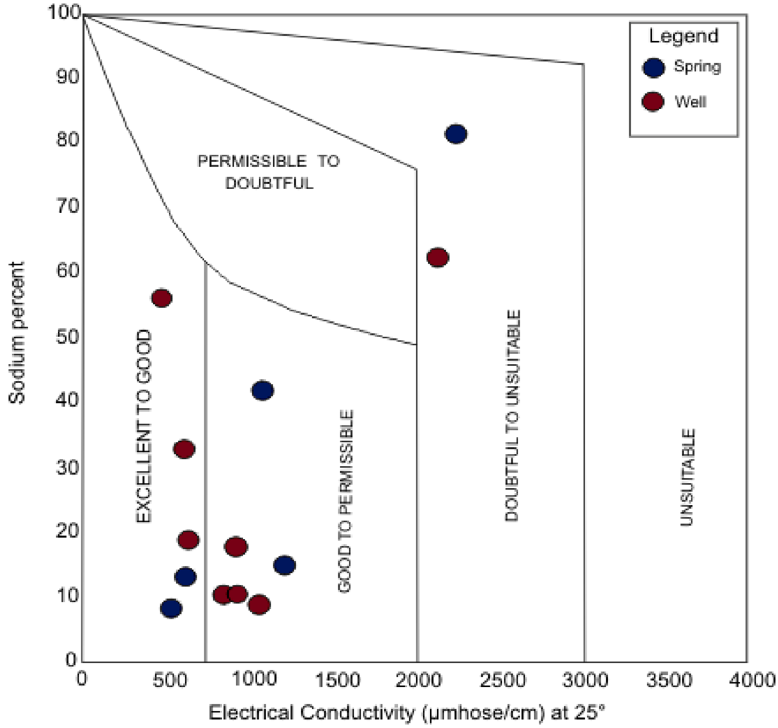

Figure 10. Percent sodium and electrical conductivity plot [36]

Conclusions

The analyzed groundwater samples of Robat-Khorramabad Plain indicate an alkaline nature form almost 85% of groundwater. The water is in the range of hard to very hard due to the calcareous nature of aquifers. Accordingly, the Piper diagram shows that Ca- HCO_3 facies are the major chemical facies in the area, suggesting that the water had a temporary hardness. The salinity of the aquifer is mainly due to the vicinity of carbonate, gypsum, and salt formations, leading to the salinity of groundwater. Due to the presence of calcareous and salt bearing formations, 46%, 26%, and 20% of all samples show a higher concentration of Ca^{2+}, Na^{+}, and Mg^{2+}, respectively, which exceed the permissible limits. Sulfate and fluoride concentrations are less than the permissible limit. However, 100%, 26%, and 20% of all samples show a higher concentration of HCO_3^-, Cl^-, and NO_3^- than a permissible limit. This difference is due to the presence of calcareous formation, salt bearing Formation, and the use of agricultural fertilizers. Moreover, TDS had a good significant correlation with all cations and Cl^- and HCO_3^- anions. On the other hand, TDS had a statistically positive correlation with EC and a negative correlation with pH. Correlation coefficients between total hardness (TH) and Ca^{2+}, Mg^{2+}, Na^{+}, Cl^-, and HCO_3^- were statistically significant. The plot of the cluster with Ward's linkage in the study area revealed that cluster II had a higher salinity than cluster I. This cluster is Cl^- and Na^+-dominated.

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