# Hydrogeochemical Assessment of Groundwater Quality and Suitability for Drinking and Agricultural Use. The Case Study of Fars Province, Iran

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## ABSTRACT

**This study aims to evaluate the hydrogeochemistry of aquifers in Fars province, Iran, from 2007 to 2017 and assess the groundwater's suitability for drinking and agricultural uses. A total of 35,000 samples were collected from wells and qanats across the province. Piper, Gibbs, and Durov diagrams were used to assess the hydrochemical facies and processes. Cross plots of different ions were investigated to assess ion exchange and determine the effects of anthropogenic activities, as well as the weathering and dissolution of different rocks and minerals in the aquifers. Groundwater quality and suitability for agricultural and drinking purposes were also assessed using physicochemical parameters including pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), Total Hardness (TH), and calcium, magnesium, sodium, potassium, bicarbonate, sulfate, and chloride concentrations. Suitability for domestic purposes was assessed by comparing these values with the WHO standards. Sodium and alkalinity hazards, including Sodium Adsorption Ratio (SAR), sodium percentage (Na%), Permeability Index (PI), Magnesium Hazard (MH), and Residual Sodium Carbonate (RSC) were used to assess irrigation suitability, along with plotting Wilcox and USSL diagrams.**

***Keywords-groundwater chemistry; Geographic Information System (GIS); hydrochemical facies; suitability analysis***

## I. INTRODUCTION

Groundwater resources, especially in arid and semi-arid regions, are important for the social and economic development. Iran, a developing country with a high population growth rate and relatively dry climate, suffers from severe decline in groundwater levels and is considered a hotspot for groundwater depletion. Easy groundwater access and inadequate supervision have exposed these valuable resources to over-exploitation in different parts of Iran. Excessive groundwater extraction has had a significant impact on both groundwater level and quality. There are many environmental challenges as well, including saline intrusion and severe quality effects from both environmental and anthropogenic factors. Since it is important to rely on an efficient and healthy water resource to meet Iran's drinking, agricultural, and industrial needs, water quality assessment, especially for groundwater, (between 55 and 80% of water demand in Iran is supplied from groundwater resources) has become significant. Water quality refers to the natural, physical, and chemical characteristics of water and any type of change that occurs for any reason [1-10]. Groundwater quality, which is usually controlled by physiochemical parameters, represents a response to all the processes and reactions that occur due to natural changes and anthropogenic activities [11]. Many factors including soil type, regional geology and topography, land use, the recharge source, climate change, atmospheric inputs, and interactions between surface and groundwater can affect groundwater chemistry [12-14]. Investigating the major ions to determine chemical indices and their spatial distribution can provide a clear picture of hydrochemical processes in aquifers. To this end, molar ion ratios can clarify the origins of solutes and characterize the occurring processes. Groundwater quality assessment in Iran is mostly limited to specific areas and periods, presenting significant gaps in knowledge, since there is a limited number of sampling wells and it is difficult to examine these sources over a long period. Thus, there is a need for a more thorough investigation of the issue. Considering the importance of investigating groundwater quality in Iran, the main objectives of this research were (1) to assess the groundwater's major ion chemistry and identify the hydrogeochemical processes affecting it and (2) to characterize the groundwater's suitability for agricultural and drinking purposes using relevant methods, diagrams, indices and standards based on a rich and reliable dataset.

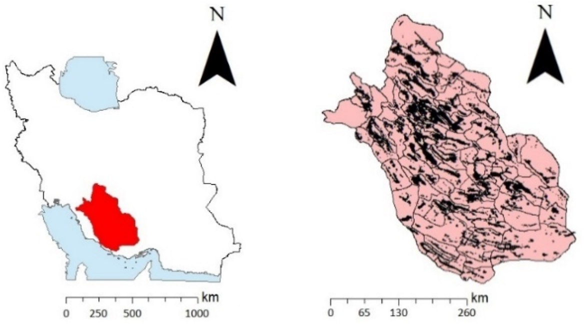
## II. MATERIAL AND METHODS

### A. Study Area

Fars Province covers approximately 122,400km$^2$ (6.7% of the country). It is located in the southwest of Iran. The average annual minimum and maximum temperatures vary between -7 and 2°C, and 25 and 40°C in this province. The average annual rainfall has been 320mm since about 2000, representing about $40\times10^9$m$^3$ [15]. The province's four climate zones are cold, temperate, hot, and very hot. Agriculture is important in Fars, with the main products being cereal (wheat and barley), citrus fruits, dates, sugar beet, and cotton. Some 71% of the province's agricultural area is allocated to irrigation farming and 29% to dry farming. Annual water consumption is approximately $10.5\times10^9$m$^3$, of which $8\times10^9$m$^3$ is supplied from groundwater. About 95% of the water used goes to the agricultural sector. Fars is a diverse province with varied geological characteristics. Different geological features in Fars, including the Zagros Mountains, are part of the Alpine-Himalayan orogenic belt and are composed of sedimentary and metamorphic rocks, Fars ophiolite complex that contains a variety of igneous, metamorphic, and sedimentary rocks, including pillow lava, sheeted dikes, gabbros, serpentinites, and cherts as well as Miocene-Pliocene sedimentary rocks, Quaternary volcanic rocks, and active faults.

### B. Data Analysis

The physiochemical parameters of 72 different districts in Fars, each with more than 1000 sampling locations, were investigated. Some 35,000 samples were collected from wells and qanats from 2007 to 2017. The sampling frequency depends on several factors including the type of well and the purpose of the sampling and the regulations and guidelines set by the local and national authorities. In Iran, the Ministry of Energy is responsible for managing and regulating the use of groundwater resources. The recommended frequency of sampling wells for drinking water is once per month. However, some regions in Fars province were required to be sampled more frequently up to 4 times per month.



(a) (b)

Fig. 1. (a) Fars province, (b) schematic view of well (sampling point) distribution in Fars.

In order to manage the sampling point data and determine the groundwater hydrochemistry and its suitability for different purposes, the data were clustered with variables such as cations, anions, pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), and Total Hardness (TH). The suitability of groundwater resources for drinking use was assessed by comparison of the water samples' physiochemical characteristics and state variables with the limits recommended by the World Health Organization (WHO) [16], salinity laboratory and Wilcox diagrams [17, 18], and the interpretation of several indices, including the Sodium Absorption Ratio (SAR) [19], sodium percentage (Na%) [18], Magnesium Hazard (MH), Residual Calcium Carbonate (RSC), and permeability index (PI) for all zones [20]. Piper, Durov, and Gibbs diagrams were used to determine the dominant water types and hydrochemical processes in Fars sub-basins [21-23]. All groundwater samples used were taken and analyzed under the supervision of the Iran Water Resources Management Company [24]. Groundwater quality data were measured in trusted water and wastewater laboratories licensed by Iran's Department of Environment, using the standard methods suggested by the American Public Health Association [25]. Groundwater quality data included major cations (i.e., $\mathrm{Ca}^{2+}$, $\mathrm{Mg}^{2+}$, $\mathrm{Na}^{+}$ and $\mathrm{Na}^{+}$), major anions (i.e., $\mathrm{HCO}_3^-$, $\mathrm{SO}_4^{2-}$, $\mathrm{Cl}^-$), pH, EC, TDS, and TH. Analytical accuracy was calculated from (1):

$$B = \frac{(C-A)}{(C+A)} \times 100 \tag{1}$$

where C and A are the sums of the cationic and anionic concentrations determined, respectively, in meq/L, and B is the ionic balance error (%) [26]. The ionic balance error did not exceed 8% in any sample analysis. Kriging interpolation, in Arc-GIS, was used to investigate groundwater quality spatially for drinking and irrigation. The statistical results of the analyzed samples are shown in Table I.

TABLE I. DESCRIPTIVE STATISTICS OF EC, PH, TDS, AND MAJOR IONS, DETERMINED IN THE GROUNDWATER SAMPLES.

| **Parameter** | **Unit** | **Minimum** | **Median** | **Mean** | **Maximum** | **Variance** | **Std. deviation** |
|---|---|---|---|---|---|---|---|
| $Ca^{2+}$ | mg/L | 40.07 | 100.2 | 159.21 | 551.25 | 12,974.67 | 113.9064 |
| $Mg^{2+}$ | mg/L | 6.99 | 60.76 | 85.64 | 413.98 | 4,569.25 | 68.07734 |
| $Na^{+}$ | mg/L | 5.98 | 69.00 | 227.99 | 1,293.865 | 101,534.60 | 318.645 |
| $K^{+}$ | mg/L | 0.78 | 3.13 | 5.55 | 34.79 | 30.93 | 5.561512 |
| $HCO_3^-$ | mg/L | 170.82 | 244.04 | 252.89 | 366.06 | 1,434.63 | 37.87644 |
| $SO_4^{2-}$ | mg/L | 73.88 | 222.86 | 342.16 | 1,597.24 | 100,883.30 | 317.6213 |
| $Cl^-$ | mg/L | 8.88 | 124.25 | 491.65 | 5,145 | 506,802.70 | 711.9007 |
| TDS | mg/L | 245.27 | 1,229.99 | 1,917.94 | 8,734.18 | 2,573,619.00 | 1,604.25 |
| EC | µs/cm | 429 | 1,887 | 2,984.8 | 14,218 | 6,290,427 | 2,508.072 |
| pH | - | 6.77 | 7.54 | 7.54 | 8.33 | 0.009,052 | 0.095,144 |
| TH | mg/L | 170.669 | 715.94 | 928.18 | 3075 | 436,500.00 | 656.01 |

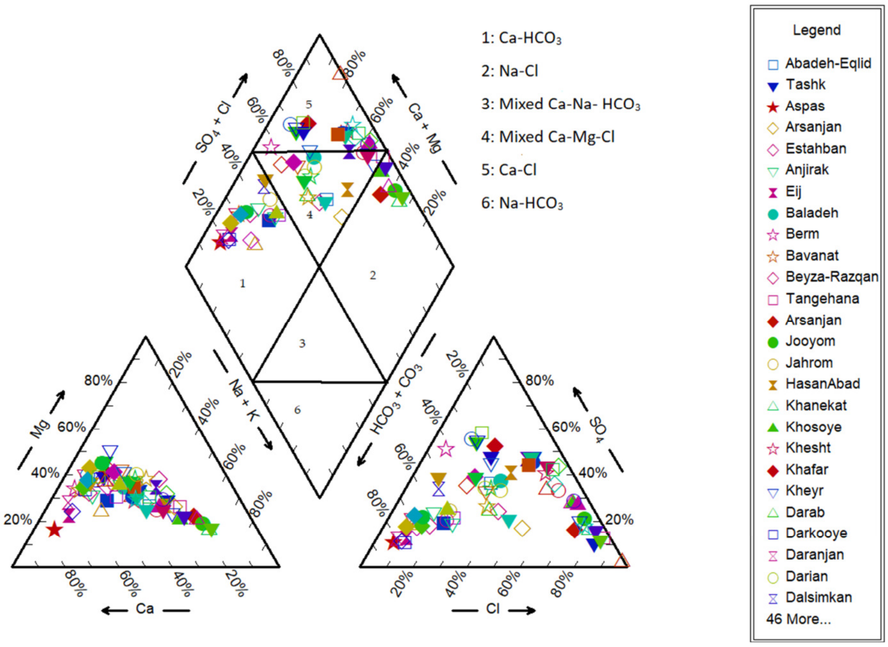


Fig. 2. Piper diagram.

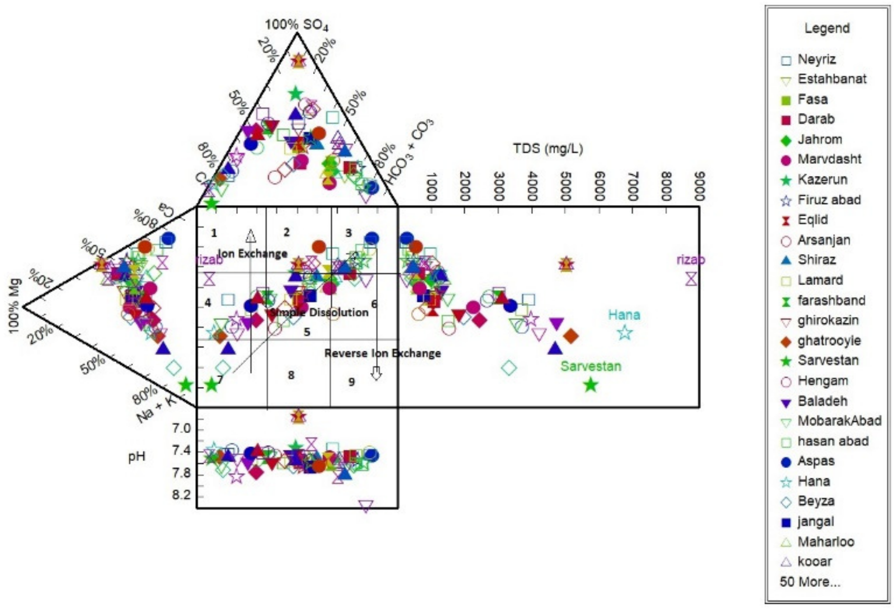


Fig. 3. Durov diagram.

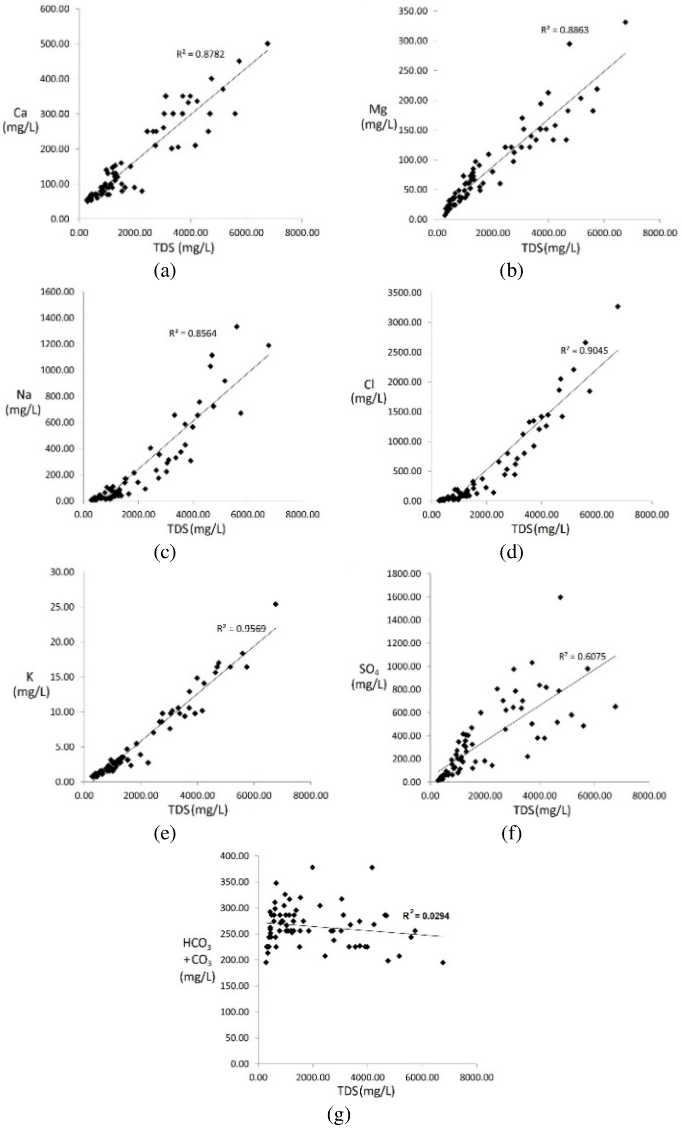
## III. RESULTS AND DISCUSSION

### *A. Ionic Types and Hydrogeochemical Facies*

Piper and Durov diagrams were used in this study to determine hydrochemical facies. In the Piper diagram, $Ca^{2+}$ and $Mg^{2+}$ (alkaline earth metals) and $Na^{+}$ (alkali metal) are the most common cations, while $HCO_3^-$ (a weak acid) and $SO_4^{2-}$ and $Cl^-$ (strong acids) are the most abundant anions. To determine the groundwater's hydrogeochemical facies, the analytical results were plotted on a Piper ternary diagram [20], using AqQa software [27] (Figure 2). The two basal triangles in the Piper diagram show that $Ca^{2+}$ is the dominant cation in 42 of the 72 districts, and $HCO_3^-$, followed by $Cl^-$, are the dominant anions. The calcium-bicarbonate type indicates that alkaline earth metals and weak acidic anions exceed alkali metals and strong acidic anions, respectively. Such water has temporary hardness. The dominance of these ionic species is evidence of anthropogenic activity. While calcium bicarbonate is the dominant water type, mixed types, and calcium chloride waters are also present. The plots show that most water samples fell in the alkaline earth metal field ($Ca^{2+}, Mg^{2+}$), which dominates the alkali metals ($Na^+$, $K^+$), while the weak acid ($HCO_3^-$) dominates the strong acids ($Cl^-$, $SO_4^{2-}$). Fresh recharge waters rich in $Ca^{2+}$ are characteristic of most zones in Fars. The Durov diagram [21, 22] in Figure 3 was plotted to determine the dominant hydrochemical processes and the type of ion exchange. It is clear from the Durov diagram that most of the water lies along the dissolution or mixing line, i.e. ion exchange and reverse ion exchange are both feasible. The increasing trend of both TDS concentration and pH can also be seen in the graph.

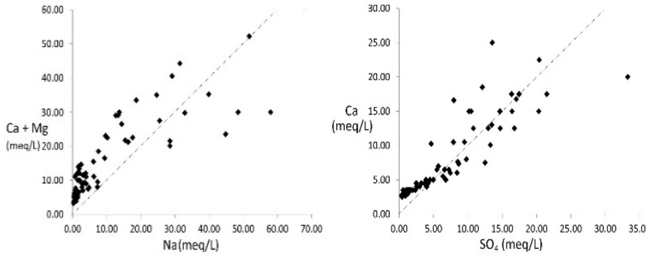
### *B. Hydrochemical Process Identification*

Scatter plots of ion concentrations enable interrelationships between the ions and the chemical reactions occurring in the aquifers to be recognized. Major ion concentrations were plotted as a function of calculated TDS values to identify the effective ions in groundwater mineralization. As shown in Figure 4, $K^+$, $Cl^-$ and $Mg^{2+}$ are correlated strongly with TDS with correlation coefficients of 0.96, 0.9, and 0.88, respectively. These ions contribute the most to the groundwater mineralization and salinization in the study area. A plot of $Ca^{2+}$ + $Mg^{2+}$ versus $Na^+$ (Figure 5) is used to identify the ion exchange process. The data points fall above the 1:1 line, indicating reverse ion exchange, which normally takes place in the presence of clays. The plot of $Ca^{2+}$ versus $SO_4^{2-}$ provides evidence of predominating cation exchange [28]. Plotting $Na^+/Cl^-$ versus EC (Figure 6(a)) is used to determine the effect of evaporation on groundwater chemistry. The graph should have a horizontal line to indicate the effect of evaporation and evapotranspiration [29]. The graph's trendline is inclined, showing that evaporation cannot be the main groundwater hydrochemical process in the area. TDS changes can arise from land use and/or pollution. In rural areas, nitrate, sulfate, sodium, and chloride ions originate from agricultural fertilizers, animal wastes, and wastewater [30]. The high correlation coefficient, 0.843 (Figure 6(b)), between TDS and ($NO_3^{2-}$ + $Cl^-/HCO_3^-$) shows the effects of human activity on water chemistry [31, 32].



(a) (b) (c) (d) (e) (f) (g)

Fig. 4. Plots of major ion concentrations versus TDS. (a) $Ca^{2+}$, (b) $Mg^{2+}$, (c) $Na^+$, (d) $Cl^-$, (e) $K^+$, (f) $SO_4^{2-}$, and (g) $HCO_3^-$ and $CO_3^{2-}$.

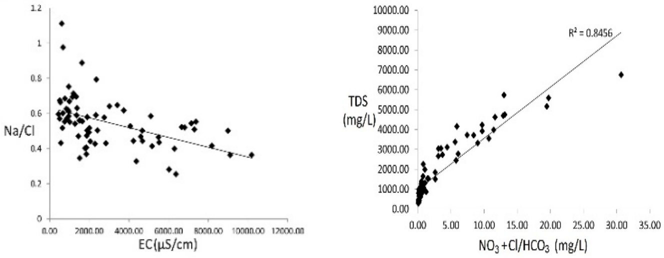


(a) (b)

Fig. 5. Plots of (a) $Ca^{2+}$ and $Mg^{2+}$ versus $Na^+$ and (b) $Ca^{2+}$ versus $SO_4^{2-}$.

### *C. Ion Exchange*

Generally, groundwater is rich in sodium where there is the precipitation of calcite and/or cation exchange. In contrast, $Ca^{2+} - Cl^-$ type water commonly arises from reverse ion exchange. Both cation exchange and reverse ion exchange are encouraged by aquifer materials leading to Na or Ca release into groundwater and Ca or Na adsorption, respectively [33-35]. As the Piper diagram indicates the possibility of ion exchange reactions, Schoeller chloralkali indices were employed to understand them. Chloroalkaline indices 1 and 2 (CAI 1 and CAI 2) were calculated for the study region groundwater using (2) and (3) [36, 37].



(a) (b)

Fig. 6. (a) $Na^+/Cl^-$ versus EC and (b) TDS versus $NO_3^{2-}$ and $Cl^-/HCO_3^-$.

$$\mathrm{CAI\ 1} = Cl^- - (Na^+ + K^+)/Cl^- \qquad (2)$$

$$\mathrm{CAI\ 2} = Cl^- - (Na^+ + K^+)/(SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^{2-}) \qquad (3)$$

If the index values are negative materials are exchanged with $Mg^{2+}$ and $Ca^{2+}$ in the water, whereas the reverse process will give a positive value ($Cl^- > Na^+ + K^+$). The host rocks are the primary sources of dissolved solids in the water. The chloralkali indices for 21% of the study area were negative, indicating an exchange between $Na^+$ and $K^+$ in the water and $Cl^-$ and $Mg^{2+}$ in the soil. In 79% of the areas, however, reverse ion exchange occurred.

The Gibbs diagram (Figure 7) is widely used to establish the relationship between solutes in water and aquifer lithology. The diagram shows three fields: precipitation, evaporation, and rock-water interaction-dominated areas [23]. Gibbs plots of log TDS against $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ were used to identify groundwater interactions that reflect that rock-water interaction and evaporation occur in this groundwater system. The dense clustering of points in the evaporation domain can be a sign of anthropogenic activity [37].

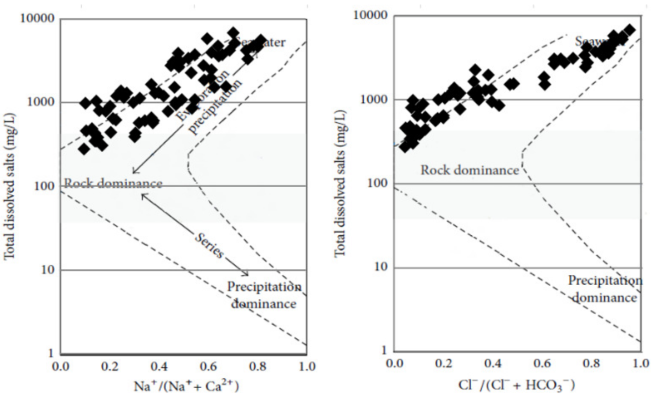


Fig. 7. Gibbs diagram.

It should be mentioned that several sources of contamination and anthropogenic activities affect the groundwater quality in Fars Province. Agricultural activities, which are the main source of income in the Province, and the extensive use of fertilizers, pesticides, and herbicides, can lead to groundwater contamination. The excess use of nitrogen and phosphorus fertilizers can lead to nitrate and phosphate contamination. Industrial activities including oil and gas extraction, mining, and manufacturing can generate hazardous waste that may contaminate groundwater. The discharge of industrial wastewater into surface waters can also lead to groundwater contamination. Besides, the rapid urbanization and population growth in Fars Province has led to increased wastewater generation and disposal.

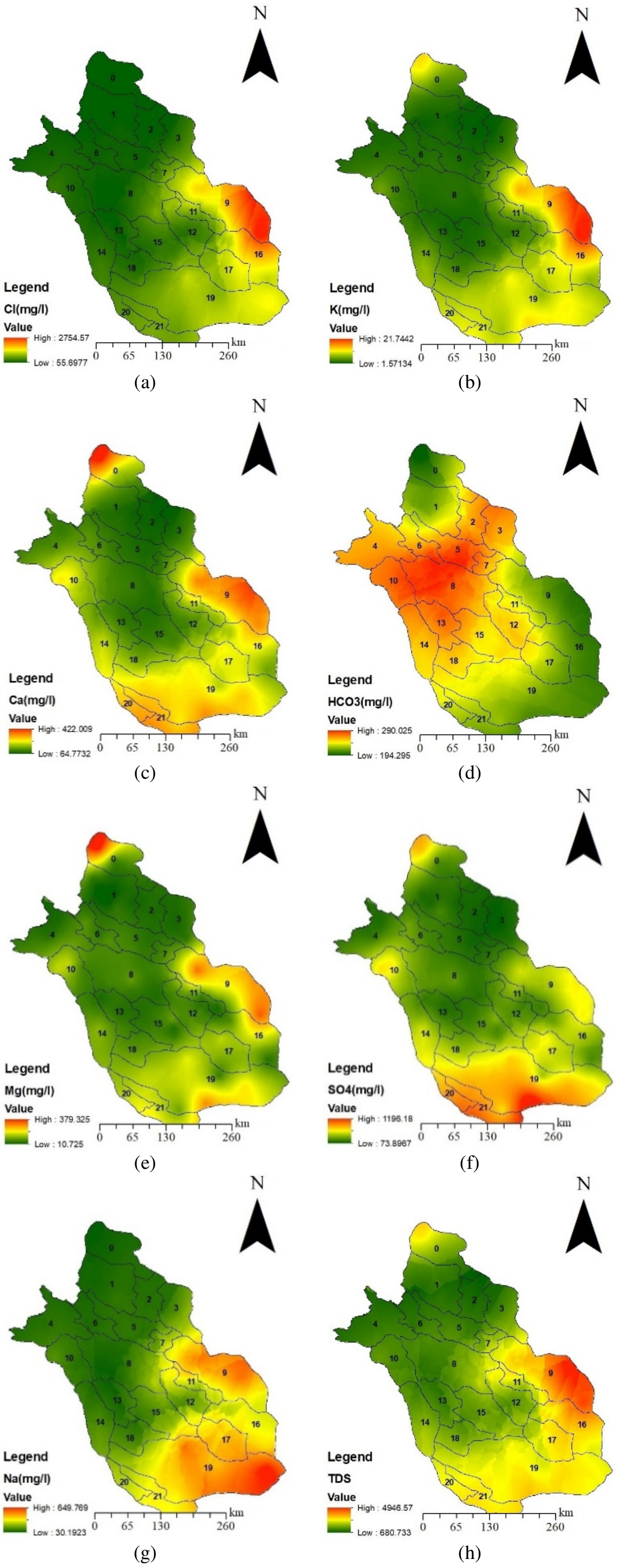
### *D. Groundwater Quality Evaluation*

#### *1) Drinking Suitability*

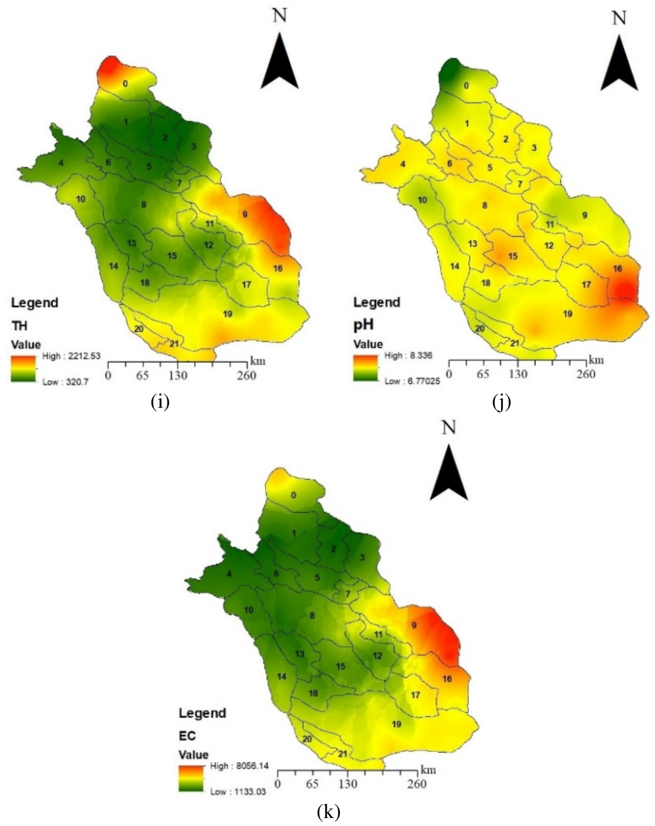
There are several groundwater quality assessment studies that regard fluoride concentration in regions facing groundwater contamination problems using the Water Quality Index (WQI) and other physiochemical parameters [38-40]. Cations, anions, pH, EC, TDS, and TH are used to determine the groundwater's suitability for drinking in this study. The concentration minima, maxima, means, and standard deviations of contributing parameters are shown in Table I. The values were compared with WHO's guideline recommendations. Figure 8 shows the spatial distribution of all parameters.

TABLE II. CHEMICAL PARAMETER CONCENTRATIONS COMPARED WITH WHO RECOMMENDATIONS

| **Water quality parameters** | **WHO max allowable limit (1993)** | **Percentage of samples exceeding the standard** | **Concentration in the study area** | **Undesirable effect produced beyond the maximum allowable limit** |
|---|---|---|---|---|
| $Ca^{2+}$ (mg/L) | 200 (mg/l) | 31.95 | (40.07-551.98) | Essential for human bone growth, high concentration cause hardness and inefficiency |
| $Mg^{2+}$ (mg/L) | 150 | 18 | (6.99-413.16) | Essential for human bone growth, but high concentrations cause water hardness |
| $Na^+$ (mg/L) | 200 (mg/l) | 31.95 | (5.98-1293.865) | High blood pressure or posing a risk for people suffering from kidney or heart diseases |
| $K^+$ (mg/L) | 12 (mg/l) | 13.89 | (0.78-34.79) | High blood pressure, blood lipids due to $K^+$ deficiency |
| $HCO_3^-$ (mg/L) | 300 (mg/l) | 9.72 | (170.82-366.06) | Unknown |
| $SO_4^{2-}$ (mg/L) | 400 (mg/l) | 31.95 | (73.88-1197.24) | Dehydration, gastrointestinal irritation-laxative effect |
| $Cl^-$ (mg/L) | 600 | 26 | (8.88-5145) | Salty taste |
| TDS (mg/L) | 1500 | 39 | (245.89-8761.21) | Taste-gastrointestinal irritation |
| pH | 6.5-8.5 | 0 | (6.98-8.33) | Taste effects on mucus membrane and adverse effects on the water supply system |
| TH as $CaCO_3$ (mg/L) | 500 | 50 | (170-3075) | Encrustation in water supply and adverse effects on domestic uses |



(a) (b) (c) (d) (e) (f) (g) (h)



(i) (j) (k)

Fig. 8. Spatial distribution of major ions and hydrochemical parameters related to drinking suitability: (a) $Cl^-$, (b) $K^+$, (c) $Ca^{2+}$, (d) $HCO_3^-$, (e) $Mg^{2+}$, (f) $SO_4^{2-}$, (g) $Na^+$, (h) TDS, (i) TH, (j) pH, (k) EC. City names: 0: Abadeh, 1: Eqlid, 2: Khorrambid, 3: Bavanat, 4: Mamasani, 5: Marvdasht, 6: Sepidan, 7: Arsanjan, 8: Shiraz, 9: Neyriz, 10: Kazerun, 11: Estahban, 12: Fasa, 13: FiruzAbad, 14: Farashband, 15: Jahrom, 16: Darab, 17: Zarrindasht, 18: Qirkazin, 19:Larestan, 20:Mohr, 21:Lamerd.

The average values of individual groundwater parameter concentrations were all within WHO's recommended limits, whereas some individual samples reported higher concentrations (see Table II). To investigate groundwater suitability for any purpose, it must be classified depending on its hydrochemical properties based on its TDS content [41, 42]. According to Table III, 63.91% of the samples were brackish water, and 36.09% were fresh water. In the classification based on [43], 15.27% of the samples were desirable and 20.82% were considered permissible for drinking purposes based on TDS (Table IV).

TABLE III. NATURE OF GROUNDWATER BASED ON TDS VALUES

| TDS | Nature of water | Percentage |
|---|---|---|
| Up to 1000 | Freshwater | 36.09 |
| 1000-10000 | Brackish water | 63.91 |
| 10000-100000 | Saline water | 0 |
| >100000 | Brine water | 0 |

The groundwater classification based on TH shows that 13% of the water is hard, and the rest is very hard. The WHO recommended maximum for TH for drinking is 500mg-$CaCO_3$/L, and 66% of the study area exceeds that limit. The pH value suitable for drinking water is specified as 6.5-8.5. The pH value of most groundwater samples in the study area was between 6.98 to 8.33, with an average of 7.33 indicating an overall alkaline nature.

TABLE IV. CLASSIFICATION OF GROUNDWATER BASED ON TDS

| TDS | Water type | Percentage |
|---|---|---|
| Up to 500 | Desirable for drinking | 15.27 |
| 500-1000 | Permissible for drinking | 20.82 |
| <3000 | Useful for irrigation | 70.83 |
| >3000 | Unfit for drinking or irrigation | 29.17 |

TABLE V. CLASSIFICATION OF GROUNDWATER BASED ON TH [44]

| Total hardness as $CaCO_3$ (mg/l) | Water class |
|---|---|
| < 75 | Soft |
| 75 – 150 | Moderately hard |
| 150 – 300 | Hard |
| > 300 | Very hard |

EC is a measure of water's capacity to convey an electric current. The recommended EC limit for drinking water is 1500μS/cm [16]. The EC of the groundwater varies from 429 to 14184μS/cm with an average value of 2984μS/cm (Table I). Higher ECs indicate higher salt concentrations. The EC can be classified as type I if the enrichments of salts are low (EC < 1,500μmhos/cm), type II if the enrichment of salts is medium (EC 1,500 and 3,000μmhos/cm), and type III if the enrichments of salts are high (EC > 3,000μmhos/cm). According to the above classification, 56% of the total groundwater samples fell under type I and 26% under type II. The remaining 18% of zones fell into the high salinity class and thus have wide applicability with respect to agricultural use. However, for drinking use, a high value of EC denotes a proportionately high value of calcium, magnesium, sodium, and potassium. Calcium and magnesium are the most abundant elements in the planet's surface, and groundwater $Ca^{2+}$ concentrations vary from 40.1 - 551.9 (Table II). The desirable limit of calcium concentration for drinking water is 75mg/l [16] and 32% of the zones fell beyond the permissible limit. Higher $Ca^{2+}$ content can cause hardness and is undesirable for domestic uses as it causes encrustation and scaling. Magnesium content varies between 6.99 and 413.98mg/l (Table II). The maximum permissible limit of Mg concentration for drinking water is 150mg/l [16]. The concentration of $Na^+$ varies between 5.98 and 1,293.865mg/l. Its maximum permissible limit is 200mg/l and 32% of the samples exceeded it (Table II). Groundwater with high sodium content is not suitable for agricultural use as it tends to deteriorate the soil. Potassium concentrations are low compared to $Ca^{2+}$, $Mg^{2+}$, and $Na^+$, with those in drinking water seldom reaching 20mg/l. The sample $K^+$ concentration varied between 0.78 and 25.4mg/l. The maximum permissible limit of $K^+$in drinking water is 12mg/l, and it was found that 86% of the samples had concentrations below it (Table II). The value of $HCO_3^-$ was between 170.03-366.06mg/l, and only 10% of the samples exceeded the WHO limit. Sulfate is one of the major anions occurring in natural waters. The upper limit for sulfate concentration in drinking water is 400mg/l [16]. The sulfate concentration in the study area ranged between 73.88 and 1,196.24mg/l with an average concentration of 342.16mg/l, indicating that 68% of the samples were within the allowable limit. The chloride in groundwater may come from diverse sources [45]. In the study area, the concentration of chloride was between 8.88 and 5,145mg/l. The excess chloride in the water is usually taken as an index of pollution and considered a tracer for groundwater contamination [46]. Chloride determination may indicate water intrusion of different compositions, or trace and measure the rates and volumes of water mass movements.

### 2) *Irrigation Suitability*

It is important to develop successful projects supplying irrigation water in addition to controlling salts and alkalis in the soil. In this regard, salinity indices such as Na%, SAR, RSC, PI, and MH were examined. Salinity and alkalinity hazards are important parameters for determining the suitability of groundwater for agricultural use and influence crop yields. United States Salinity Laboratory (USSL) classification and the Wilcox diagram were also used for better assessment.

#### a) *Salinity and Alkalinity Hazards*

EC is a good measure of salinity hazard to crops, as it reflects the TDS in groundwater and is the most important parameter in determining water suitability for irrigation. TDS refers to any minerals, salts, metals, cations, or anions dissolved in the water. Excess salinity reduces the osmotic activity of plants and thus interferes with water and nutrient absorption from the soil [47]. Different types of water based on EC values are presented in Table VI and EC and TDS spatial distribution in Figure 8. According to the Wilcox diagram, only 47% of the samples were below the permissible limit of EC. According to the AqQa software results, 33%, 40%, and 26% of samples were reported in the range of very high, high, and medium salinity hazards, respectively. Based on TDS classification, the groundwater in around 80% of the study area was classified as permissible for agricultural use at TDS < 3000.

SAR is an important parameter in determining the suitability of groundwater for irrigation because it is a measure of alkali/sodium hazard to crops as excess sodium in water can cause undesirable effects [48]. SAR is calculated by:

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \quad (4)$$

where sodium, calcium, and magnesium are measured in meq/l. The SAR value can be an indicator of the extent to which sodium is absorbed by soils. Sodium concentration can reduce soil permeability, deteriorate soil structure, and influence crop yield [49]. The waters were classified for irrigation based on the ranges of the SAR values [19]. Based on the SAR values, 94% of the samples were excellent and 6% were good for irrigation (Table VI). In addition, for better insight, the USSL plot presented in Figure 9 indicates that 7% of the groundwater samples fell in the C1S1 (low salinity-low sodium), and 18% of the samples fell in the C2S1 category. About 20% of the groundwater samples fell in the C3S1, indicating high salinity or high sodium type. Only 9% fell in the very high salinity to low sodium category (C4S1), and the rest of the samples had very high salinity and are not shown in the diagram.

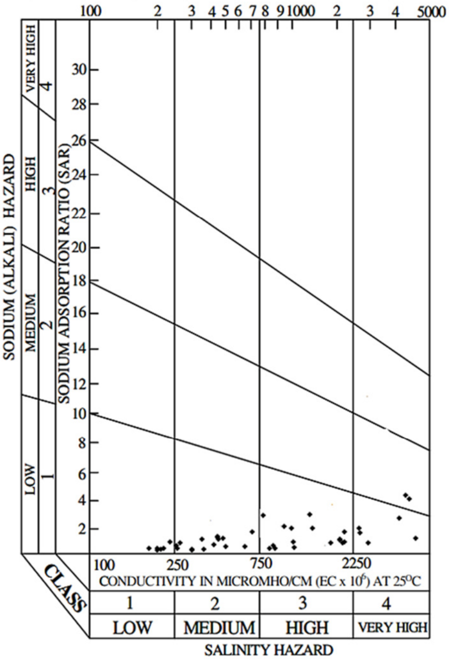


Fig. 9. USSL diagram used to classify irrigation water suitability.

In addition to the sodium adsorption ratio, Na% can be a risk indicator for soil in agriculture. High sodium in the soil can be detrimental to soil structure, aeration, and infiltration [26, 49]. The sodium in irrigation waters is usually denoted as a percent of sodium. In all natural waters, Na% is a common parameter for the evaluation of their suitability for irrigational purposes [50]. Na% values are obtained by:

$$\text{Na\%} = \frac{\text{Na}^{+} \times 100}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^{+} + \text{K}^{+}} \quad (5)$$

All ionic concentrations are expressed in meq/l.

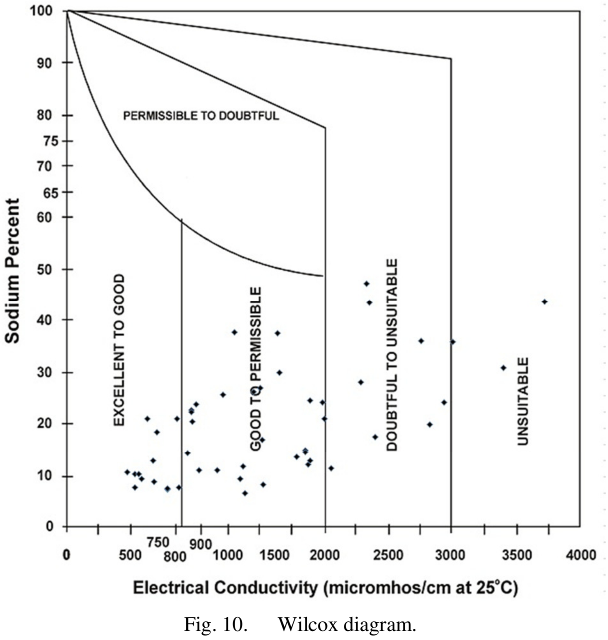


Fig. 10. Wilcox diagram.

TABLE VI. CLASSIFICATION OF GROUNDWATER BASED ON TH, EC, SAR, NA%, RSC, MH, AND PI

| Classification | Category | Range | Sample % |
|---|---|---|---|
| **TH [44]** | Soft | Less than 75 | 0 |
| | Moderately hard | 75-150 | 0 |
| | Hard | 150-300 | 20 |
| | Very hard | More than 300 | 80 |
| **EC [18]** | Excellent | Less than 250 | 0 |
| | Good | 250-750 | 13.88 |
| | Permissible | 750-2250 | 47.88 |
| | Doubtful | 2250-5000 | 17.12 |
| | Unsuitable | More than 5000 | 21.12 |
| **SAR [19]** | Excellent | Less than 10 | 94.38 |
| | Good | 10-18 | 5.62 |
| | Doubtful | 18-26 | 0 |
| | Unsuitable | More than 26 | 0 |
| **Na% [18]** | Excellent | 0-20 | 38.02 |
| | Good | 20-40 | 0 |
| | Permissible | 40-60 | 36.62 |
| | Doubtful | 60-80 | 19.71 |
| | Unsuitable | More than 80 | 4.22 |
| **RSC [53]** | - | - | - |
| | Good | Less than 1.25 | 98.6 |
| | Medium | 1.25-2.5 | 1.41 |
| | Bad | More than 2.5 | 0 |
| **MH [52]** | Good | Less than 50 | 81.69 |
| | Poor | More than 50 | 18.3 |
| | - | - | - |
| **PI [51]** | Class 1 | More than 75 | 0 |
| | Class 2 | 75-25 | 97.2 |
| | Class 3 | Less than 25 | 2.8 |

As shown in Table VI, 38%, 36%, 19.71%, and 4.22% of the samples are considered excellent, good, permissible, and doubtful, respectively, based on Na%. Na% is plotted against EC in a Wilcox diagram [18]. As shown in Figure 10, 16% of the groundwater samples were excellent to good, 41% good to permissible, 10% doubtful to unsuitable, and the rest of the samples were considered unsuitable for irrigation due to the aforementioned reasons.

### *b) Permeability Index*

A water suitability classification for irrigation was developed in [51] based on the PI, as soil permeability is impacted by the long-term use of water containing sodium, calcium, magnesium, and bicarbonate. The PI is calculated by:

$$\text{PI} = 100 \times \frac{\text{Na}^{+} + \sqrt{\text{HCO}_3^{-}}}{\text{Na}^{+} + \text{Ca}^{2+} + \text{Mg}^{2+}} \quad (6)$$

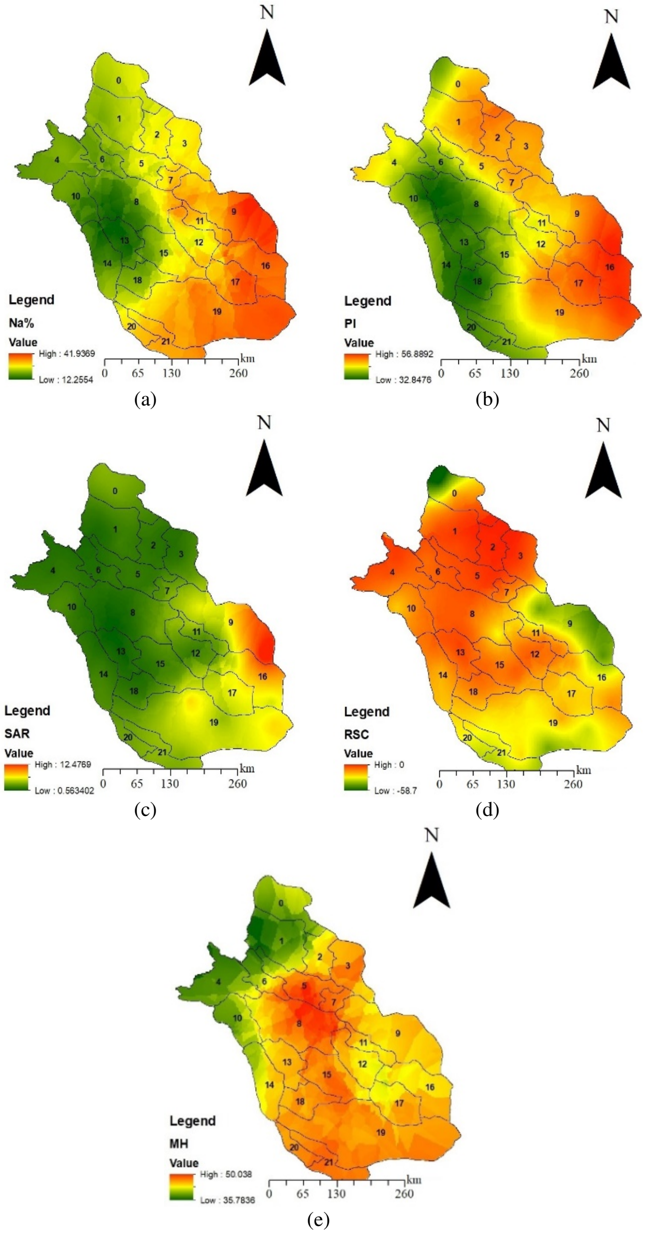
All ion concentrations are expressed in meq/l. The PI in the study area was between 1.93 and 28.14 with an average value of about 15.48 (Table VI). A classification based on PI was proposed by WHO for assessing the suitability of groundwater for irrigation purposes. According to the PI values, 97.2% of the samples fell into class 2, and only 2.8% belonged to class 3 which is considered unsuitable for irrigation.

### *c) Magnesium Hazard*

In most waters, calcium and magnesium maintain a state of equilibrium. There is evidence that $\text{Mg}^{2+}$ can be detrimental to soil texture in water with a high sodium content in particular. MH index was developed in 1972 [52]. High MH harms crop yields as the soil becomes more alkaline.

$$\text{Magnesium ratio} = \frac{Mg^{2+}}{(Ca^{2+}+Mg^{2+})} \times 100 \qquad (7)$$

In the study area, the MH ranged between 14.28% and 59.45%. The 81.69% of the collected samples showed an MH ratio below 50% (suitable for irrigation), while 18.4% were unsuitable and can cause adverse effects on agricultural yields (Figure 11).



(a) (b) (c) (d) (e)

Fig. 11. Spatial distribution of (a) Na%, (b) PI, (c) SAR, (d) RSC, (e) MH.

### *d) Residual Sodium Carbonate*

The RSC index of water samples in the study site was estimated by [19]:

$$RSC = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+}) \qquad (8)$$

All ion concentrations are expressed in meq/l. Irrigation water based on RSC is classified as good, medium, and bad [33, 53]. For irrigation purposes based on RSC values, 98.6% of the groundwater samples were found good for irrigation, and the remainder belonged in the medium category.

## IV. CONCLUSIONS

Groundwater is a major water source for domestic and agricultural uses. Groundwater quality and its suitability for drinking and agricultural use, as well as hydrogeochemical processes, in Fars province, Iran, were assessed in this paper. In this regard, 35,000 groundwater samples were collected from 2007 to 2017 and analyzed for pH, electrical conductivity, major ion concentrations, total dissolved solids, and total hardness. Interpretation of the hydrochemical analyses revealed that in most zones, the groundwater was hard to very hard, fresh to brackish, and alkaline in nature. Based on the Piper diagram, $Ca^{2+}$ was the dominant cation in 42 out of the 72 districts, and bicarbonate followed by chloride, were the dominant anions in the province. Effects of anthropogenic activities were evident in this region due to the dominance of the aforementioned ions. The dominant type in the province was calcium bicarbonate, followed by mixed types and calcium chloride. According to the Durov diagram, the hydrochemical reactions in this area were mixed reactions with different origins, mixing and reverse cation exchange reactions, and water infiltration with calcium bicarbonate types. $K^{+}$, $Cl^{-}$, and $Mg^{2+}$ were strongly correlated with TDS, which shows that these ions contribute the most to the mineralization and salinization of the study area's groundwater. The plot of calcium versus sulfate can be evidence of cation exchange predominance. The high correlation coefficient between TDS and $((NO_3^{2-} + Cl^{-})/HCO_3^{-})$ also shows the effect of human activities on water chemistry-agricultural fertilizers. Based on the chloralkali index, 21% of the areas had a negative value, indicating the exchange between sodium and potassium in water, chlorine, and magnesium in the soil. The plot of $Ca^{2+} + Mg^{2+}$ versus $Na^{+}$ was used to identify the ion exchange process indicating the occurrence of ion reverse exchange in about 90% of the study area. The same was observed in 79% of the districts according to the chloralkali index. The Gibbs diagram demonstrated the rock dominance domain towards the evaporation dominance domain, which reflects that rock-water interaction and evaporation occurring in the groundwater system. Assessment of water samples according to WHO standards indicated that, except a few places, the concentrations of major ions in groundwater were within the permissible limits for drinking. The suitability of groundwater for irrigation use was assessed by SAR, RSC, Na%, MH, and PI. The results ranged from good to permissible and indicated that most of the samples were suitable for this purpose. Based on EC, due to high to very high salinity hazards, the groundwater in nearly 40% of the study area was beyond the maximum allowable limit for irrigation, even though it had a low alkalinity hazard. Therefore, the groundwater in a few places can be used for plants that have a good salt tolerance, but it also restricts its suitability for irrigation, especially in soils with restricted drainage. The spatial distribution of different parameters either related to drinking or irrigation purposes was presented to grant a better insight into the general condition of groundwater quality in Fars.

The results of this study demonstrate the basic requirements for Fars's groundwater quality adaptation process, considering the water requirements for different allocation purposes. Based on the groundwater hydrogeochemical characteristics, policymakers and stakeholders in Fars Province should consider monitoring and controlling anthropogenic activities and implementing proper waste management practices that are essential for the protection of groundwater resources. Regular and systematic monitoring of groundwater quality is essential for understanding the hydrogeochemical characteristics of the aquifers and identifying potential sources of contamination. Policymakers and stakeholders should develop and implement groundwater monitoring programs that use appropriate sampling and analytical methods to assess groundwater quality parameters and track changes over time. Promoting sustainable groundwater use is of great importance because groundwater resources in Fars are under stress due to the increasing demand and over-extraction. Policymakers and stakeholders should promote sustainable groundwater use practices that balance water demand with the natural recharge rates of the aquifers including regulating groundwater pumping, promoting water conservation measures, and promoting the use of alternative water sources such as recycled wastewater. Implementing proper waste management practices is another step that should be taken including the treatment and disposal of hazardous waste and wastewater, to prevent the contamination of groundwater resources.

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