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Spatial and temporal assessment of groundwater quality and hydrogeochemical processes in Urmia Lake Basin, Iran

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ABSTRACT

The evaluation of groundwater quality and geochemistry have an important role in the management of water resources in arid and semi-arid regions. In the present study, the spatio-temporal assessment of groundwater quality and hydrogeochemical processes, as well as, statistical analyses in the Azarshahr and Ajabshir planes located in the Urmia Lake basin were investigated. The results revealed that within six years (from 2014 to 2019), the value of total hardness was higher than the permissible level and the quality of groundwater for drinking was very hard and fresh in both planes. In 2019, 84 and 67% of the samples fell within the range of good to poor groundwater quality in the Azarshahr and Ajabshir planes, respectively. The temporal assessment with the help of water quality index values for both planes revealed a good groundwater quality for the Azarshahr plane and a good to poor groundwater quality for the Ajabshir plane. However, deterioration of water quality was observed in both planes from 2014 to 2019. The level of water quality for irrigation was better in the Azarshahr plane than in the Ajabshir plane, due to the presence of fewer salty sites. In addition, Ca–Mg–HCO_3 and rock dominance were identified as hydrochemical facies and the controlling factor in the groundwater of both planes, respectively. Multivariate statistical analyses indicated both natural and anthropogenic sources (such as weathering, fertilizers, and wastewater) for hydrochemical parameters. It was suggested to develop a comprehensive regulation to control the entry of pollutants into the groundwater of the study area.

Key words: drinking and irrigation, groundwater quality, hydrogeochemistry, Urmia Lake

HIGHLIGHTS

- The level of water quality for drinking and irrigation was better in the Azarshahr plane than in the Ajabshir plane.
- Ca–Mg–HCO_3 and rock dominance were identified as hydrochemical facies and the controlling factors in the groundwater of the study area.
- The groundwater resources in the Urmia Lake Basin were found to be threatened by different sources of pollution.

INTRODUCTION

In the last decades, water demand has been significantly increased due to water shortage caused by global warming and climate changes (Fallahati *et al.* 2020). The groundwater is considered as one of the most valuable water resources for drinking, agricultural, and industrial purposes (Raju *et al.* 2015; Jalili *et al.* 2018; Li *et al.* 2019a, 2019b). According to Qasemi *et al.* (2018, 2019), agricultural purposes rank first and account for more than 80% of groundwater consumption in Iran. In arid and semi-arid areas, the high demand for groundwater resources leads to reduction in the water table of groundwater aquifers (Abbasnia *et al.* 2019). Moreover, pollution of water resources is rapidly increasing due to urbanization, industrialization, and agricultural activities (Rao *et al.* 2017; Haghnazar & Saneie 2019; Rahman *et al.* 2020). The anthropogenic sources including industrial effluents, municipal sewage, overuse of pesticides and fertilizers, and mining operations along with the natural sources such as weathering of parent materials are the main sources of water quality reduction (Taghipour *et al.* 2012; Brindha *et al.* 2017; Ezugwu *et al.* 2019; Onwuka *et al.* 2019; Haghnazar *et al.* 2020). Groundwater quality is mainly affected by hydrological properties, geological structures, fertilizers, industrial pollution, sewage, and sand river mining (Mirzabeygi *et al.* 2017; Yousefi *et al.* 2017; Abboud 2018; Rezaei & Hassani 2018; Adimalla & Qian 2019). Therefore, control and assessment of groundwater quality are considered to be essential.

Various studies have focused on the hydrochemical monitoring, geochemical processing, sources of pollution, and applicability of water for agricultural and drinking purposes (Alaya *et al.* 2014; Li *et al.* 2016; Abd El-Aziz 2017; Rezaei *et al.* 2018; Zhang *et al.* 2018; Berhe 2020). The sources of contamination can be determined by multivariate statistical analyses such as correlation matrix and principal component analysis (PCA). These approaches are useful in finding the complicated relationships among the physicochemical parameters of water resources (Wang *et al.* 2014; Ustaoğlu *et al.* 2020). Control of groundwater quality can be done using the water quality index (WQI), which has been widely used by numerous researchers (Sahu & Sikdar 2008; Bhuiyan *et al.* 2016; Sethy *et al.* 2016; Rawat & Singh 2018; Sharmin *et al.* 2020). One of the advantages of WQI is its capability of overall assessment of physicochemical parameters (Abtahi *et al.* 2015). So far, different types of methods, such as Wilcox, Piper, and Gibs diagrams, have been used for groundwater quality assessment in previous studies (Choramin *et al.* 2015; Li *et al.* 2016; Narsimha & Sudarshan 2017; Kawo & Karuppannan 2018; Sahoo & Khaoash 2020). The suitability for agricultural purposes can be assessed using Wilcox diagrams (Khoramabadi Shams *et al.* 2014). Furthermore, hydrochemical facies and factors for controlling the groundwater chemistry are evaluated by Piper and Gibs diagrams, respectively (Srinivasamoorthy *et al.* 2014; Koffi *et al.* 2017). Urmia Lake, as the second great salt lake in the world, is one of the most important and valuable ecosystems located in the Northwest of Iran (Hassanzadeh *et al.* 2012). In the last 10 years, the surface water tabel in the Urmia Lake has dropped dramatically due to climate changes, continuous droughts, development of cultivated areas, land-use changes, and construction of dams (Ghale *et al.* 2018). The hypersalinity of the Urmia Lake has highlited the critical role of groundwater in supplying the water required for drinking, agricultural, and industrial purposes in the urban areas around the lake. In the last decade, the groundwater resources in the Urmia Lake Basin have been threatened by chemical pollution due to the significant increase of agricultural activities and population around the lake. Therefore, it is vital to assess the spatio-temporal status of the quality of the multi-purpose groundwater in this area.

Considering the condition of the Urmia lake in recent years, which is threatening the groundwater quality due to the continuous drying of the salty lake, it is of great importance to investigate the groundwater quality and determine the effect of the salt water of the lake in the area. Accordingly, the present study aimed to investigate groundwater quality variation in recent years in a large area. In addition, the temporal status of groundwater for drinking purpose together with identification of sources of the major ions in the Eastern lake is well documented for the first time.

In this study, the spatio-temporal variations of groundwater quality have been evaluated using the WQI and diagram-based methods. In addition, the sources of chemical parameters were determined using the multivariate statistical techniques.

The objectives of this study were: (1) to evaluate the spatio-temporal variations of the hydrochemical parameters of groundwater, (2) to determine the status of the groundwater quality for drinking and irrigation purposes, and (3) to assess the hydrogeochemical process of groundwater in the study area. This study was carried out in Azarshahr and Ajabshir cities in 2019.

MATERIALS AND METHODS

Characteristics of the study area

The study area is located in East-Azerbaijan province in the North-West of Iran. The groundwater wells in the Azarshahr plane, with an area of 168 km^2, and the Ajabshir plane, with an area of 144 km^2, in the eastern part of Urmia Lake were selected for sampling (Figure 1). The study area has a semi-arid and cold climate. In the Azarshar and Ajabshir planes, the average annual temperatures are 13 °C and 12 °C and the average annual precipitation is 221.2 and 300 mm, respectively (Docheshmeh Gorgij & Asghari Moghaddam 2017; Gorgij *et al.* 2017; Moghaddam *et al.* 2018). The mean water table depths of the aquifers are in the range of 0.7–29.8 m in the Azarshar plane and 0.5–37.7 m in the Ajabshir plane (Rezaei & Gurdak 2020). In recent years, the groundwater aquifers in the study area have been faced with over-extraction due to overpopulation, industrialization, and overuse of fertilizers. Since the study area is located in the vicinity of the hypersaline region of the Urmia Lake, where there is an imbalance between precipitation and evaporation, water consumption is completely dependent on groundwater resources (Gorgij *et al.* 2019). For example, in the Azarshahr plane, 100% of the water for drinking, domestic, and industrial purposes and 80% of the water for agricultural purposes are supplied by the groundwater resources (Gorgij *et al.* 2017).

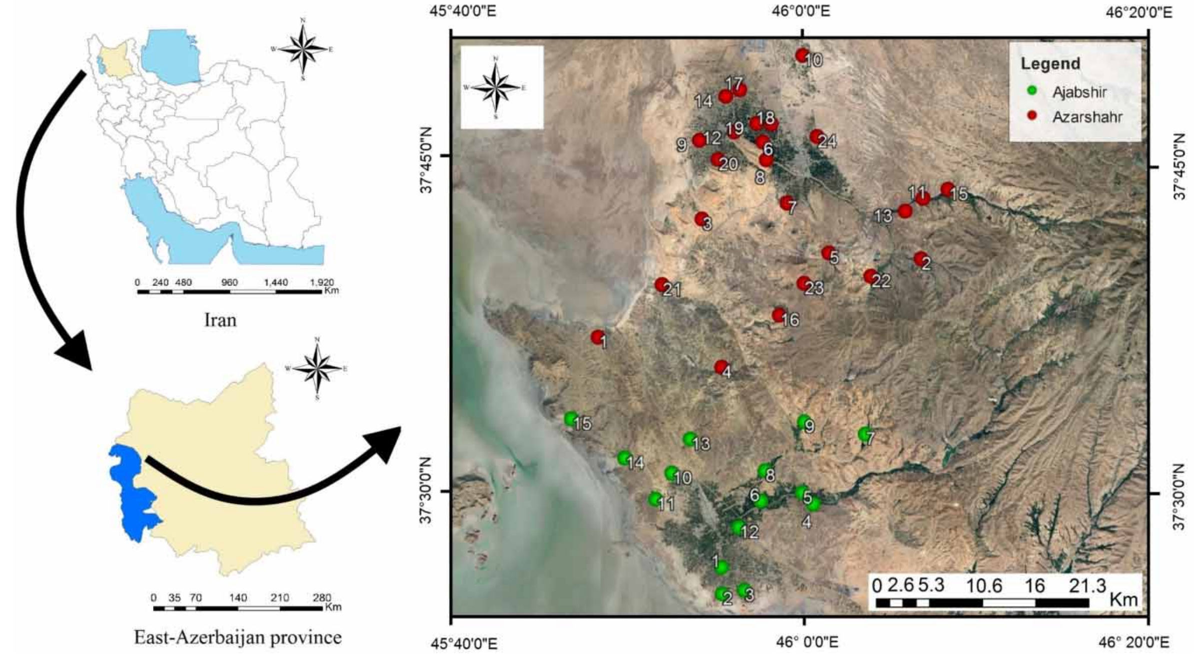

Figure 1 | Geographic location of the study area with the sampling sites in the Azarshahr and Ajabshir planes in the vicinity of Urmia Lake.

Sampling and analysis

Totally, 24 and 15 groundwater samples (39 samples) were collected from the Azarshahr and Ajabshir planes in October 2019, respectively. For temporal assessment of the groundwater quality, the data on hydrochemical parameters of the sampling sites from 2014 to 2018 was obtained from the Regional Water Company of East-Azerbaijan. Water of wells was pumped for 10 min to remove the impact of stagnant water (Adimalla 2019). 250 ml polyethylene bottles were washed with deionized water and used for collecting the samples. The collected samples were stored at 4 °C in a refrigerator and transferred to the laboratory to be studied for hydrochemical parameters. Accordingly, the groundwater hydrochemical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness as $CaCo_3$ (TH), cations [potassium (K^+), sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+})], and anions [sulfate (SO_4^{2-}), nitrate (NO^{3-}), chloride (Cl^-), bicarbonate (HCO_3^-), fluoride (F^-)] were analyzed. After sampling, pH and EC were detected *in situ* using a portable pH/EC meter. Moreover, TDS was calculated by multiplying a factor (0.64) to EC. HCO_3^-, SO_4^{2-}, and Cl^- were determined by titrimetric methods, and NO^{3-} and F^- were obtained using a spectrophotometer. Na^+ and K^+ were analyzed by flame atomic absorption spectrometry, while TH, Mg^{2+} and Ca^{2+} were measured by EDTA titrimetric method. All the samples were tested in two replicates to ensure the accuracy of the analyses.

Assessment of groundwater quality

Groundwater quality for drinking

WQI is a useful index-based method for overall assessmnet of groundwater quality for drinking purposes (Ramakrishnaiah *et al.* 2009; Khan & Jhariya 2017). To calculate the WQI, weights of 2–5 were assigned to the hydrochemical parameters of groundwater based on their significance in groundwater quality. In the first step, the relative weights (W_i) were computed using (Equation (1)).

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \tag{1}$$

The values of weights and relative weights for each parameter are presented in Table 1 (Khalid 2019).

In the second step, the quality rating scale (Q_i) for each hydrochemical parameter was calculated by the ratio of the measured parameters' values to the relevant standard value proposed by WHO (2011)

Table 1 | Standard values, weights, and relative weights for each hydrochemical parameter

Elements	WHO (2011) (mg/L)	Weight (w_i)	Relative weight (W_i)
pH	6.5–8.5	4	0.087
EC	1,500	4	0.087
TDS	1,000	4	0.087
SO_4^{2-}	250	5	0.109
NO_3^-	45	5	0.109
Cl^-	250	4	0.087
HCO_3^-	500	3	0.065
F^-	1.5	5	0.109
TH	100	3	0.065
K^+	12	2	0.043
Na^+	200	3	0.065
Mg^{2+}	50	2	0.043
Ca^{2+}	75	2	0.043
		$\sum w_i = 46$	$\sum W_i = 1$

according to (Equation (2)).

$$Q_i = \frac{C_i}{S_i} \times 100 \tag{2}$$

where, C_i and S_i are the measured value and the standard value of parameters, respectively.

In the final step, the water quality sub-index and the WQI are obtained using (Equation (3)) and (Equation (4)).

$$SI_i = Q_i \times W_i \tag{3}$$

$$WQI = \sum_{i=1}^{n} SI_i \tag{4}$$

The WQI was classified into five clasess as presented in Table 2 (Saleem *et al.* 2016).

Groundwater quality for irrigation

To assess the suitability of the groundwater for agricultural purposes, Wilcox diagrams were plotted using the value of sodium absorption ratio (SAR) versus EC (Wilcox 1955). SAR can be calculated by (Equation (5)).

$$SAR = \frac{Na^+}{\sqrt{\frac{Mg^{2+} + Ca^{2+}}{2}}} \tag{5}$$

Table 2 | The WQI classification for drinking purposes

Classification	Groundwater quality
WQI < 25	Excellent groundwater
25 < WQI < 50	Good groundwater
50 < WQI < 75	Poor groundwater
75 < WQI < 100	Very poor groundwater
WQI > 100	Unsuitable groundwater

The groundwater quality for irrigation was categorized into four classes as presented in Table 3 (Fallahati *et al.* 2020).

Controlling factors, types and facies of groundwater

Piper diagram is a useful method to determine the hydrochemical type and facies of groundwater (Patolia & Sinha 2017; Li *et al.* 2019a, 2019b; Sahoo & Khaoash 2020). According to the Piper diagram, the groundwater was classified into four dominants for major cations and anions including (a) Mg type, (b) Ca type, (c) Na & K type, (d) no dominant type, (e) SO_4 type, (f) HCO_3 type, (g) Cl type. Finally, the groundwater was classified into six faces as Face 1: Ca–Mg–HCO_3, Face 2: Na-Cl, Face 3: mixed Ca–Na–HCO_3, Face 4: Mixed Ca–Mg–Cl, Face 5: Ca-Cl, and Face 6: Na- HCO_3 (Shakerkhatibi *et al.* 2019; Sharmin *et al.* 2020).

The factors for controlling the groundwater chemistry were determined using two semilog digrams designed by Gibbs (1970). The Gibbs diagrams were plotted by TDS versus $Cl/Cl + HCO_3$ and $Na/Na + Ca$ representing the anions and cations, respectively. According to the Gibbs diagrams, the controlling factors were grouped into three dominances including rock dominance, precipitation dominance, and evaporation dominance (He & Wu 2019; Heydarirad *et al.* 2019).

Statistical analysis

For both Azarshahr and Ajabshir planes, multivariate statistical analyses were performed to determine the interactions among the hydrochemical parameters (Sethy *et al.* 2016; Sangsefidi *et al.* 2017). The Kolmogorov-Smirnov test was carried out to assess the normality of the value of the parameters (Haghnazar *et al.* 2021). Moreover, Pearson's correlation matrix was applied to identify the relationship among the parameters. The correlation coefficients in the range of 0.5–0.7 and greater than 0.7 were considered as moderate and significant, respectively (Mehraein *et al.* 2020). PCA was conducted to reduce the dimension of the dataset and determine the sources of hydrochemical parameters of the groundwater (Mosaferi *et al.* 2014). In the PCA calculation method, the rotation of principal components was carried out using Varmix rotation for better interpretation.

RESULTS AND DISCUSSION

Temporal assessment of the groundwater chemistry

Temporal assessment of the hydrochemical parameters of the groundwater in the Azarshahr and Ajabshir planes during six years (from 2014 to 2019) was studied and the values of the parameters were compared with the permissible values for drinking water proposed by WHO (2011). The mean values of the hydrochemical parameters in both planes have been presented in Table 4. The pH range of 7.2–7.5 in the groundwater of the Azarshahr and Ajabshir planes represented the alkaline groundwater in nature for six years. In addition, the dominant cations were found to be in the order of $Ca^{2+} > Na^{2+} > Mg^{2+} > K^{+}$, and the dominant anions had the order of $HCO_3^{-} > SO_4^{2-} \approx Cl^{-} > NO_3^{-} > F^{-}$ for both planes from 2014 to 2019. In the Azarshahr plane, the mean values of EC, TDS, NO_3^{-}, HCO_3^{-}, TH, Mg^{2+}, and Ca^{2+} increased in the second three years (2017–2019) compared to the first three years (2014–2016).

The mean values of all the parameters, except for TH, were found to be less than the permissible levels provided by WHO (2011). The values of TH were higher than the permissible levels in the whole six years. The minimum and maximum values of TH were 1.88 and 2.07 times greater than the permissible values in 2014 and 2019, respectively. In the Ajabshir plane, the mean values of EC, TDS, TH, Na^{2+}, and Ca^{2+} had a similar order and an increasing trend in the second three years (2017–2019). The mean values of all the parameters, except for TH and Ca^{2+}, exceeded the permissible levels. The maximum and minimum values of TH were

Table 3 | The Wilcox classification for groundwater quality

Class	Water quality for irrigation
C1S1	Sweet
C1S2-C2S2-C2S1	A little salty
C1S3-C2S3-C3S1-C3S2-C3S3	Salty
C1S4-C2S4-C3S4-C4S4-C4S3-C4S2 -C4S1	Very salty

Table 4 | Hydrochemical parameters in the groundwater of Azarshahr (Az) and Ajabshir (Aj) planes

Year	**2014**		**2015**		**2016**		**2017**		**2018**		**2019**		
Elements	**Az**	**Aj**	**Az**	**Aj**	**Az**	**Aj**	**Az**	**Aj**	**Az**	**Aj**	**Az**	**Aj**	**WHO (2011)**
pH	7.5	7.4	7.4	7.2	7.5	7.5	7.4	7.4	7.2	7.2	7.2	7.2	6.5–8.5
EC	506.5	556.5	496.1	771.4	470.6	585.7	541.8	862.0	516.2	664.6	520.0	799.8	1,500
TDS	324.1	356.2	313.7	493.7	301.2	374.9	346.7	551.7	330.4	425.4	332.7	511.9	1,000
SO_4^{2-}	48.7	32.9	34.3	54.9	30.7	32.9	47.8	53.4	39.2	42.2	40.2	47.7	250
NO_3^-	1.7	4.9	9.1	21.6	2.7	14.2	11.5	18.4	7.7	9.6	10.4	20.9	45
Cl^-	39.7	35.3	40.6	52.2	30.8	27.9	38.5	53.2	38.2	36.2	39.4	56.0	250
HCO_3^-	190.3	258.6	193.8	324.8	200.5	274.0	208.4	375.1	205.5	296.8	204.0	341.3	500
F^-	0.4	0.6	0.3	0.4	0.3	0.3	0.4	0.4	0.3	0.3	0.4	0.4	1.5
TH	188.0	232.0	182.0	286.3	178.2	214.6	209.0	331.1	200.5	232.2	207.2	310.7	100
K^+	3.4	3.2	3.5	3.9	3.1	5.5	3.3	3.2	2.8	4.8	2.8	3.1	12
Na^+	29.9	26.7	29.2	48.1	25.7	35.4	27.5	45.2	26.3	44.0	23.9	41.7	200
Mg^{2+}	11.8	16.1	12.7	24.1	12.4	14.3	14.3	25.1	13.9	16.6	14.7	19.9	50
Ca^{2+}	54.5	58.1	51.5	74.9	50.5	62.4	59.7	90.6	57.0	65.2	58.3	91.3	75

2.14 and 3.1 times greater than the permissible values in 2016 and 2019, respectively. For Ca^{2+}, the highest value was recorded as 1.2 times greater than the permissible value in 2016 and 2017.

The high concentration of TH, due to anthropogenic sources and geological structures, in both planes has led to deterioration of the groundwater quality in recent years. According to the mean values obtained for TH and TDS, the groundwater quality for drinking was found to be very hard (Sawyer & McCarthy 1967) and fresh (Freeze & Cherry 1979) for both planes.

Groundwater quality assessment

The results of groundwater quality in the Azarshahr and Ajabshir planes in the six years are illustrated in Figure 2. The mean values of WQI in the six years were lower in the Azarshahr plane than in the Ajabshir plane, indicating better quality of water for drinking. The minimum and maximum mean values of WQI in the Azarshahr and Ajabshir planes were 38.8/45.65 and 47.68/65.37, respectively, showing good groundwater quality in the Azarshahr plane and good to poor groundwater quality in the Ajabshir plane.

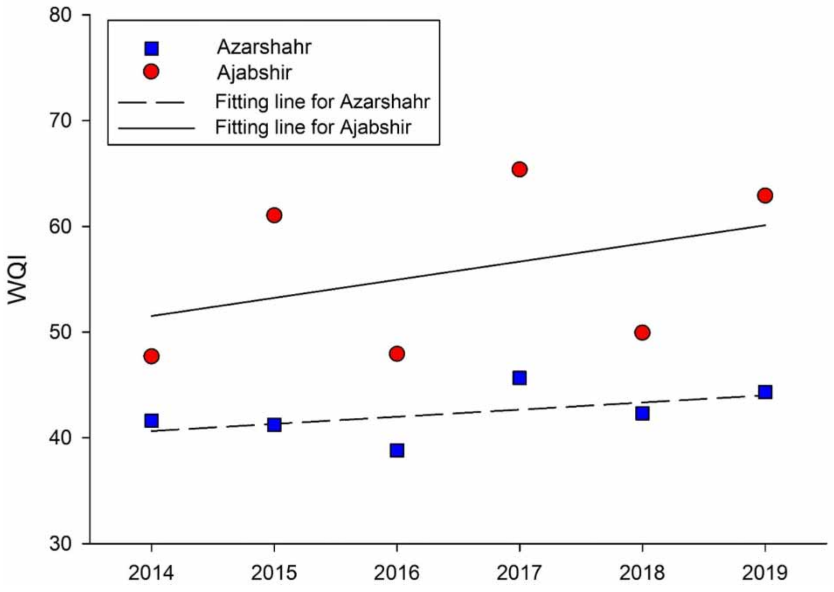

Figure 2 | Groundwater quality (WQI) in the Azarshahr and Ajabshir planes.

The regression lines for the data showed that the mean WQI values for both planes increased from 2014 to 2019, which indicated the decline of water quality over time.

The spatial distributions of WQI in the Azarshahr and Ajabshir planes in 2019 have been presented in Figure 3. The results indicated a very poor groundwater quality in two sampling points at the Eastern and Southern parts of

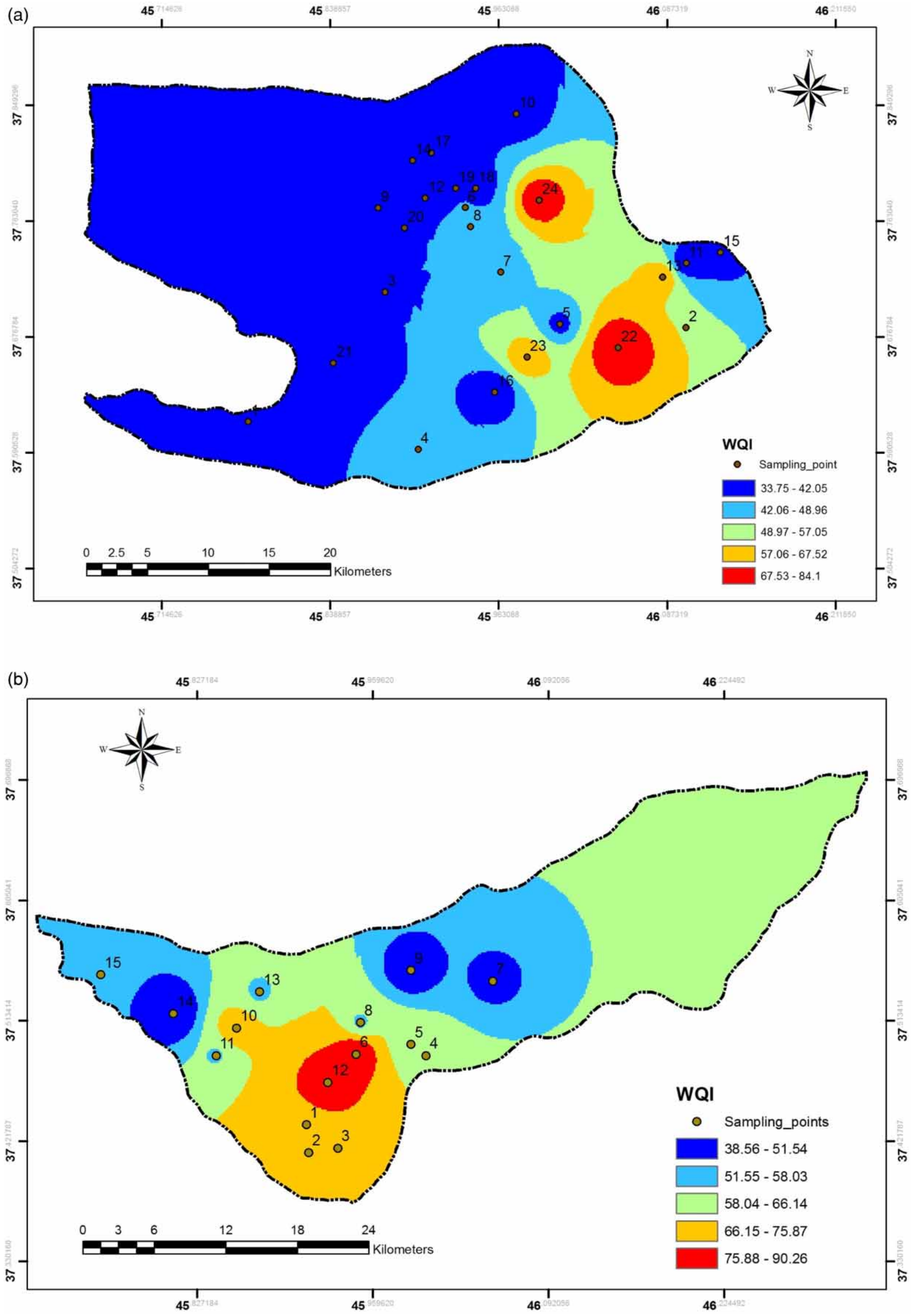

Figure 3 | Spatial distribution of WQI: (a) Azarshahr plane, (b) Ajabshir plane.

the Azarshahr and Ajabshir planes, respectively. In the Azarshahr plane, 84, 8, and 8% of the samples had a good, poor, and very poor groundwater quality, respectively. However, in the Ajabshir plane, 20, 67, and 13% of the samples showed a good, poor, and very poor groundwater quality, respectively. These hotspots located in urban and agricultural areas of the planes revealed that anthropogenic activities were responsible for the poor and very poor quality of groundwater for drinking.

SAR and EC are two major indicators for sodium hazard and salinity of groundwater. The Wilcox diagram is an effective and simple method to assess the applicability of groundwater for irrigation by combining alkalinity and salinity (Li *et al.* 2018). The Wilcox diagrams for both planes were plotted for 2019. As shown in Figure 4(a), most of the sampling points in the Azarshahr plane fall within C2S1 and C2S2, indicating a slightly salty and almost good quality for irrigation. However, four samples categorized under C3S1 and C3S2 groups proved to be salty but usable for agriculture. According to Figure 4(b), half of the samples under C2S1 and C2S2 groups and the rest of those under C3S1 and C3S2 groups could be known as slightly salty and salty, respectively. The results showed that the level of water quality for irrigation was better in the Azarshahr plane than in the Ajabshir plane due to having fewer salty sites. The sampling sites with EC >750 in the Azarshahr plane (13, 22, 23, and 24) and Ajabshir plane (1, 2, 3, 4, 5, 6, 10, and 12), located in the eastern and southern parts of the planes, were found to be affcted by leaching of soluble salts caused by anthropogenic activities (Wu *et al.* 2014; Adimalla 2019).

Geochemical characterization of groundwater

The Piper diagrams were plotted based on the dominant dissolved cations and anions to determine the hydrochemical evolution of the groundwater parameters and overall effects of reactions among major ions (Patolia & Sinha 2017; Li *et al.* 2018). According to Figure 5, the results of the Piper trilinear diagrams for both Azarshahr and Ajabshir planes were similar in 2019. Cations fell within zones B and D, indicating calcium and no dominant groundwater types, respectively. Anions belonged to zones F and D, representing bicarbonate and no dominant groundwater types, respectively. Finally, most of the sampling sites fell into zone 1, demonstrating a Ca–Mg–HCO_3 groundwater face. However, two sampling sites in the Azarshahr plane and one sampling site in the Ajabshir plane fell within zone 4, indicating the mixed Ca–Mg–Cl groundwater types.

The Gibbs diagrams were employed to analyze the mechanisms of evolution in the surface water and groundwater. The Gibbs diagrams for the Azarshahr and Ajabshir planes in 2019 were plotted according to governing cations, anions, and TDS values (Figures 6 and 7, respectively). As shown in Figures 6 and 7, all the sampling sites in both planes fell within the middle part of both cation-based and anion-based diagrams, indicating rock dominance or water-rock interaction group. The results indicated that mineral weathering was a main factor in controlling the ionic composition and the chemistry of groundwater.

Multivariate statistical analyses

Correlation analysis and PCA were conducted to determine the relationship between physicochemical variables and potential sources of minerals in the groundwater. The Pearson's correlation coefficients and PCA results,

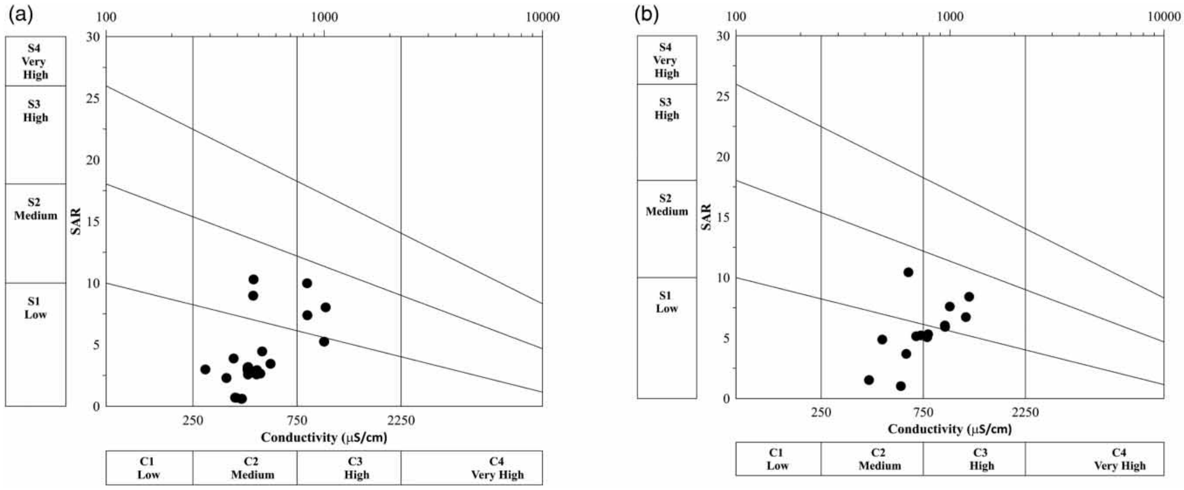

Figure 4 | Wilcox diagram of the sampling sites (a) Azarshahr plane, (b) Ajabshir plane.

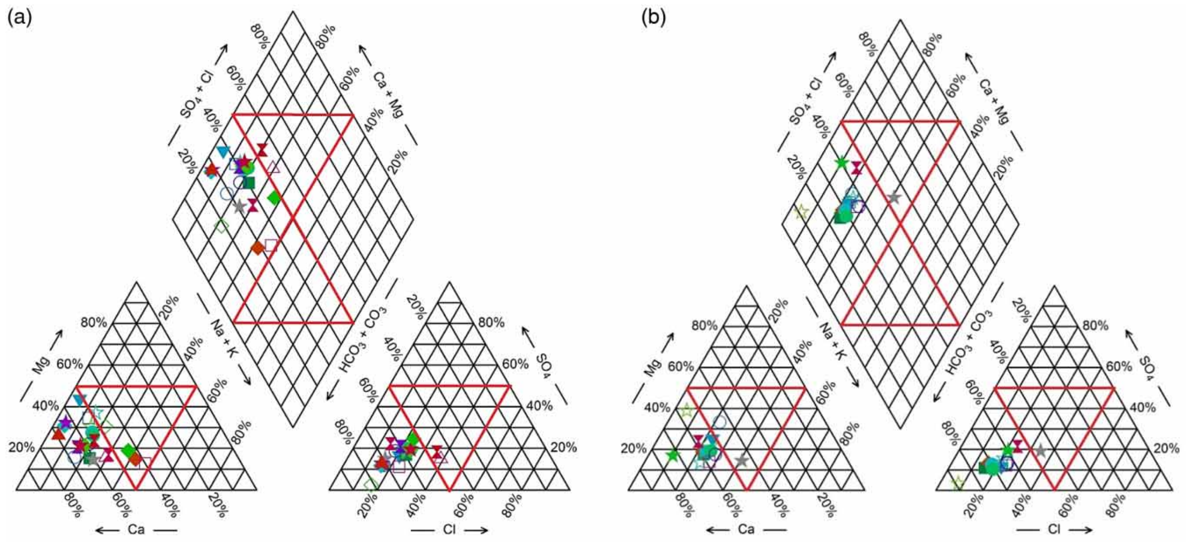

Figure 5 | Piper diagram of the sampling sites: (a) Azarshahr plane, (b) Ajabshir plane.

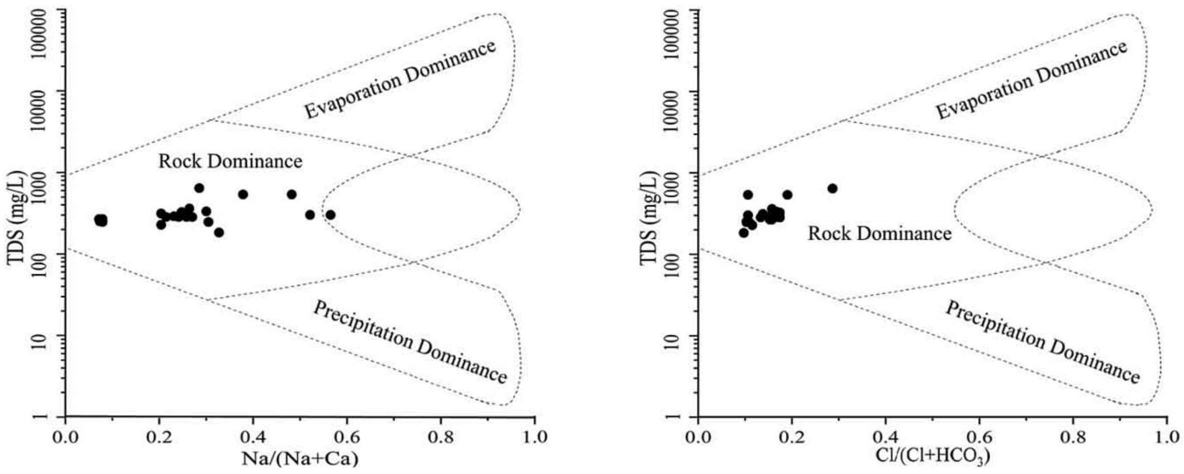

Figure 6 | The Gibbs diagrams for the sampling sites of the Azarshahr plane.

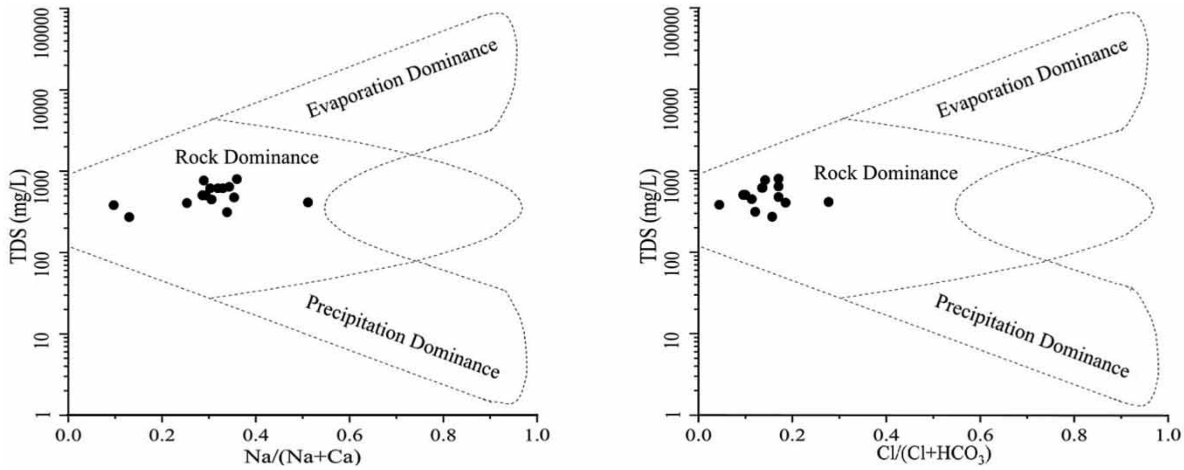

Figure 7 | The Gibbs diagrams for the sampling sites of the Ajabshir plane.

with eigenvalues greater than 1 for the Azarshahr and Ajabshir planes, were obtained based on the data related to 2019 (Tables 5 and 6). In the Azarshahr plane, the results indicated four principal components describing 84.4% of the total variance. The first component (PC1) included SO_4, Cl, Ca, Mg, EC, TDS, and TH. According to the correlation matrix, Ca had significant and moderate correlations with SO_4 (0.893) and Cl (0.549), respectively, indicating the dissolution of gypsum ($CaSO_4.2H_2O$) and $CaCl_2$ salt (Wu *et al.* 2009; Thilagavathi *et al.* 2017). The correlation of EC and TDS with other parameters in PC1 could be explained by the dominance of these ions caused by mineralization in the aquifers (Khalid 2019). The second component (PC2) was specified by Cl, Na, K, EC, and pH. The positive correlation between Na and K (0.702) could be related to weathering and mineralization (Bhuiyan *et al.* 2016). The third component (PC3) included K, Na, F, and NO_3. The correlation of Na and NO_3 (0.521) with F and K (0.562) might be related to agricultural activities (Kawo & Karuppannan 2018). The fourth component (PC4), which was specified by TDS and HCO_3, demonstrated the geogenic/anthropogenic sources. Analysis of the Ajabshir plane showed three principal components specifying 88.4% of the total variance. According to the results shown in Table 6, the first component included HCO_3, Ca, Mg, K, EC, TDS, and TH, which illustrated that EC and TDS were controlled by other parameters in PC1. The moderate correlation between HCO_3 and Mg (0.596) as well as the significant correlation of Ca and HCO_3 (0.902) with HCO_3 and K (0.829) indicated silicate and carbonate weathering and dissolution (Sethy *et al.* 2016; Wu *et al.* 2017). The second component (PC2) was specified by SO_4, Cl, F, and Na. The significant correlation between Na and Cl (0.932) showed the effects of the Urmia Lake on the dissolution of NaCl salt and interaction of halite rocks and groundwater (Muhammad & Husam 2011; Li *et al.* 2013). In addition, Na had a significant correlation with SO_4, indicating mirabilite ($Na_2SO_4.10H_2O$) due to a salt lake (Gao *et al.* 2007). Na showed a moderate correlation with F (0.589), indicating NaF salt due to the discharge of industrial wastewater from the Ajabshir Industrial City to the groundwater sources (Masindi & Abiye 2018). The third principal component (PC3) included NO_3 and pH, which demonstrated anthropogenic activities such as the use of fertilizers and domestic wastewater (Gao *et al.* 2007).

Spatial distribution of ions

The spatial distribution plots for cations and anions were extracted using the measured concentration in each sampling site for 2019 and presented in Figures S1 and S2. In the Azarshahr plane, the most concentrated areas of ions, except for Na, were located in the Eastern part. Concentration of Na in the western of the plane indicated the effects of Urmia Lake. The higher concentration of SO_4, Cl, Ca, and Mg in the western part of the plane demonstrated the types of geological layers based on the multivariate statistical results. The spatial distributions of K, F, and No_3 indicated the higher rate of agricultural activities in the eastern part of the plane. Mixed geogenic and anthropogenic activities in the eastern parts of the plane were found to be responsible for the concentrated areas of HCO_3.

In the Ajabshir plane, the concentrated areas of HCO_3, Ca, Mg, K were located in the southern and eastern parts, indicating higher amounts of weathering and natural sources in these areas. The higher concentrations of Na, Cl, and SO_4 in the western part of the plane were related to Urmia Lake. The increase of Na and F concentrations in the north-west areas was due to the industrial activities in Ajabshir Industrial City. Moreover, NO_3 showed a high concentration in the western and southern areas due to the anthropogenic activities in the agricultural and urban areas.

CONCLUSION

In this study, the groundwater in the Urmia Lake Basin was subjected to spatial and temporal assessments. For this purpose, the Azarshahr and Ajabshir planes, located at the east of the lake, were selected. The results indicated that the groundwater in nature was alkaline due to the pH range of 7.2–7.5. In both planes, the value of TH was greater than the standard level within six years (2014 to 2019). The mean values of TH and TDS in the six years showed that the groundwater quality for drinking was very hard and fresh in both planes. The results of WQI revealed a good groundwater quality in the Azarshahr plane and a good to poor groundwater quality in the Ajabshir plane for drinking purposes. In all, 84% and 20% of the samples fell within the range of good groundwater quality in the Azarshahr and Ajabshir planes, respectively. Furthermore, 8 and 67% of the samples showed poor groundwater quality, and 8% and 13% of the samples proved to be in the range of very poor groundwater quality in the Azarshahr and Ajabshir planes, respectively. Using the Wilcox diagrams, the groundwater quality for irrigation purposes was found to be slightly salty and salty in both planes. The hydrochemical facies of the

Table 5 | Correlation matrix for groundwater in Azarshahr and Ajabshir planes

Azarshahr	**HCO_3**	**NO_3**	**SO_4**	**Cl**	**F**	**Ca**	**Mg**	**Na**	**K**	**EC**	**PH**	**TDS**	**TH**
HCO_3	1.000												
NO_3	0.307	1.000											
SO_4	0.085	0.292	1.000										
Cl	0.378	0.121	0.766	1.000									
F	0.016	0.546	0.324	0.174	1.000								
Ca	0.035	0.381	0.893	0.549	0.177	1.000							
Mg	0.048	−0.323	0.439	0.421	−0.170	0.238	1.000						
Na	0.260	0.521	0.238	0.355	0.468	0.047	−0.223	1.000					
K	−0.166	0.351	0.536	0.351	0.562	0.317	−0.121	0.702	1.000				
EC	0.135	0.298	0.859	0.658	0.252	0.811	0.185	0.335	0.515	1.000			
pH	−0.187	−0.072	−0.450	−0.580	−0.059	−0.321	0.190	−0.416	−0.455	−0.591	1.000		
TDS	0.652	0.344	0.787	0.878	0.216	0.648	0.353	0.381	0.310	0.716	−0.518	1.000	
TH	0.010	0.028	0.706	0.500	−0.031	0.669	0.749	−0.189	−0.034	0.502	−0.085	0.499	1.000

Ajabshir	**HCO_3**	**NO_3**	**SO_4**	**Cl**	**F**	**Ca**	**Mg**	**Na**	**K**	**EC**	**PH**	**TDS**	**TH**
HCO_3	1.000												
NO_3	0.245	1.000											
SO_4	0.457	0.478	1.000										
Cl	0.562	0.481	0.871	1.000									
F	−0.259	0.303	0.413	0.450	1.000								
Ca	0.902	0.344	0.720	0.690	−0.122	1.000							
Mg	0.596	0.097	0.059	0.247	−0.160	0.310	1.000						
Na	0.634	0.498	0.789	0.932	0.589	0.715	0.161	1.000					
K	0.829	0.142	0.620	0.519	−0.326	0.882	0.287	0.594	1.000				
EC	0.930	0.400	0.732	0.816	0.047	0.942	0.506	0.829	0.830	1.000			
pH	−0.476	−0.626	−0.008	−0.072	0.259	−0.372	−0.163	−0.249	−0.314	−0.362	1.000		
TDS	0.930	0.400	0.732	0.816	0.047	0.942	0.506	0.829	0.830	1.000	−0.362	1.000	
TH	0.961	0.314	0.626	0.657	−0.168	0.952	0.586	0.650	0.846	0.962	−0.367	0.962	1.000

Table 6 | Principal components (PCs) of groundwater in Azarshahr and Ajabshir planes

	Azarshahr plane				**Ajabshir plane**		
	PC1	**PC2**	**PC3**	**PC4**	**PC1**	**PC2**	**PC3**
% Total variance	43.1	20.6	11.5	9.2	60.6	17.5	10.3
HCO_3	0.013	0.057	0.078	0.974	0.952	0.106	0.218
NO_3	0.076	−0.024	0.866	0.280	0.050	0.449	0.836
SO_4	0.859	0.411	0.275	0.020	0.448	0.805	0.042
Cl	0.610	0.557	0.030	0.396	0.460	0.873	0.088
F	0.077	0.074	0.836	−0.075	−0.404	0.852	−0.026
Ca	0.815	0.233	0.273	−0.018	0.878	0.337	0.184
Mg	0.734	−0.212	−0.345	0.085	0.596	−0.115	0.040
Na	−0.150	0.556	0.600	0.223	0.497	0.775	0.219
K	0.120	0.643	0.580	−0.285	0.894	0.152	0.052
EC	0.656	0.575	0.257	0.047	0.869	0.449	0.196
pH	−0.101	−0.914	0.032	−0.144	−0.294	0.168	−0.909
TDS	0.617	0.433	0.192	0.613	0.869	0.449	0.196
TH	0.930	−0.090	−0.105	0.025	0.944	0.238	0.163

groundwater was determined as $Ca–Mg–HCO_3$, and weathering of minerals was specified as a controlling factor in groundwater chemistry in both planes. The results of correlation analysis, PCA, and spatial distribution demonstrated that geological structures and agricultural and anthropogenic activities were the main sources affecting the parameters in the Azarshahr plane. Moreover, weathering and dissolution, salts of Urmia Lake, fertilizers, and wastewater were found to be the main sources affecting the parameters in the Ajabshir plane.

DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

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