

Hydro-chemical assessment and GIS-mapping of groundwater quality parameters in semi-arid regions

Afshin Honarbakhsh, Aliasghar Azma, Fahime Nikseresht, Milad Mousazadeh, Mobin Eftekhari and Yaser Ostovari

ABSTRACT

Groundwater quality assessment is vital to protect this resource. Therefore, the aims of this study were to evaluate the hydro-chemical quality of the Marvdasht aquifer located in the semi-arid region of Iran and to map the groundwater quality parameters. For this purpose, a mean data of 11 groundwater quality parameters collected from 49 wells (2010–2015) were used. Pie, Schoeller and Piper diagrams were used to determine the dominant ions and type of water. Ion ratios and Gibbs diagrams were used to illustrate the chemistry and processes in the groundwater. Spatial distribution of quality parameters were mapped using ArcGIS. Results showed that the water type is Na-Cl and Cl^- with abundance orders of $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$ and Na^+ with abundance orders of $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ are dominant anion and cation, respectively. Gibbs diagrams revealed that geological formations control the groundwater chemistry in 66% of the groundwater samples. Based on the Wilcox diagram, only 24% of the samples fell into the $\text{C}_4\text{-S}_4$ class with high salinity and alkalinity hazard. The maps showed that generally groundwater in the north of the study site has better quality than that the south of the study site, where the existence of dolomite and chalky formations leads to decreasing water quality.

Key words | Gibbs diagram, GIS, ion ratio, sodium adsorption ratio, WHO, Wilcox

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INTRODUCTION

Groundwater is a vital natural resource for economic development and for providing drinking water worldwide (Khan & Jhariya 2017). Nowadays groundwater quality due to urbanization, industrialization and agricultural activity has become one of the most serious issues throughout the globe. In recent years it has been recognized that the quality

of groundwater is of nearly equal importance as the quantity (Khan & Jhariya 2017; Honarbakhsh *et al.* 2019). Particularly in arid and semi-arid regions like Iran, groundwater is the main source of water supply and provides approximately 85% of drinking water. In the last decade, groundwater quality during prolonged drought has become one of the

most serious issues in Iran, especially in the southern provinces (Khodapanah *et al.* 2009; Ostovari *et al.* 2016). Generally, groundwater has better quality than surface water; however, it has been deteriorating due to a massive rise in the rate of industrialization and population. The quality of groundwater is influenced by various factors such as lithology, rock-water interaction, domestic waste disposal, application of fertilizers and pesticides in agriculture, and climatic conditions (Tiwari *et al.* 2017).

In view of the importance for public health of water for human consumption, the World Health Organization (WHO) has laid down various quality standards for groundwater parameters (Nag & Das 2014). Therefore, the values of the physical and chemical parameters assigned by WHO are important monitoring tools for assessing the groundwater quality for drinking. In most developing countries, 80% of all diseases are significantly attributed to poor quality drinking water and unsanitary conditions. Protecting groundwater quality is essential because it is too difficult to rehabilitate if it becomes polluted. For the best control and management of groundwater quality, it is important to know the spatial distribution of groundwater quality parameters. Hence, Geographic Information Systems (GIS) can be a powerful tool for the assessment of groundwater quality (Reza & Sing 2010; Tiwari *et al.* 2017). It has been used in addressing issues and managing geographical information in a holistic manner without losing spatial variability, which is often critical in assessment and decision-making (Machiwal *et al.* 2011; Ostovari *et al.* 2015).

The importance of groundwater quality for drinking has recently attracted a great deal of interest. In recent years, due to the necessity of monitoring groundwater quality, assessment and mapping of groundwater quality for drinking has been widely conducted by many researchers. Hosseinzadeh-Talaei (2014) assessed the groundwater quality of Ardabil plain (north of Iran) using GIS. The results showed that the quantity of salinity was higher than 2.5 dSm^{-1} in 2% of the study area. According to WHO (2011), the results also revealed that other quality parameters had good quality and their concentrations were lower than the corresponding threshold values. Jaihouni *et al.* (2014) evaluated the groundwater of Tabriz City for drinking purposes using GIS. The maps created using 70 wells showed that the groundwater quality increases from north to south

and from west to east of the study area. Ostovari *et al.* (2016) assessed the Lordegan aquifer in Iran using a GIS-based groundwater quality assessment. Their results showed that the Lordegan aquifer had good drinking water quality with a mean Groundwater Quality Index (GWQI) of 83. The GWQI map indicates that drinking water quality decreases moving north from the southwest; this may be attributed to the existence of agricultural activities, municipal effluent and gypsum formations present north of the plain.

Khan & Jhariya (2017) used GIS for the assessment of the Raipur City groundwater for drinking. Eight water quality parameters including pH, Cl^- , F^- , Ca^{2+} , Mg^{2+} , alkalinity, hardness and nitrate content were evaluated. The results showed that 76% of the area falls under excellent, very good and good water quality classes and 24% of the area falls under poor and very poor classes. Jafari *et al.* (2018) assessed the groundwater quality of Abhar city in the north of Iran for drinking. The results showed higher concentrations of electrical conductivity (100%), total hardness (66.7%), total dissolved solids (40%), magnesium (23%), and sulfate (13.3%) which, according to WHO, indicated signs of deterioration for drinking consumption.

Khetwani & Singh (2018) assessed a spatio-temporal analysis of the hydrological drought in Marathwada Region, India. They used the water level index to investigate the hydrological drought intensity during pre- and post-monsoon seasons between 2001 and 2015. The spatio-temporal maps of hydrological drought showed significant spatial expansion of hydrological drought during the period 2011–2015. Honarbakhsh *et al.* (2019) used a GIS-based approach with the GWQI to analyze groundwater quality in Marvdasht, located in the semi-arid region of Iran. They used groundwater quality data of 49 wells during 2010–2015. The GWQI map showed that only 2% of the study area (11 km^2) was below the low quality class located in the south of the study site. Sensitivity analysis revealed that Mg^{2+} , TH and Na^+ were identified as the most sensitive water quality parameters. Elubid *et al.* (2019) investigated the geospatial distribution of groundwater quality in the southern part of Gedaref State in eastern Sudan using GIS and drinking water quality index. They used data of major anions and cations from 40 wells. Their results proved that groundwater quality was controlled by sodium and bicarbonates ions that defined the composition of the water type to be Na HCO_3 .

Although assessment and mapping of groundwater quality is very important to manage this valuable resource, there are only a few published works evaluating the groundwater quality for drinking in southern Iran. Marvdasht groundwater is the most important aquifer in the province of Fars, because it supplies drinking water for more than 300,000 people and irrigation water for agricultural activities. Therefore, hydro-chemical assessment of groundwater of the Marvdasht aquifer is vital for the use of this valuable water resource for drinking and irrigating. Moreover, GIS-mapping of the groundwater quality determines hotspot areas (low quality) and can help to make a plan for preserving these areas. Hence, the objectives of this study are to assess the hydro-chemical analysis of the Marvdasht groundwater parameters and to map the groundwater quality parameters using GIS.

MATERIALS AND METHODS

Study area

The Marvdasht Plain with an area of 3,926.3 km² is located between 29°19'–30°20' N and 52°15'–53°27' E in the

northern part of Fars province, Iran. The Marvdasht aquifer with an area of 1,986.4 km² includes eight sub-aquifers (Figure 1). Marvdasht city with a population over 200,000 people and around 200 villages with more than 100,000 people are located in the study site and Marvdasht groundwater is the only resource to provide drinking water for those populations. In addition, Marvdasht groundwater also supplies irrigation water for thousands of hectares of agricultural farms because agriculture is the main activity in the study site. The study site has a semi-arid climate with a mean annual precipitation of 350 mm. The soils are calcareous with more than 45% calcium carbonate and are categorized in two main groups: Entisols and Inceptisols.

Geology of the area

The altitude of the study area varies in the range of 1,500–2,460 m with a mean of 2,070 m above mean sea level. The center of the study area is a flat plain with intensive agricultural activities, while the elevated zones of the study area are predominantly mountainous. The prominent geological formations in the study area are soluble dolomite and calcite limestone of Sarvak formation, quaternary

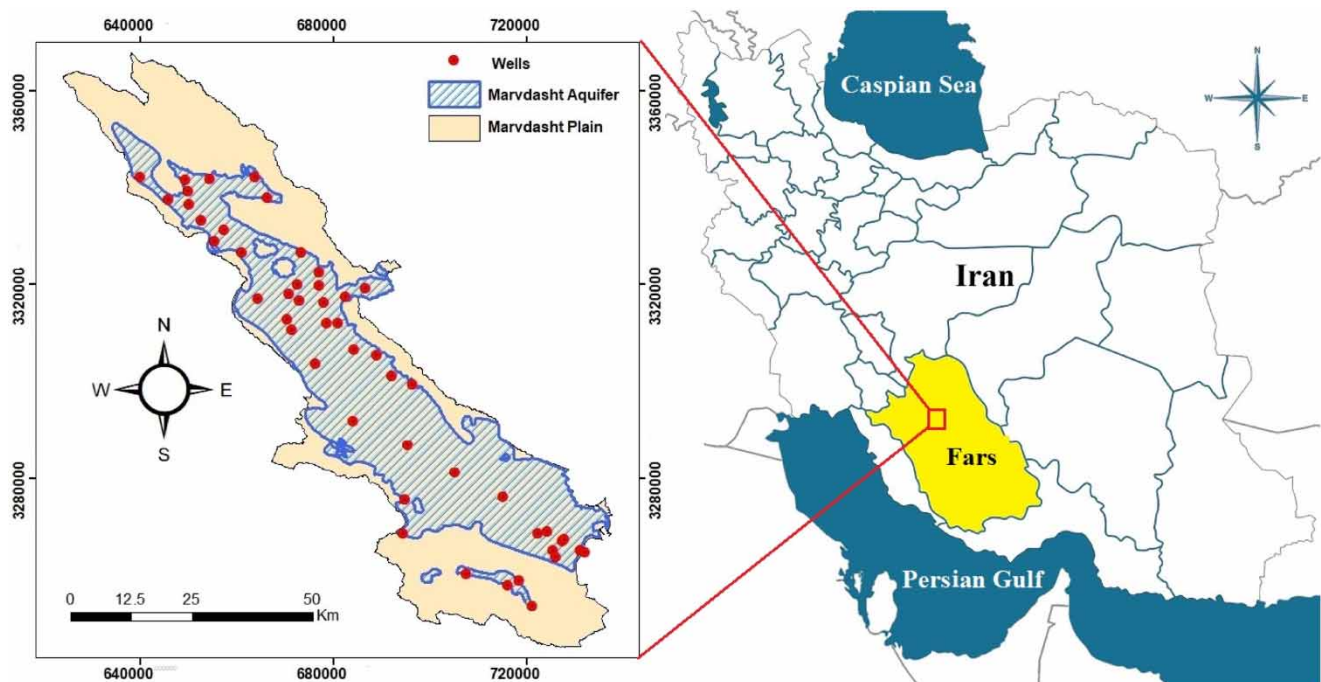


Figure 1 | Study area in Fars Province, Iran and the locations of sample sites.

conglomerates, and alluvial deposits Q1 to Q3 (Sangab Zagros Co 2009). In addition, Hormuz and Cachon (in the southeast) and Asmari-Jahrome (in the northwest), which have some soluble materials such as chalky-salty marl and argillaceous limestone, are found in the study site (Sangab Zagros Co 2009).

Sampling and analysis

In order to evaluate the groundwater quality, mean 5-year (2010–2015) data of 49 agricultural wells over the study area (Figure 1) were used. Geographical locations of the sample sites were obtained using a hand-held GPS. The mean water table over the experimental area was approximately 35 meters (Ostovari *et al.* 2015). Groundwater samples were analyzed for 11 chemical parameters following the APHA (1998) standard. EC and pH were measured by the pH-EC meter model ZX44XL. The total dissolved solids (TDS) was obtained based on the evaporation method; 100 mL of water sample was heated to boiling point to evaporate the water and then the residual materials from the boiled water were weighed and considered as the TDS. Chloride (Cl^-) was measured immediately after transfer to the laboratory by titration with silver nitrate. Sodium (Na^+) and potassium (K^+) were determined by flame photometry using a flame photometer model XP. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were analyzed by titration with EDTA. Bicarbonate (HCO_3^-) was measured by the titration with sulfuric acid and sulfate (SO_4^{2-}) was measured by

spectrophotometry using spectrophotometer model REY-LEIGH-1800 UV. Ca^{2+} and Mg^{2+} were then used to calculate total hardness (TH) as follows (Boyd 2000):

$$\text{TH (mg of CaCO}_3\text{)} = (\text{Ca}^{2+} + \text{Mg}^{2+}) \times 50 \quad (1)$$

where Ca^{2+} and Mg^{2+} are calcium and magnesium (meq/L).

Hydro-chemical analysis and mapping

Statistical analyses including description statistic and correlation matrix were conducted using Statista 8.0 software. The hydro-chemical analysis of groundwater quality parameters was carried out in Aqua software. In order to map the spatial analysis of groundwater quality parameters, maps of all 11 chemical parameters were created using inverse distance weighting in ArcGIS 10.0 software (ESRI Inc 2008).

RESULTS

Groundwater description

The statistical summary for the physio-chemical parameters is presented in Table 1 which also shows the maximum allowable limits of various parameters according to WHO (2017). The pH value of the groundwater varied from 7.30 to 8.25 with an average value of 7.70 (Table 1). The EC values

Table 1 | Statistical summary for the physio-chemical parameters of Marvdasht groundwater

Chemical parameter	unit	Mean	Min	Max	Standard deviation	Coefficient variation	WHO (2017)
pH	–	7.53	6.9	8.0	0.2	2.8	7.5–8.5
EC	$\mu\text{S/cm}$	4,001.2	35.9	14,697.0	2,635.1	127.1	1,500
TDS	mg/L	2,400.7	347.2	10,270.5	2,823.0	117.1	1,000
TH	mg/L	1,123.2	199.6	5,470.4	1,364.5	121.1	500
HCO_3^-	mg/L	309.1	100.0	552.1	89.6	29.4	300
SO_4^{2-}	mg/L	301.5	13.2	1,501.6	377.3	125.2	200
Cl^-	mg/L	941.6	13.5	5,117.7	1,418.1	150.5	200
Ca^{2+}	mg/L	217.1	52.0	838.6	235.1	108.2	75
Mg^{2+}	mg/L	146.1	12.2	840.5	187.4	128.2	30
K	mg/L	7.4	0.5	32.0	0.8	51	12
Na^+	mg/L	398.6	6.0	2,200.4	548.8	137.7	200

Table 2 | Pearson correlation coefficient among various groundwater quality parameters

	pH	EC	TDS	TH	TA	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	K ⁺
EC	-0.67*									
TDS	-0.68*	0.99*								
TH	-0.68*	0.96*	0.97*							
TA	0.24	-0.14	-0.21	0.85*						
SO ₄ ²⁻	-0.53*	0.86*	0.87*	0.90*	-0.21					
Cl ⁻	-0.71*	0.98*	0.99*	0.96*	-0.23	0.81*				
Ca ²⁺	-0.69*	0.94*	0.96*	0.97*	-0.34	0.87*	0.94*			
Mg ²⁺	-0.65*	0.94*	0.96*	0.98*	-0.16	0.88*	0.94*	0.93*		
K ⁺	-0.67*	0.98*	0.99*	0.96*	-0.20	0.85*	0.99*	0.95*	0.93*	
Na ⁺	-0.66*	0.90*	0.97*	0.89*	-0.16	0.79*	0.97*	0.93*	0.87*	0.97*

*Significant differences at 95% level.

ranged from 35.9 to 14,697.0 $\mu\text{S}/\text{cm}$ with an average value of 4,001.2 $\mu\text{S}/\text{cm}$ (Table 1). The mean of TDS in the Marvdasht groundwater is 2,400 mg/L (Table 1) and based on this value, groundwater is unsuitable for drinking (WHO 2011). According to Table 1, Ca²⁺ concentration varied from 52.0 to 838.6 mg/L with an average of 217.1 mg/L. The concentration of Na⁺ varied from 6.0 to 2,200.4 mg/L (Table 1). Sixty-one per cent of the samples are below the maximum desirable limit (<200 mg/L) as recommended by WHO (2017). Minimum, maximum and mean of bicarbonate concentration are 100.0, 552.1 and 309.1 mg/L, respectively (Table 1). Almost half the samples are within the maximum permissible limit of HCO₃⁻ (300 mg/L). The Cl⁻ varied between 13.5 and 5,117.7 mg/L with an average value of 941.6 mg/l (Table 1). According to WHO (2011), 28.5% of groundwater samples exceed the maximum allowable limit of Cl⁻ (600 mg/L). The Pearson correlation among groundwater quality parameters is presented in Table 2.

Hydro-geochemical assessment

Pie and Schoeller diagrams are given in Figure 2. According to Figure 2(a), Cl⁻ is the dominant anion with abundance orders of Cl⁻ > SO₄²⁻ > HCO₃⁻ (meq/L) (Figure 2(a)). Na⁺ is the dominant cation with abundance orders of Na⁺ > Mg²⁺ > Ca²⁺ > K⁺ (Figure 2(b)). According to the Piper diagram, all samples fall into two water types including Ca-Mg-SO₄-Cl (45% of the samples) and Ca-Mg-HCO₃ (55% of the samples). Figure 3 depicts the Piper diagram

of the Marvdasht groundwater. Ca²⁺, Mg²⁺ and N⁺ plus K⁺ are the dominant cations in approximately 25, 25 and 50% of the samples, respectively. The dominant anion in 48% of the samples is Cl⁻, in 28% of the samples it is SO₄²⁻ and in 24% of the samples it is HCO₃⁻.

The Wilcox diagram of the Marvdasht wells is shown in Figure 4. No water sample falls into the C₁S₁ (very low EC and very low SAR) or 'Very good' class (Figure 3). As can be seen in Figure 4, 11 samples (22% of the groundwater samples) fall into the C₂-S₁ class. Forty-three per cent of the samples (21 samples) fall into the C₃-S₁ class, indicating high salinity and low sodium. Five samples (10% of the samples) lie in the C₄-S₁ and C₄-S₂ classes, which show very high salinity hazard and medium alkalinity hazard (Figure 4). Only 12 (24%) samples, including five samples in the C₄-S₃ and seven samples in the C₄-S₄ class, have a very high salinity and alkalinity hazard.

Figure 5 shows the relationship between TDS and some groundwater quality parameters in Marvdasht Aquifer. Magnesium has a strong linear relationship with TDS ($R^2 = 0.92$) (Figure 5(a)). The concentration of HCO₃⁻ is relatively constant with increasing TDS (Figure 5(b)), while Ca²⁺, Na⁺, Mg²⁺, Cl⁻ and SO₄²⁻ concentrations increase linearly with increasing TDS.

Ionic ratio

The ratio between cations and anions of the Marvdasht groundwater is given in Figure 6. As mentioned before,

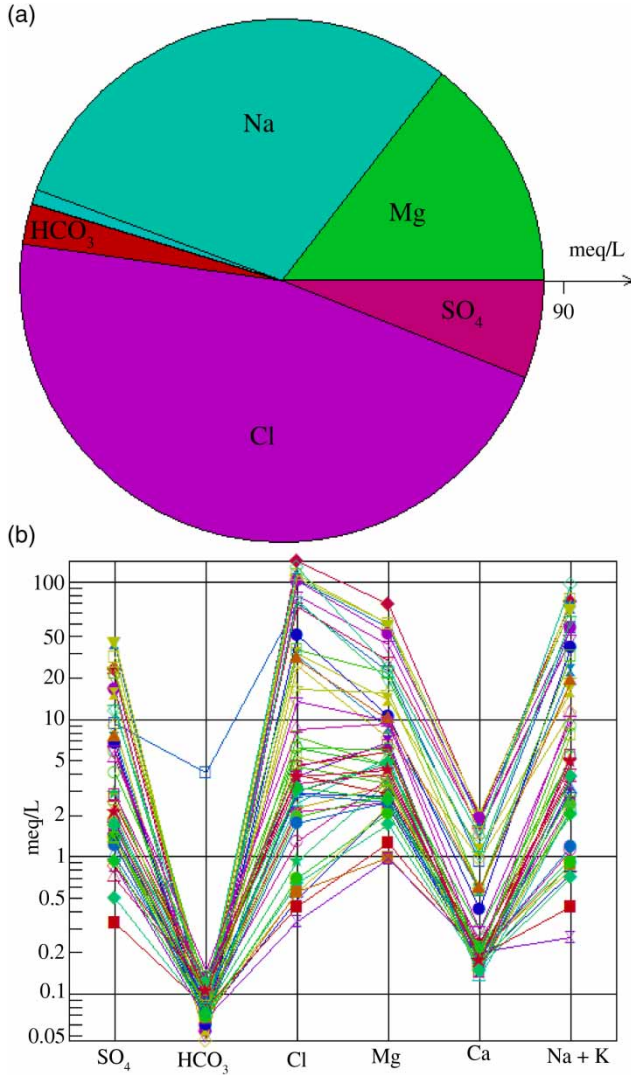


Figure 2 | Pie diagram (a) and Schoeller diagram (b).

Na^+ and Mg^{2+} are the dominant cations and Cl^- is the dominant anion in the Marvdasht groundwater.

Gibbs plot

Many factors such as rock weathering, soil type, and climate conditions such as precipitation, temperature and evaporation control groundwater chemistry, which can be related to the physical situation of the aquifer, bedrock mineralogy and weather conditions. Gibbs (1970) suggested TDS versus $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ for cations and TDS versus $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ for anions to illustrate the natural mechanism controlling groundwater chemistry, including

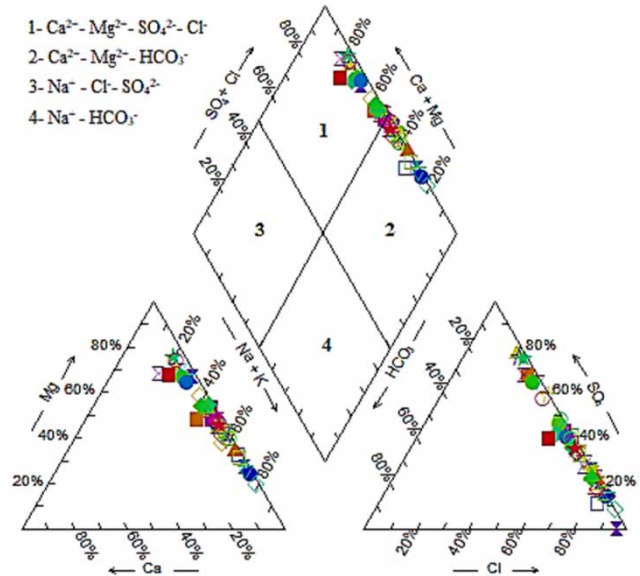


Figure 3 | Piper diagram of the Marvdasht groundwater.

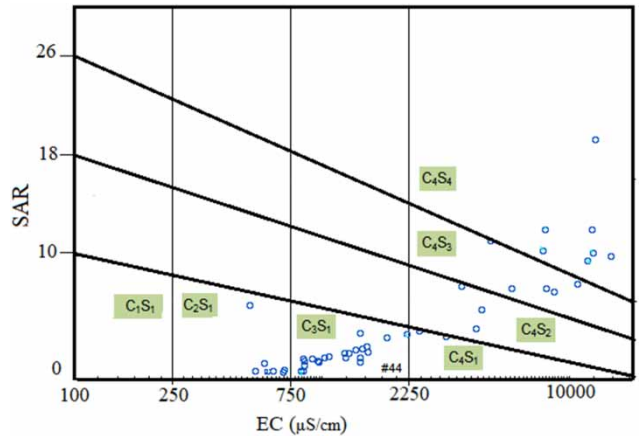


Figure 4 | Wilcox diagram (USSS classification) of the Marvdasht groundwater.

the rainfall dominance, rock weathering dominance, and evaporation plus participation dominance (Figure 7).

Spatial variability of groundwater parameters

The spatial distribution of groundwater quality parameters of the Marvdasht aquifer is illustrated in Figure 8. As can be clearly seen in Figure 8, due to the charge of the aquifer by the Kor River and existence of the Dorudzan Dam, the northern part of the aquifer has the best groundwater for drinking and irrigation purposes because all groundwater quality parameters are below the desirable values suggested

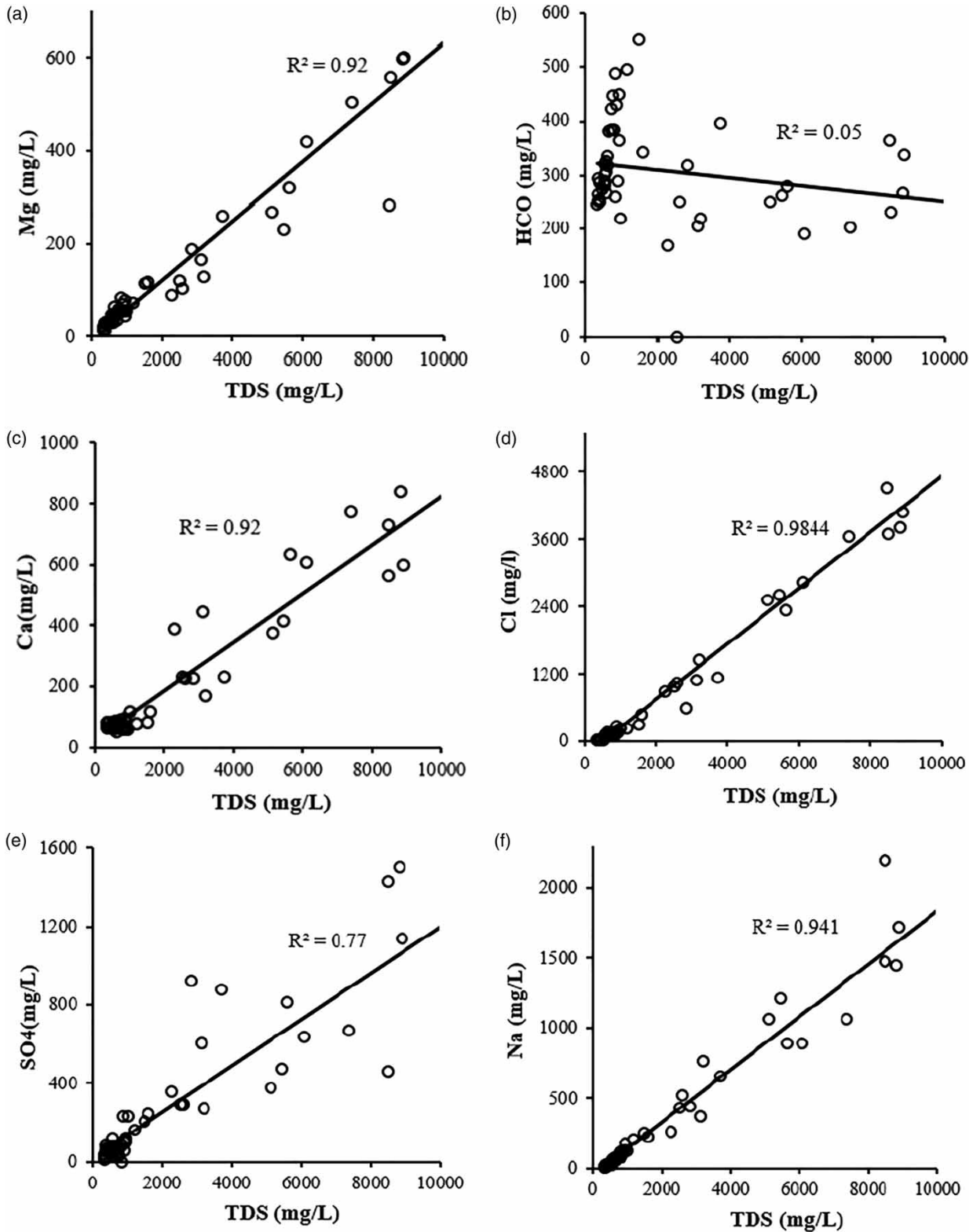


Figure 5 | Combined diagrams of various geochemical processes affecting TDS of Marvdasht groundwater.

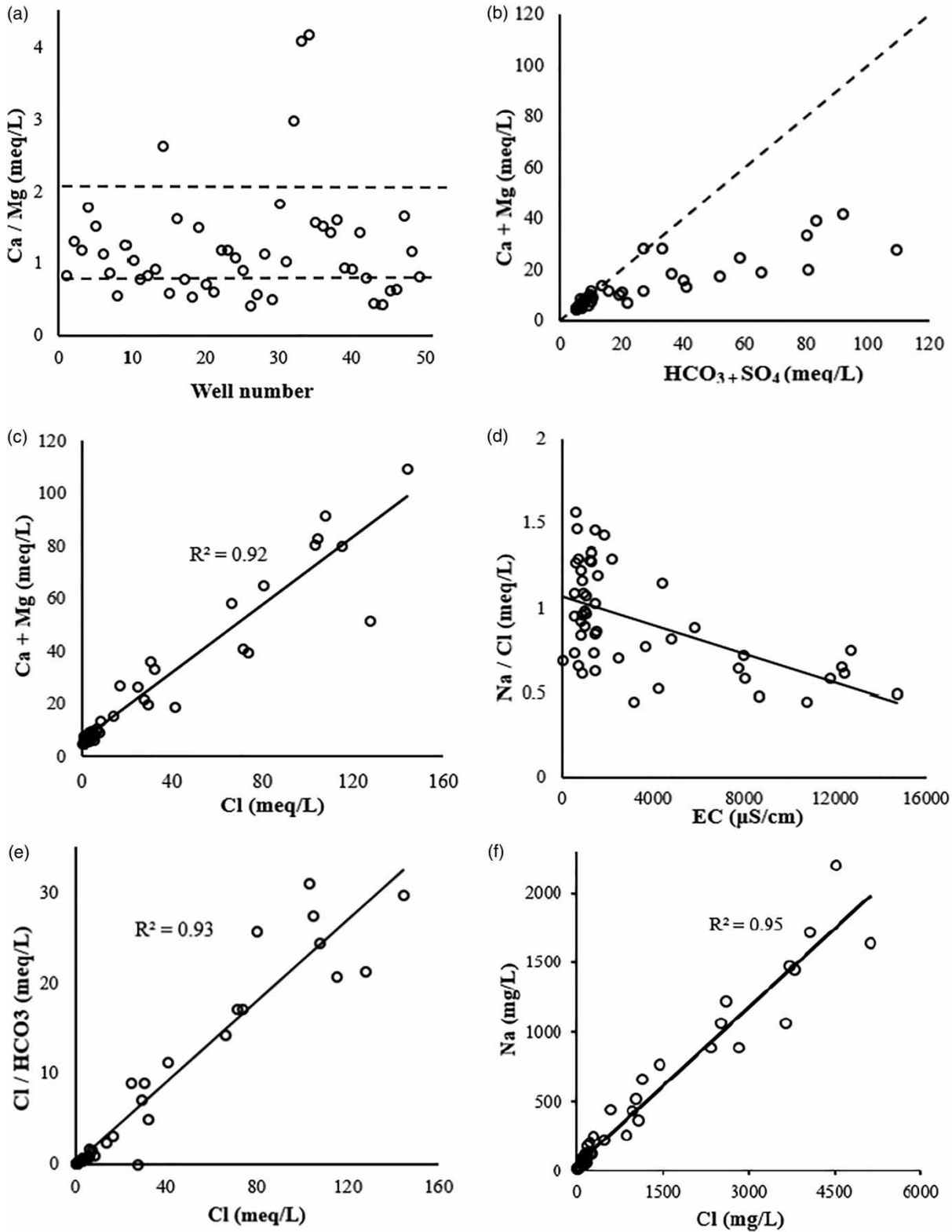


Figure 6 | Ionic ratio in Marvdasht groundwater.

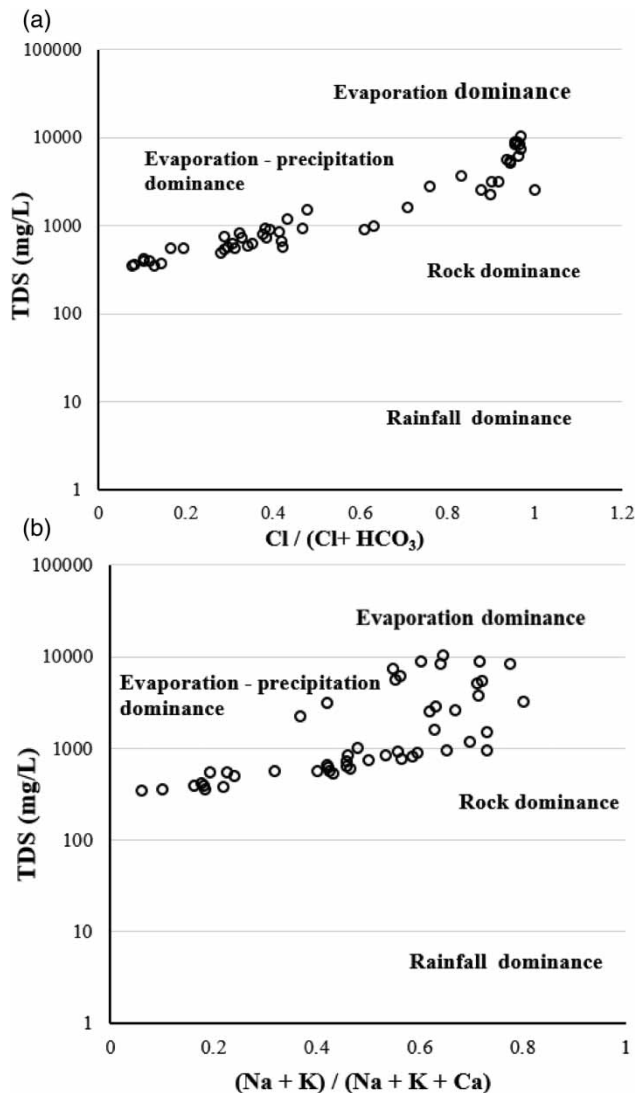


Figure 7 | Gibbs diagram of the Marvdasht aquifer.

by WHO (2011). Maps of Ca^{2+} , Mg^{2+} and TH are similar, and their values vary from north to south due to the existence of the soluble carbonate formations such as dolomite in the south of the study area.

DISCUSSION

Groundwater description

The results show that the groundwater of the study area is mainly alkaline. It was found that EC values in 57.1% of

samples were within the desirable limit (0–1,500 $\mu S/cm$). The results also showed that only 28.5% of the samples are below 600 mg/L of TDS, which are generally considered as desirable for drinking water without any risk (WHO 2011). The results also showed that the majority of the groundwater samples are below the allowable limit of TH (500 mg/L) for drinking water.

The pH has a negative significant correlation with all quality parameters except total alkalinity (TA), which is in agreement with the finding of Ramakrishnaiah *et al.* (2009), Jeihouni *et al.* (2014), Acharya *et al.* (2018) and Honarbakhsh *et al.* (2019). There is a significant correlation between Mg^{2+} with Cl^- ($r = 0.94$; $p < 0.05$) and Ca^{2+} ($r = 0.93$; $p < 0.05$). Mehrjerdi *et al.* (2008) and Kalantari *et al.* (2009) highlighted a relatively strong correlation between Mg^{2+} with Cl^- and Ca^{2+} . This correlation could be due to the existence of a sensitive formation with high amounts of calcite and dolomite (Zagros Streets Co 2009). In addition, Na^+ has a strong significant correlation with Cl^- ($r = 0.97$; $p < 0.05$) and Mg^{2+} ($r = 0.93$; $p < 0.05$). Ostovari *et al.* (2011) found a significant correlation between Ca^{2+} and Mg^{2+} in the Lordegan aquifer. Heshmati (2011) also showed a high correlation between Ca^{2+} and Mg^{2+} with Cl^- and SO_4^{2-} in the Shahrekord aquifer. Total alkalinity (TA) is well correlated with total hardness (TH) with a correlation of 0.85. Rafferty (2000), Mehrjerdi *et al.* (2008) and Ostovari *et al.* (2016) reported a significant correlation between TA and TH. High Ca^{2+} and Mg^{2+} concentrations may have originated from calcite and dolomite weathering or silicate rock dissolution. Ca^{2+} and Mg^{2+} constitute the possible sources of total hardness, common in the limestone aquifers.

Hydro-geochemical assessment

The type of water in the Marvdasht aquifer is Na-Cl, which could be supported by a mean TDS value of 2,400.7 mg/L and EC of 4,001.2 $\mu S/cm$. Ostovari *et al.* (2016) and Honarbakhsh *et al.* (2019) also reported that the type of groundwater in Marvdasht groundwater is Na-CL. Mg^{2+} is an important cation in this aquifer due to carbonate and marl formation that consists of large quantities of dolomite, which is in agreement with the findings of Honarbakhsh *et al.* (2019); however, Elubid *et al.* (2019)

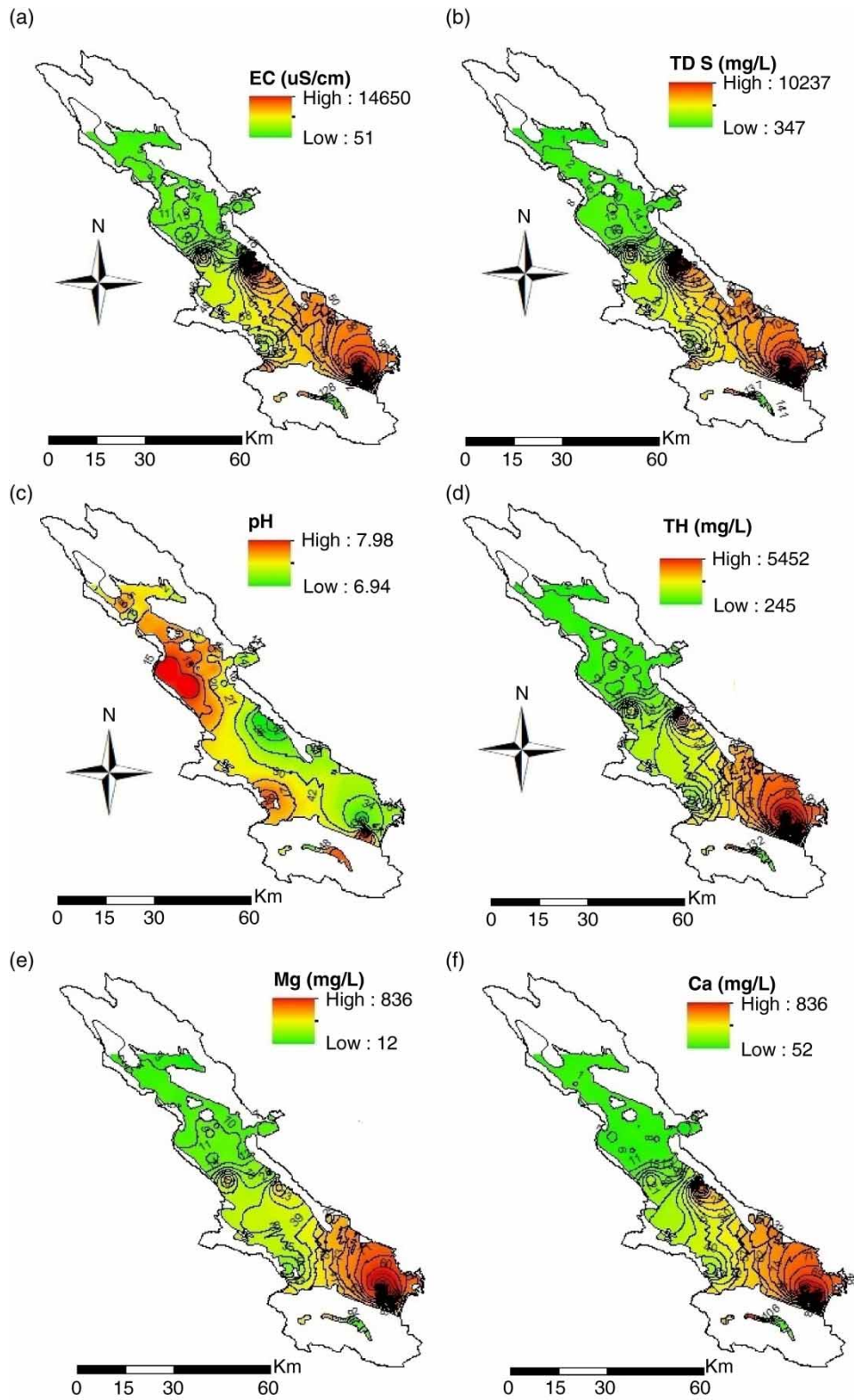
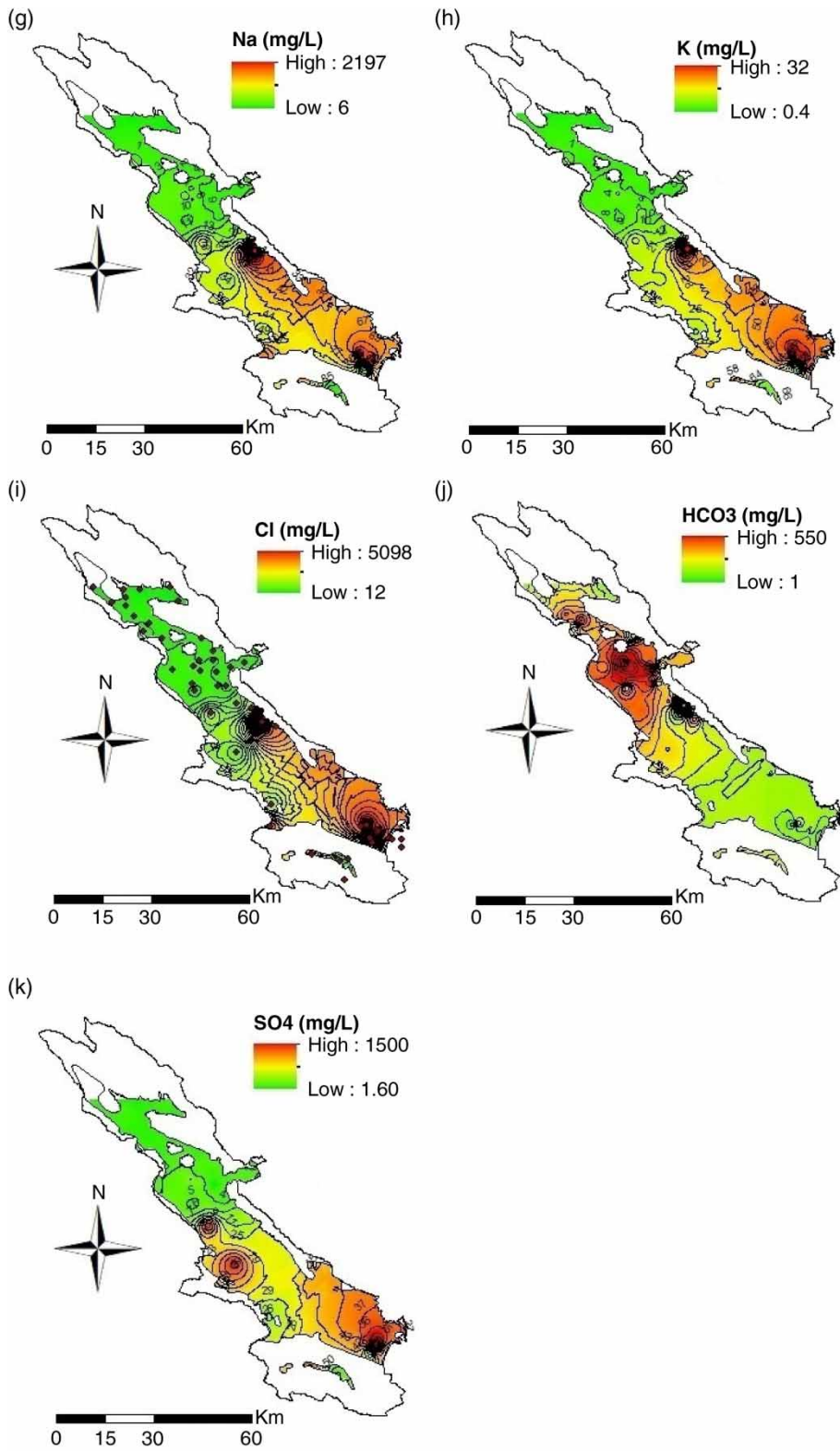


Figure 8 | Maps of Marvdasht groundwater quality parameters. (Continued.)

**Figure 8** | Continued.

reported that Na^+ is able to control the groundwater quality. Generally, the main type of water in this aquifer is Na-Cl. Charging the Marvdasht aquifer with the Kor River, which passes through the chalky-saline formation of Gachsaran, transports large amounts of urban sewage with high concentration of Cl^- . This could be a reason for the existence of Mg^{2+} in the Marvdasht aquifer (Ostovari *et al.* 2015, 2016). Heshmati (2011) showed that Mg^{2+} was the main cation on the Shahrekord groundwater.

The Wilcox diagram indicates that water samples generally have medium EC and low Na^+ that can be applied for irrigation purposes in all types of soil with no danger of exchangeable sodium. The $\text{C}_5\text{-S}_1$ class can be used for irrigation in all soil types without the need for concern for exchangeable sodium. Only plants that have good salt tolerance can be irrigated with this kind of water (Nag & Das 2014). The waters in $\text{C}_4\text{-S}_3$ and $\text{C}_4\text{-S}_4$ classes are not appropriate for irrigation; however, they could be used under very particular conditions such as providing considerable leaching and additional flocculating substances such as gypsum to soil (Acharya *et al.* 2018).

On one hand, with increasing TDS calcium increases linearly in the Marvdasht groundwater (Figure 5(c)). On the other hand, there is a strong linear relationship between SO_4^{2-} and TDS ($R^2 = 0.77$; Figure 5(e)), which indicates the process of dissolving gypsum in the aquifer. Because the ratio $\text{Mg}/\text{Ca} + \text{Mg}$ in most samples is less than 0.5, the origin of Mg^{2+} is due to the weathering of dolomite. Concentration of the Cl^- ion is linearly increased with increasing the TDS ($R^2 = 0.98$) (Figure 5(d)), which indicates possible origins for Cl^- such as the Kor River and salty and chalky formations. The concentration of Na^+ increases linearly ($R^2 = 0.94$) with increasing TDS (Figure 5(f)). As the ratio of $\text{HCO}_3^-/\text{total anions}$ is less than 0.8 in 20 samples and the content of SO_4^{2-} is high, the role of gypsum dissolution in the change of quality groundwater is confirmed (Hounslow 1995).

Ionic ratio

The high concentration of Na^+ and Cl^- in the groundwater could be related to the weathering of salt domes, the evapotranspiration process and river water intrusion. The abundance of Ca^{2+} and Mg^{2+} in the groundwater is attributed to the presence of carbonate formation. The

ratio $\text{Ca}^{2+}/\text{Mg}^{2+}$ can show the dissolution of calcite and dolomite in the groundwater. The ratio >2 may indicate the dissolution of silicate minerals into the groundwater, while the ratio between 1 and 2 represents a more dominant calcite contribution from the rocks. In 41% of the groundwater samples, the ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ is between 1 and 2, indicating the dominance of the calcite in the groundwater (Figure 6(a)). In 38% of the samples the ratio is >2 , which shows the effects of silicate mineral on the groundwater. Therefore, more than half of the samples have the ratio <1 , which indicates dolomite rock dissolution, resulting in domination of Mg^{2+} . Dissolution of carbonate formations is a simple and common weathering reaction in aquifers in semi-arid regions (Kalantari *et al.* 2009). This is clarified by the ratio $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ in the groundwater. The lower value of $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ is observed in about 5% of the samples, indicative of other sources of HCO_3^- in the study area such as silicate weathering. In around 18% of samples, the ratio of $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ is higher than 10 indicating the excess of Ca^{2+} and Mg^{2+} balanced by Cl^- and SO_4^{2-} , which is consistent with Kalantari *et al.* (2009). According to Figure 6(b), the distribution of the samples tends to the right (below the 1:1 line) which shows the excess of SO_4^{2-} plus HCO_3^- , which are derived from gypsum in line with Aghazadeh & Asghari-Mogaddam (2010).

The scatter plot of Na^+/Cl^- versus EC explicitly indicates that the salinity increases with decreasing the ratio of Na^+/Cl^- . The scatter plot of Ca^{2+} plus Mg^{2+} versus Cl^- (Figure 6(c)) shows the reversion of ion exchange in the clay/weathered layer. There is a strong positive relationship between $\text{Cl}^-/\text{HCO}_3^-$ and Cl^- ($R^2 = 0.93$, $p < 0.01$). The $\text{Cl}^-/\text{HCO}_3^-$ ratio indicates the impact of salinization because of the river water mixing with the groundwater. About 36% of the groundwater samples have a ratio of $\text{Cl}^-/\text{HCO}_3^-$ lower than 0.5, which means the groundwater is fresh water. The ratio of Na^+/Cl^- is used to determine the process that controls the salinity and saline intrusion in arid and semiarid regions (Kalantari *et al.* 2009). The average molar ratio of Na^+/Cl^- is 0.92, which indicates lower Na^+ values than Cl^- values (Figure 5(f)). A new number of samples having the Na^+/Cl^- ratio equal to or greater than 1 may represent Na released due to the silicate weathering process. Silicate weathering is the reaction of the feldspar minerals with the carbonate acid in the water, which is specified by

bicarbonate as a dominant anion in the groundwater. Eight percent of the samples have the ratio of Na^+/Cl^- equal to 1, which indicates that halite dissolution could be a cause of Na^+ concentration in the water samples.

Gibbs plot

Only 34% of the samples (17 samples) fall into the evaporation-precipitation dominance and 66% of the samples (32 samples) fall into the rock dominance. It seems that the ion chemistry is related to the carbonate and silicate weathering process on the south of the study site.

Spatial variability of groundwater parameters

High groundwater quality in the northern part of the study site could be due to: (i) the greater capacity of the vadose zone to attenuate contaminant percolation in this area; (ii) recharging of this area with the seepage from the Droudzan dam, which leads to higher quality groundwater. The quality of groundwater decreases from the central to the southern regions of the aquifer. At the southern regions, groundwater quality is influenced by recharging with saline water coming from the Kor River and urban wastewater of Marvdasht city. Ostovari *et al.* (2015) reported that the southern parts of the Marvdasht groundwater, with high levels of EC and sodium absorption ratio (SAR), were unsuitable for irrigation. Furthermore, in this part of the aquifer, dissolution of saline and chalky formations has increased salinity, TDS and TH levels. In addition, in the semi-arid regions, groundwater salinity may also be attributed to the formation of salt layers by leaching from the soil surface due to high evaporation during the dry seasons. In less than 20% of the study site located in the northern part of the area, values of EC and TDS are less than $750 \mu\text{S}/\text{cm}$ and $500 \text{ mg}/\text{L}$, respectively, which are suitable for drinking. In the remaining area of the study site (from center to south), the groundwater is unsuitable for drinking (Figure 8(a) and 8(b)).

CONCLUSIONS

The present study was carried out to evaluate the hydrochemical analysis of the Marvdasht, which is the main

resource of water supply for drinking and irrigating purposes located in the semi-arid region of Iran, and map the groundwater quality parameters. Pie and Schoeller diagrams showed that Cl^- and Na^+ were the dominant anion and cation, respectively, and generally, the type of water was Na-Cl. Mg^{2+} is the second most important anion in the study site due to weathering of carbonate components, especially dolomite in the aquifer. Gibbs diagrams showed that in 66% of the samples rock (geological formation) is the main process of water chemistry involved in controlling the groundwater quality. The Wilcox diagram shows that only 12 (24%) samples, including five samples in $\text{C}_4\text{-S}_3$ and seven samples in $\text{C}_4\text{-S}_4$ class, have very high salinity and alkalinity hazard. The maps of groundwater quality parameters show that north of the Marvdasht aquifer has better groundwater quality than that of the central and southern areas. In the southern aquifer, there are two soluble formations including dolomite and gypsum that lead to decreasing water quality. We suggest planting crops that are resistant to high salinity in the south of the study site where groundwater has a high amount of salinity and sodium ($\text{C}_4\text{-S}_4$ and $\text{C}_4\text{-S}_3$ classes). In addition, we highly recommend using a water purifier for potable water in southern areas.

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