



## Research Article

# Groundwater quality evaluation of Shiraz City, Iran using multivariate and geostatistical techniques



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## Abstract

Groundwater is vital water resource for domestic, agricultural and industrial purposes in Shiraz City, Iran. Management of groundwater with respect to quality and quantity is decisive subject in order to accomplish the increasing requirements for water. In the present paper, evaluation of groundwater parameters, viz., pH, electrical conductivity (EC), major cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ), major anions ( $Cl^-$  and  $HCO_3^-$ ),  $NO_3^-$ ,  $SO_4^{2-}$ , total dissolved solids (TDS), alkalinity, hardness, sodium absorption ratio (SAR) and Na% were done from Shiraz City, Iran. Consequently, 80 groundwater samples were collected from different sites in June 2017. The results of different parameters were compared with the standard guideline prescribed by the World Health Organization (WHO) for drinking and public health purposes. From the results, it was concluded that 62.5% samples exceeded for EC values, 12.5% samples for  $Na^+$ , 30% samples for  $Ca^{2+}$ , 97.5% samples for  $Mg^{2+}$  and TDS, 28.7% samples for  $Cl^-$ , and 40% samples for  $SO_4^{2-}$  contents as recommended by WHO. The Na% values ranged from 5.25 to 38.59, whereas SAR values varied from 0.21 to 6.64 meq/L. Results of Na% and SAR indicated that groundwater is good for irrigation and domestic purposes. The results of MGI and BEI showed that 83.75% sampling sites showed shallow meteoric percolation type and  $Na + SO_4$  type with less than one value respectively. Multivariate statistical analysis (cluster analysis and principal component analysis) and spatial maps showed that both anthropogenic activities such as cement factory, gas power plant, Rishmark factory and vegetable Oil Company, and natural processes like rock weathering are responsible for the contents of groundwater parameters.

**Keywords** Groundwater · SAR · Multivariate techniques · NMDS · Geostatistical analysis

## 1 Introduction

The good quality of drinking water is far behind for utmost populations throughout the world [1]. This is due to the reason that resources are contaminated at incessant rate due to unorganized industrialization and urbanization [2]. Presently, water quality is of key issue, because it is the source of poor health in major countries of the world [3, 4]. The countries which are growing, inappropriate access to clean drinking water is harmfully influencing the human health [5]. Population explosion and growing living standards are enhancing the requirement of water in urban areas and this requirement has put enormous pressure

on the inadequate water resources [6]. The over utilization of groundwater associated with nominal renew leads to groundwater degradation and scarcity [7].

European Environment Agency framed policies regarding management of groundwater and to recognize point source pollutants as the primary initiative for the remediation. However, in many urbanized regions, pollutant plumes formed by single point sources commonly synchronize with prevalent pollution originated from diverse point sources [8]. The proper attention should be given to prevent and control the groundwater contamination in order to avoid expensive remediation, because groundwater contamination is invisible, complex and has prolonged

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effects. To assess the probable effects of any contaminant in the groundwater pollution is an efficient strategy for management of groundwater [9, 10].

Aquifer systems are affected by the spatial and temporal alterations of natural as well as human activities. The associations and spatial variability of these aspects, limits and hierarchy of their associations between the constituents, statistically elucidated [11–13]. Geostatistics is important for spatial mapping of groundwater parameters, variograms are employed to determine spatial relationship, and the kriging variance is a role of geometric pattern. The kriging determination variances are independent and are associated to model variogram and the spatial organization of the sampling statistics. Kriging interpolation is applied to give the good variable nearness value of an approximate in association to the real value employing least square approach [14, 15]. Multivariate techniques have been used to find the information from the large data and such techniques applied in exploratory data assessment as approaches to categorize samples and recognize pollution sources [16, 17]. Cluster analysis and principal component analysis techniques helps in interpretation of enormous parameters to accomplish a great understanding of the hydrochemical mechanisms engaged [18, 19]. To improve organization of water resources on a local level, the objective of this research is to recognize and assess the interfering natural and human factors concerning with groundwater hydrochemistry in an urban area. Because of the multifaceted interactions between human and geogenic features influencing groundwater hydrochemistry, this study is distinctive in its application of integrated techniques hydrochemical exploration, geostatistics, and multivariate techniques in urban areas. To protect and maintain the speedily diminishing groundwater resources in urban regions, sophisticated evaluation methods are required to better recognize the relationships among land-use and natural and, human causes of pollution.

## 2 Materials and methods

### 2.1 Study area

The present study was accomplished in Shiraz megacity, 5th populated city of Iran with 223.4 km<sup>2</sup> area positioned at 29°37'8"N lat. and 52°31'14"E longitude (Fig. 1). About 1500 m is the surface elevation of this city from the sea level. The main direction of the Shiraz aquifer is from northwest to south east. The 1009 km<sup>2</sup> Shiraz basin partly comprises of the watershed of the Khoshk seasonal river, which runs to Maharloo salt lake located to the south of the city. The hydraulic gradient of the eastern part is less than that of central and western parts. According to the

Iran Meteorological Organization (IRIMO) reports, the annual mean temperature and precipitation are 18.7 °C and 324.2 mm respectively. The climatic condition in the surrounding study area is semi-arid. Approximate half of the water used for domestic and industrial purposes is supplied from deep and semi-deep wells dispersed in the area. Due to improper sewage system in the city, about 80–85% of the municipal water used, i.e., 250 L per cap. per day moves into the groundwater, mainly goes to Maharloo Salt Lake [20]. The area is waterlogged during wet years when the level of Khoshk River is high.

### 2.2 Hydrological settings and aquifer formation

The geophysical investigations in the Shiraz have established that Shiraz water bearing layer in more depths, it suffers from unsuitable quality. Studies showed that groundwater of Shiraz comprises of surface unconstrained aquifer and a deep aquifer [20]. Two seasonal rivers Khoshkrud and Chenarrahdar occurred in Shiraz area. The seasonal Khoshkrud River enters in Golestan and Ghalat mountains heights after connecting with Khoshk River, it arrives in the Shiraz city. Agricultural runoff and industrial wastewater arrives into the river at the south eastern part of Shiraz. The geological information showed that the development that takes place in the area are from old to new such as Formation of Tarbor takes place during Campanian to Maastrichtian, Pabdeh–Gurpi developments occurred in Paleocene, formation of Sachun takes place in Paleocene, Jahrom formation occurred in Eocene, Asmari establishments takes place in Oligocene, Razak formation during Miocene, Agha Jari development occurred in Miocene to Pliocene, formation of Bakhtyari made in Pliocene to Pleistocen, and quarternary alluvial deposits [21].

Shiraz alluvial aquifer is formed during the Quaternary alluvium that comprises of grain sediments and moderate to fine grained clay particles carried by stream and flood wash of catchment geological units. The northern side comprises of coarse alluvium. Oligo-miocene carbonate formed from the Asmari-Jahrom, Miocene marl formed from Razak and Plio-Pleistocene conglomerate developed from the Bakhtyari form the catchment geological settings in Shiraz [22]. In addition to Shiraz alluvial aquifer, many karstic anticlines adjoining the Shiraz also provides drinking water to the peoples of city. The northern karstic aquifer is linked with the alluvial aquifer. Comprehensive pumping in the northern karstic aquifer has reversed the ground water flow route, taking place in alluvial aquifer water arriving the karstic aquifer [22].

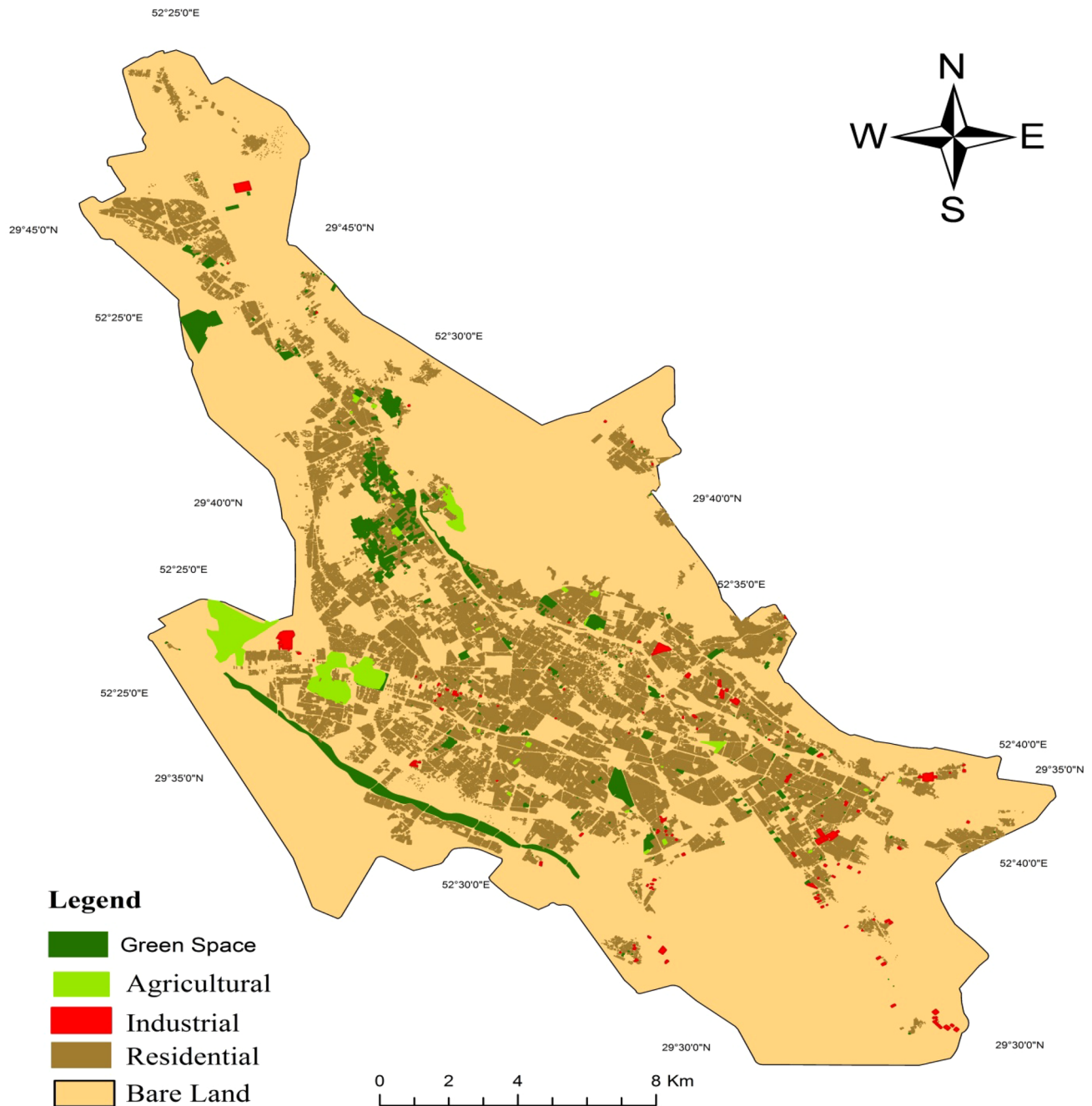


Fig. 1 Study area and location of sampling sites

### 2.3 Sampling and analysis

For the assessment of groundwater quality, samples were collected from 80 sites from the deep wells distributed throughout the area. Geographic coordinates of each sampling site was noted using geographic positioning system apparatus. All the samples were filtered and stored in 250-mL polypropylene bottles cleaned with water samples and kept at temperatures below 4 °C to avoid unforeseeable

variations in chemical constitution [23]. pH was determined by using pH meter (Metrohm 827). EC and TDS were measured by using EC meter (Hanna EC214).  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  content were measured in the groundwater by using HACH DR 5000 UV-Vis spectrophotometer.  $\text{Na}^+$  and  $\text{K}^+$  were determined by using flame photometer (Feter Electronic 405).  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  were measured by EDTA titration method.  $\text{Cl}^-$  was measured in the groundwater samples base on ASTM [24] method. Alkalinity

was measured in the samples by using ETDA titration. Total hardness (TH) was calculated by  $TH (mg/L) = 2.497 Ca + 4.115 Mg$  [25].

### 2.4 Spatial maps

Spatial distribution maps for all the groundwater parameters were made in ArcGis software v. 10 using kriging approach.

### 2.5 Statistical analysis

The results were statistically analyzed by using descriptive statistics in PAST software v. 3.15. The data was also analyzed by using various multivariate techniques such as Pearson’s correlation analysis R programming software v. 3.1.3, Cluster analysis (CA) and principal component analysis (PCA) by SPSS software v. 16 and non-metric multidimensional scaling (NMDS) by PAST software v. 3.15. CA is mainly applied in hydrology with the objective to find out relationship among the variables [26, 27]. In present work, we conducted a hierarchical CA following Ward’s method and Euclidean distance [28, 29]. Ward’s method indicates that proximity between two clusters is the enhancement in squared error. The outcomes are shown in the form of dendrograms [30]. PCA is conducted to decrease the data and determine the common arrangements within a large data [31]. In hydrology, PCA is mainly applied in hydrochemical and hydrogeological works [32]. It permits

decreasing the dimensions of data with a great number of correlated variables. The decrease is made by converting original data into a new set of data called principal components. The data was rotated by varimax rotation to enhance the precision of results [33].

## 3 Results and discussion

The physiochemical characteristics and statistical analysis for all the 80 groundwater samples were determined. Table 1 presents the mean, minimum, maximum, standard deviation, skewness, kurtosis and coefficient of variation for the groundwater samples. The pH of the groundwater samples ranged from 6.8 to 8.31, indicating acidic to slightly alkaline nature of water. The pH values of present study were found within the range of world health organization [34] for drinking and public health purposes. The electrical conductivity varied from 518 ( $\mu S/cm$ ) to 12160 ( $\mu S/cm$ ) with average value of 1877.74 ( $\mu S/cm$ ) for the present study. The maximum permissible limit of EC prescribed by WHO [34] is 1500 ( $\mu S/cm$ ). About 62.5% samples exceeded WHO [34] limit for drinking water. The higher EC values indicate enrichment of salts in the groundwater [35]. The  $K^+$  content ranged from 39 to 2952.3 mg/L with mean value of 246.14 mg/L. All the samples for  $K^+$ , exceeded the value of WHO [34] for drinking water, i.e., 12 mg/L. The  $Na^+$  varied from 8.28 to 963.7 mg/L with average value of 113.6 mg/L. About 12.5% samples exceeded the WHO [34] limit for drinking water. The maximum

**Table 1** Descriptive statistics of groundwater parameters from Shiraz

	Min	Max	Mean	SE	SD	Skewness	Kurtosis	C.V.	WHO (2011)
pH	6.8	8.31	7.17	0.03	0.24	1.66	5.63	3.30	6.5–8.5
EC ( $\mu S/cm$ )	518	12,160	1877.74	148.98	1332.56	6.03	45.55	70.97	1500
$K^+$ (mg/L)	39	2952.3	246.14	37.54	335.76	6.91	54.80	136.41	12
$Na^+$ (mg/L)	8.28	963.7	113.60	12.91	115.45	5.24	37.26	101.63	200
$Ca^{2+}$ (mg/L)	36.8	134	63.13	1.96	17.57	0.90	1.71	27.82	75
$Mg^{2+}$ (mg/L)	33.6	874.8	125.69	10.67	95.41	6.36	49.07	75.91	50
$HCO_3^-$ (mg/L)	146.4	463.6	358.07	7.33	65.57	-0.82	0.23	18.31	500
$Cl^-$ (mg/L)	28.4	2272	246.64	32.43	290.04	4.91	30.87	117.60	250
$SO_4^{2-}$ (mg/L)	4.8	2457.6	280.56	37.48	335.19	4.08	22.91	119.47	250
$NO_3^-$ (mg/L)	0.16	8.96	4.31	0.29	2.59	-0.72	-0.92	60.12	45
Alkalinity (mg/L)	144	456	352.20	7.21	64.50	-0.82	0.23	18.31	600
Hardness (mg/L)	230	3980	681.69	47.58	425.56	6.13	46.50	62.43	600
TDS (mg/L)	331.52	7782.4	1201.75	95.35	852.84	6.03	45.55	70.97	500
Na (%)	5.25	38.59	24.05	0.93	8.29	-0.04	-0.50	34.45	-
SAR meq/L	0.21	6.64	1.76	0.12	1.04	1.56	4.78	58.82	-



allowable limit prescribed by WHO [34] is 200 mg/L. High EC contributes to saline soil formation, while high  $\text{Na}^+$  concentration forms alkaline soil [36].  $\text{Ca}^{2+}$  ranged from 36.8 to 134 mg/L with average value of 63.13 mg/L. The limit prescribed by WHO [34] for drinking water are 75 mg/L. 30% samples exceeded the WHO limit for  $\text{Ca}^{2+}$  in the present study.  $\text{Mg}^{2+}$  varies from 33.6 to 874.8 mg/L, and about 97.5% samples exceeded the limit of WHO [34] for drinking water.  $\text{HCO}_3^-$  content ranged from 146.4 to 463.6 mg/L with average value of 358.07 mg/L. For all the sampling sites,  $\text{HCO}_3^-$  content was found lower than the WHO [34] for drinking water, i.e., 500 mg/L.  $\text{Cl}^-$  content varied from 28.4 to 2272 mg/L with average value of 246.6 mg/L. The maximum allowable limit for  $\text{Cl}^-$  is 250 mg/L as recommended by WHO [34] and about 28.7% samples exceeded the WHO [34] limit.  $\text{SO}_4^{2-}$  content ranged from 4.8 to 2457.6 mg/L with mean value of 280.56 mg/L. The limit prescribed by WHO [34] for  $\text{SO}_4^{2-}$  is 250 mg/L and about 40% samples exceeded this limit for  $\text{SO}_4^{2-}$  content.  $\text{NO}_3^-$  content varied from 0.16 to 8.96 mg/L with average value of 4.31 mg/L. The limit recommended by WHO [34] for  $\text{NO}_3^-$  is 45 mg/L, and all samples were found below this limit for  $\text{NO}_3^-$  content. TDS content ranged from 331.5 to 7782.4 mg/L with average value of 1201.7 mg/L. The limit prescribed by WHO [34] for TDS is 500 mg/L, and 97.5% samples exceeded this limit for TDS. The hardness values varied from 230 to 3980 mg/L with average value of 681.69 mg/L. The level of hardness is categorized as: 0–75 soft, 75–150 moderately hard, 150–300 hard, and > 300 very hard [37]. 97.5% samples showed that hardness content is very hard for the present study. The alkalinity values ranged from 144 to 456 mg/L with mean value of 352.2 mg/L. The alkalinity values were found lower than the maximum limits recommended by WHO [34] for drinking water such as 600 mg/L. The skewness and kurtosis of pH, EC,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , hardness and TDS were found greater than one representing right handed skewness and leptokurtic [38].  $\text{K}^+$  followed by  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  showed greatest variation in the groundwater samples of the present study. Figure 2 presents the spatial distribution of pH, EC,  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3$ , alkalinity, hardness and TDS for the present study on the basis of kriging method. From the spatial maps, it was predicated that both anthropogenic activities like cement factory, gas power plant, Rishmark factory and vegetable Oil Company, and natural processes like rock weathering are responsible for the contents of groundwater parameters.

Pearson's correlation analysis was applied to groundwater parameters to find relationship among different

parameters (Fig. 3). They presented efficient method to indicate the associations between diverse variables and consequently useful in understanding the contributing aspects and sources of chemical constituents. pH showed correlation with  $\text{HCO}_3$  and alkalinity. Correlation of  $\text{NO}_3$  found with Ca. The correlation of EC existed with K, Na, Ca, Mg, Cl,  $\text{SO}_4$ , Hardness, TDS and SAR. The K, Na, Ca and Mg showed correlation with Cl,  $\text{SO}_4$ , hardness, TDS and SAR. Cl,  $\text{SO}_4$ , hardness, TDS and SAR showed correlation with each other. The correlation of EC and TDS is attributed by the fact that dissolved constituents cause enhanced ionic content and EC content [39]. The correlations results of different ions showed that these ions involve diverse physical as well as chemical processes such as oxidation/reduction reactions as well as ion exchange in groundwater aquifers, indicating that similar factor have strong influence on them [40, 41]. The correlation of Cl and  $\text{SO}_4$  usually used to recognize the processes of salinity in arid and semiarid places [42].

### 3.1 Sodium (Na)% and Sodium absorption ratio (SAR)

Na% is a widespread index calculated to evaluate the acceptability of groundwater. Na concentration in groundwater is exchanged with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  of clay particles of the soil, which leads to decrease of soil permeability, internal drainage and air circulation. % Na is computed by following Wilcox [43]:

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

Higher percentage of Na in groundwater decreases the permeability of the soil. The Na% varies from 5.25 to 38.59 with average value of 24.05. The 31.2% samples showed < 20 Na%, indicating excellent for irrigation and agricultural practices, and 68.7% samples were fall in the category of 30–40 Na%, indicating good category of groundwater and suitable for irrigation and agricultural practices. Figure 2 presents the spatial distribution of % Na for the present study on the basis of kriging approach.

SAR is vital parameter to evaluate the groundwater quality. It represents the impact of relative cation content on  $\text{Na}^{2+}$  accumulation in the soil, is applied to assess the Sodidity risk of water. Soil permeability reduces with the enhancement in  $\text{Na}^{2+}$  in relation to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations. It is computed by following Hem [44]:

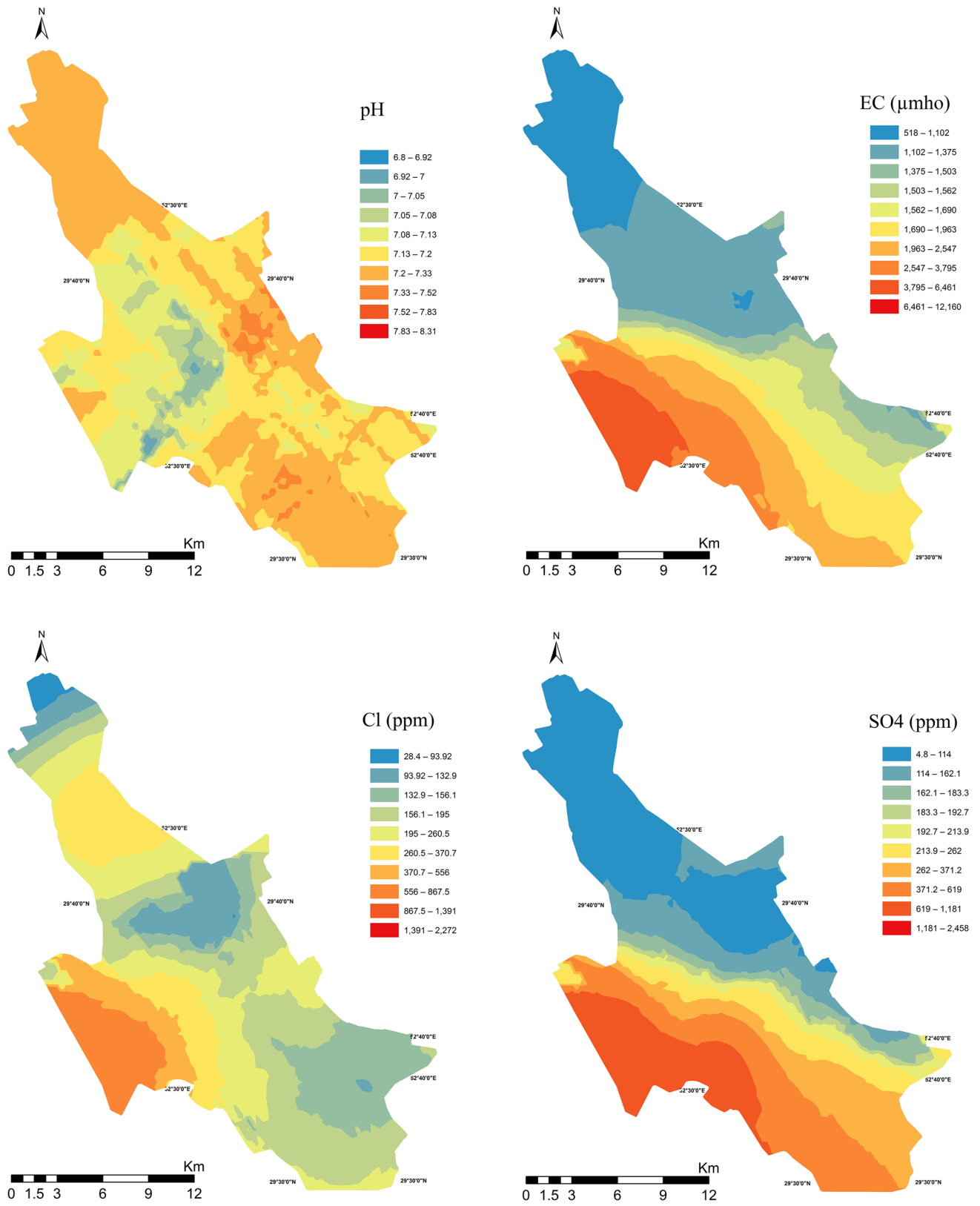


Fig. 2 Spatial distribution of groundwater parameters (pH, EC, Cl, SO<sub>4</sub>, NO<sub>3</sub>, alkalinity, hardness, TDS, Na% and SAR)

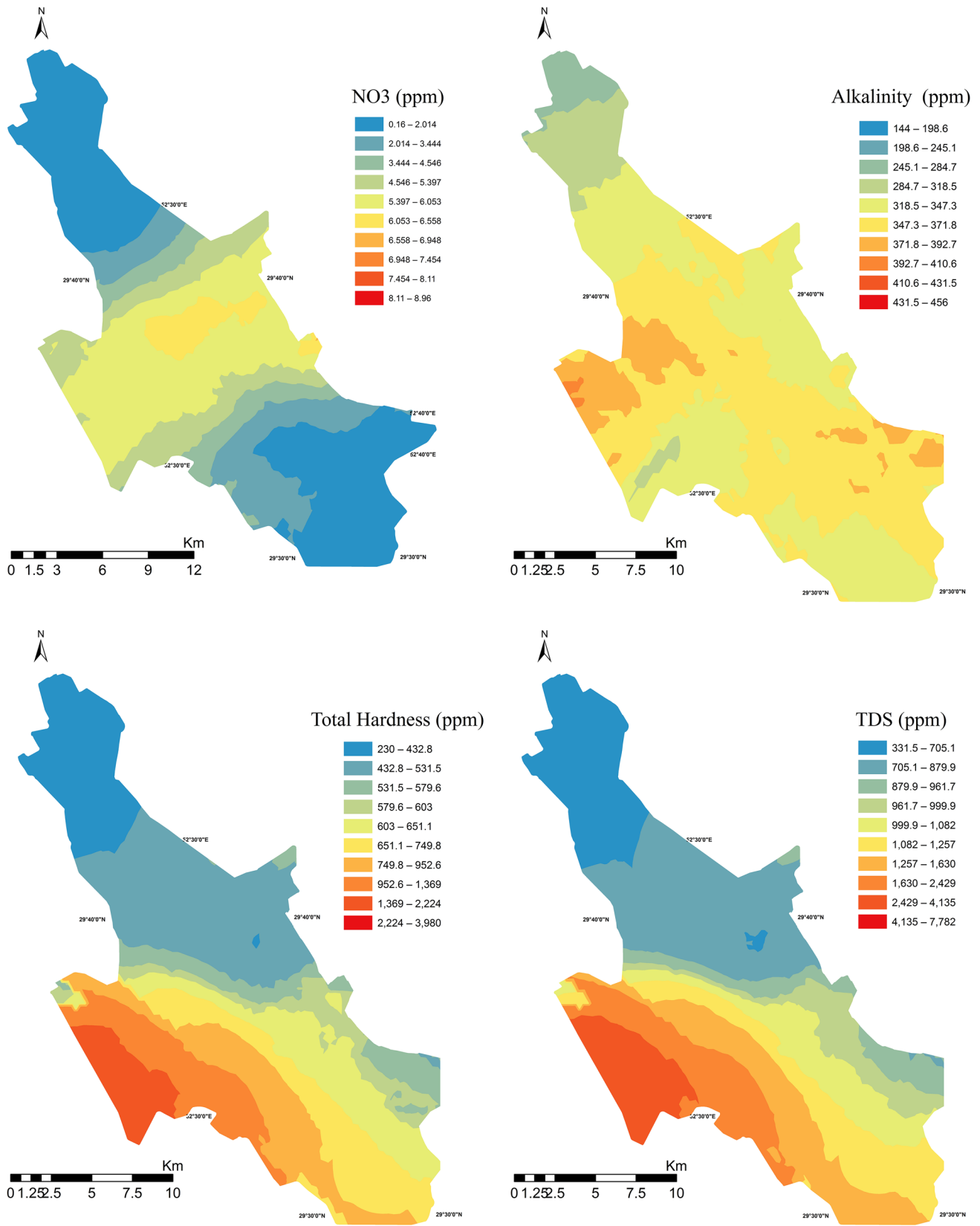


Fig. 2 (continued)

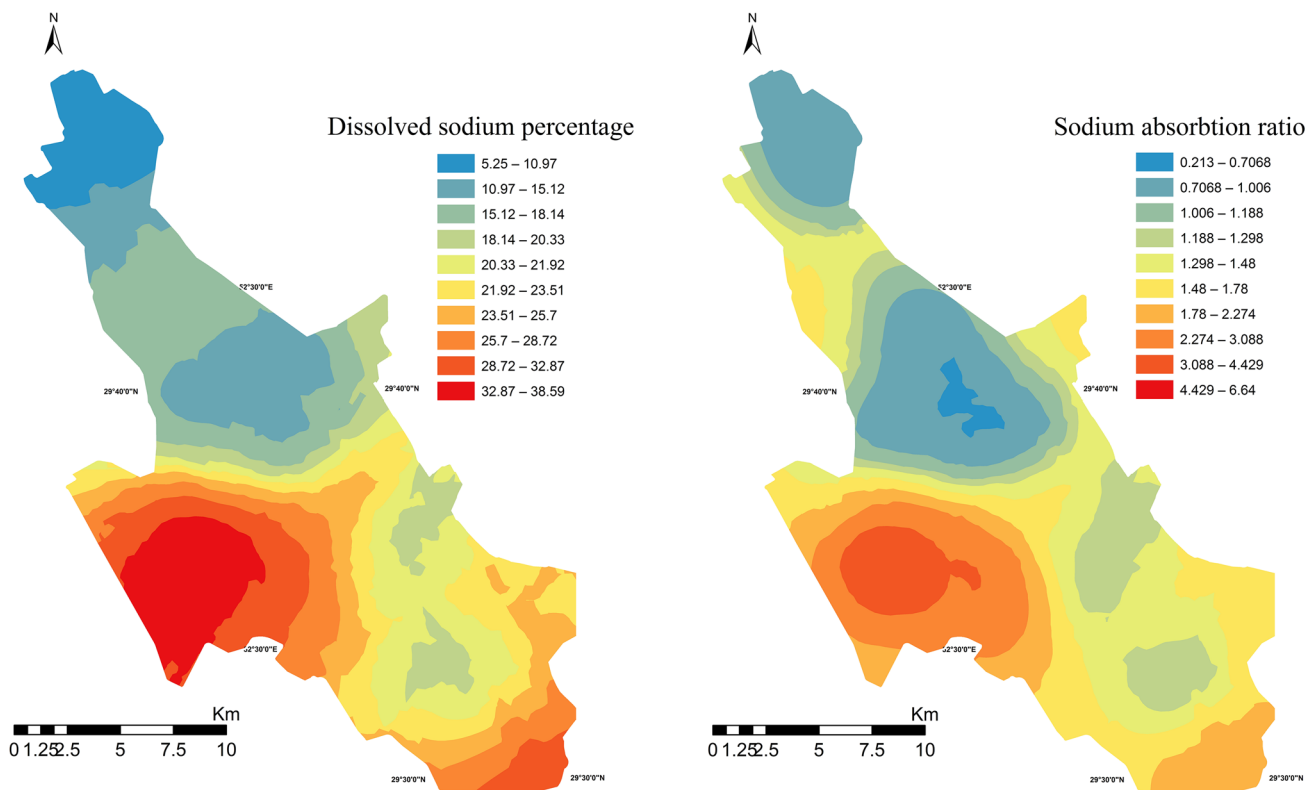


Fig. 2 (continued)

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

SAR levels were presented in meq/L and varied from 0.21 to 6.64 with mean value of 1.76. SAR values were found below < 10, belongs to excellent category. Richards [45] suggested following grades to classify the SAR: < 10: excellent, 10–18: good, 18–26: doubtful and > 26: unsuitable. The skewness and kurtosis of SAR values were also recorded greater than one indicating right handed skewness and leptokurtic [38]. SAR values for all the samples were excellent for irrigation and agricultural practices. Figure 2 presents the spatial distribution of SAR values for the present study on the basis of kriging approach.

### 3.2 Base-exchange indices (BEI) and meteoric genesis indices (MGI)

The BEI and MGI were determined by following Matthes [46], Soltan [47, 48] and are calculated by following equations:

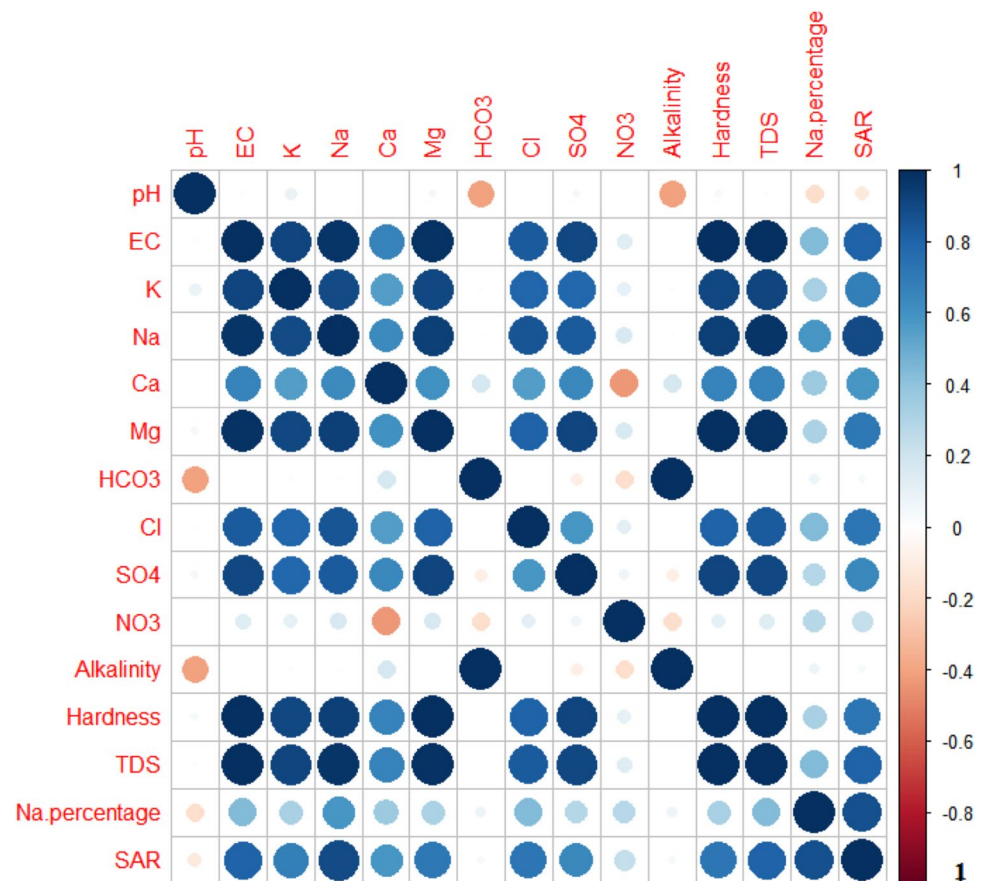
$$BEI = \frac{Na^+ - Cl^-}{SO_4^{2-}}$$

$$MGI = \frac{[(Na^+ + K^+) - Cl^-]}{SO_4^{2-}}$$

On the basis of these indices, groundwater is grouped as:  $Na^+ - HCO_3^-$  type if  $BEI > 1$  and  $Na^+ - SO_4^{2-}$  type if  $BEI < 1$ .



**Fig. 3** Pearson's correlation analysis of groundwater parameters



If  $MGI < 1$ , then water type is of deep meteoric type and if  $MGI > 1$ , then it is of shallow meteoric percolation type. The results of BEI and MGI are presented in Table 2. From the results of MGI, it was found that 83.75% sampling sites showed shallow meteoric percolation type, while 16.25% sampling sites indicated deep meteoric percolation type. 83.75% sampling sites showed BEI values less than one and indicated  $Na + SO_4$ , while 16.25% sampling sites showed  $Na + HCO_3$  water type.

### 3.3 Multivariate statistical analysis of groundwater parameters

Cluster analysis (CA) was prepared to classify the different parameters (Fig. 4). CA mainly categorized the groundwater parameters into two groups such as alkalinity and  $HCO_3^-$  in one group and rest of the parameters are

included in other cluster which is further grouped into two subgroups: subgroup I ( $NO_3^-$ , pH, Na% and SAR) and subgroup II (EC, TDS,  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$ ,  $Cl^-$ , hardness and K).

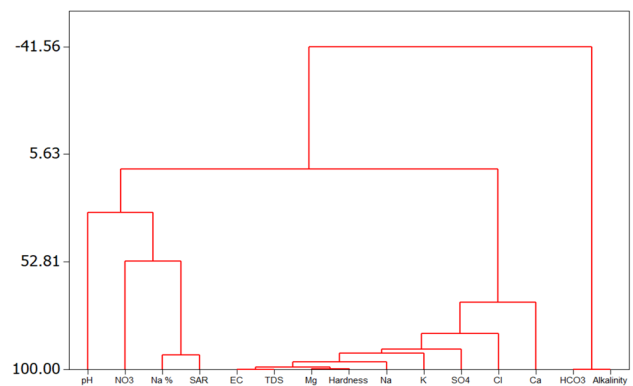
CA was also prepared for different sampling sites on the basis of groundwater parameters (Fig. 5). Mainly three clusters were formed for sampling sites which are further categorized into subgroups. Cluster 1 comprises of sites (1, 24, 13, 2, 8, 5, 45, 53, 74, 78, 6, 19, 77, 60, 76, 11, 14, 25, 9, 18, 17, 20, 10, 23, 26, 15, 16 and 21) which is categorized in four sub-clusters (1, 24, 13, 2 and 8), (5, 45, 53, 74 and 78), (6, 19, 77, 60, 76, 11, 14 and 25), and (9, 18, 17, 20, 10, 23, 26, 15 and 16). Site 21 formed a separate cluster 2 which may be attributed to high Na, K, Cl,  $SO_4$ , hardness and alkalinity of the groundwater. Rock containing minerals are responsible for the contribution of these parameters in the area. Cluster 3 comprises of three sub-groups: (3, 12, 36,

**Table 2** Groundwater classification according to base-exchange index (BGI) and meteoric genesis index (MGI) criteria

Sampling sites	BEI	Water type	MGI	Water type
1	-0.14	Na + SO <sub>4</sub>	0.28	Shallow meteoric
2	-0.05	Na + SO <sub>4</sub>	0.37	Shallow meteoric
3	-1.74	Na + HCO <sub>3</sub>	-0.42	Deep meteoric
4	-30.96	Na + HCO <sub>3</sub>	3.98	Shallow meteoric
5	-1.02	Na + HCO <sub>3</sub>	0.16	Shallow meteoric
6	-0.13	Na + SO <sub>4</sub>	0.65	Shallow meteoric
7	-0.23	Na + SO <sub>4</sub>	0.74	Shallow meteoric
8	-0.08	Na + SO <sub>4</sub>	0.28	Shallow meteoric
9	-0.07	Na + SO <sub>4</sub>	0.22	Shallow meteoric
10	-2.83	Na + HCO <sub>3</sub>	-1.08	Deep meteoric
11	0.09	Na + HCO <sub>3</sub>	0.61	Shallow meteoric
12	-3.96	Na + HCO <sub>3</sub>	4.43	Shallow meteoric
13	-0.22	Na + SO <sub>4</sub>	0.26	Shallow meteoric
14	-1.16	Na + HCO <sub>3</sub>	-0.004	Deep meteoric
15	-1.89	Na + HCO <sub>3</sub>	-0.86	Deep meteoric
16	-5.86	Na + HCO <sub>3</sub>	-0.98	Deep meteoric
17	-0.52	Na + SO <sub>4</sub>	0.06	Shallow meteoric
18	-0.25	Na + SO <sub>4</sub>	0.56	Shallow meteoric
19	-0.27	Na + SO <sub>4</sub>	0.42	Shallow meteoric
20	-0.57	Na + SO <sub>4</sub>	2.08	Shallow meteoric
21	-0.53	Na + SO <sub>4</sub>	0.67	Shallow meteoric
22	-0.19	Na + SO <sub>4</sub>	1.92	Shallow meteoric
23	-0.80	Na + SO <sub>4</sub>	-0.20	Deep meteoric
24	-0.04	Na + SO <sub>4</sub>	0.36	Shallow meteoric
25	-0.27	Na + SO <sub>4</sub>	0.61	Shallow meteoric
26	-2.11	Na + HCO <sub>3</sub>	-0.73	Deep meteoric
27	-0.82	Na + SO <sub>4</sub>	0.22	Shallow meteoric
28	-0.16	Na + SO <sub>4</sub>	0.53	Shallow meteoric
29	-0.11	Na + SO <sub>4</sub>	0.45	Shallow meteoric
30	-0.02	Na + SO <sub>4</sub>	0.69	Shallow meteoric
31	-0.50	Na + SO <sub>4</sub>	0.17	Shallow meteoric
32	-0.87	Na + SO <sub>4</sub>	0.27	Shallow meteoric
33	-0.12	Na + SO <sub>4</sub>	2.47	Shallow meteoric
34	-0.56	Na + SO <sub>4</sub>	0.25	Shallow meteoric
35	-0.87	Na + SO <sub>4</sub>	0.23	Shallow meteoric
36	-0.74	Na + SO <sub>4</sub>	-0.05	Deep meteoric
37	-0.72	Na + SO <sub>4</sub>	-0.16	Deep meteoric
38	-0.43	Na + SO <sub>4</sub>	1.01	Shallow meteoric
39	-0.34	Na + SO <sub>4</sub>	0.25	Shallow meteoric
40	-0.06	Na + SO <sub>4</sub>	0.28	Shallow meteoric
41	-0.45	Na + SO <sub>4</sub>	0.21	Shallow meteoric
42	-1.12	Na + HCO <sub>3</sub>	0.58	Shallow meteoric
43	-0.81	Na + SO <sub>4</sub>	0.27	Shallow meteoric
44	-0.53	Na + SO <sub>4</sub>	0.12	Shallow meteoric
45	-0.61	Na + SO <sub>4</sub>	-0.06	Deep meteoric
46	-0.20	Na + SO <sub>4</sub>	0.07	Shallow meteoric
47	-0.24	Na + SO <sub>4</sub>	0.72	Shallow meteoric
48	-0.59	Na + SO <sub>4</sub>	-0.05	Deep meteoric

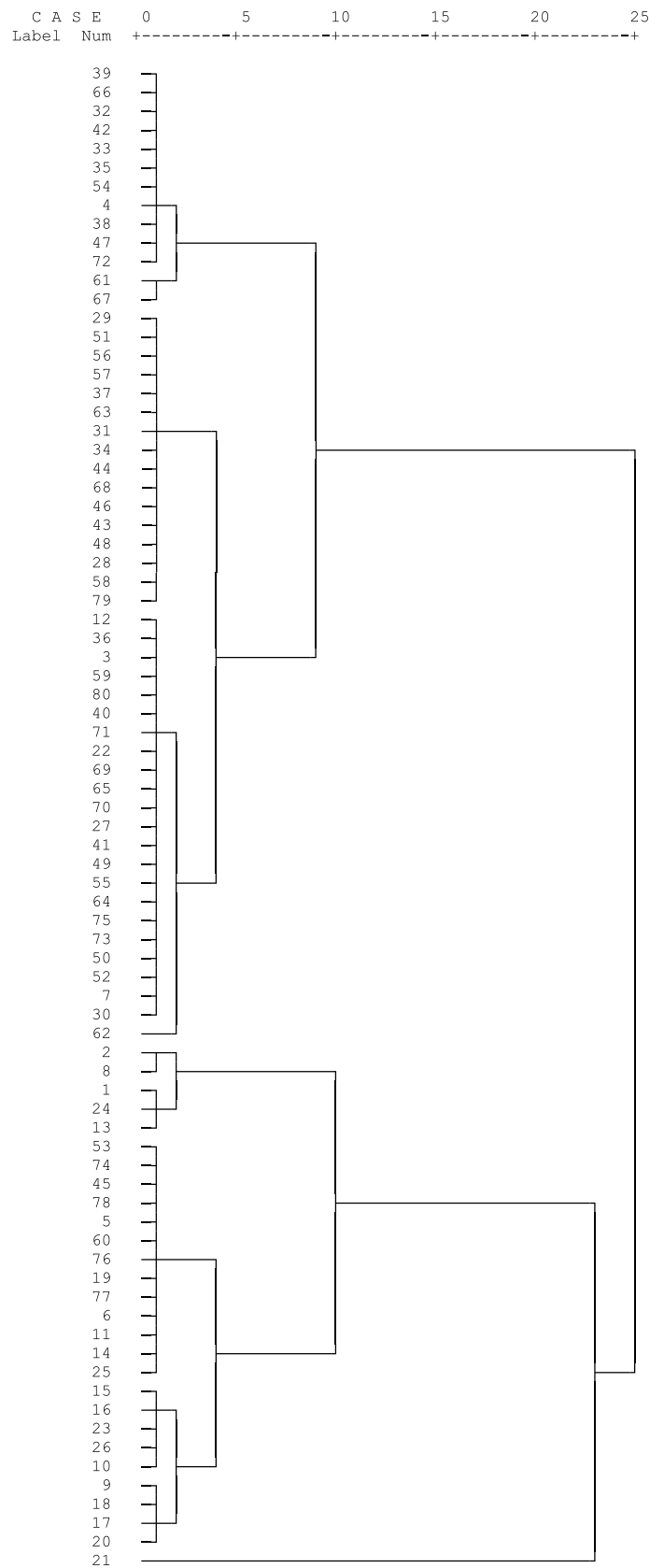
**Table 2** (continued)

Sampling sites	BEI	Water type	MGI	Water type
49	-0.32	Na + SO <sub>4</sub>	0.60	Shallow meteoric
50	-0.13	Na + SO <sub>4</sub>	0.70	Shallow meteoric
51	-0.16	Na + SO <sub>4</sub>	0.39	Shallow meteoric
52	-0.34	Na + SO <sub>4</sub>	0.63	Shallow meteoric
53	-0.37	Na + SO <sub>4</sub>	0.38	Shallow meteoric
54	-0.89	Na + SO <sub>4</sub>	0.04	Shallow meteoric
55	-0.18	Na + SO <sub>4</sub>	0.74	Shallow meteoric
56	-0.23	Na + SO <sub>4</sub>	0.58	Shallow meteoric
57	-0.34	Na + SO <sub>4</sub>	0.78	Shallow meteoric
58	-0.13	Na + SO <sub>4</sub>	0.50	Shallow meteoric
59	-0.56	Na + SO <sub>4</sub>	0.32	Shallow meteoric
60	-0.18	Na + SO <sub>4</sub>	0.38	Shallow meteoric
61	-0.14	Na + SO <sub>4</sub>	-0.02	Deep meteoric
62	-4.26	Na + HCO <sub>3</sub>	-3.92	Deep meteoric
63	-0.34	Na + SO <sub>4</sub>	0.10	Shallow meteoric
64	-0.32	Na + SO <sub>4</sub>	0.26	Shallow meteoric
65	-0.22	Na + SO <sub>4</sub>	0.78	Shallow meteoric
66	-0.40	Na + SO <sub>4</sub>	0.23	Shallow meteoric
67	-0.28	Na + SO <sub>4</sub>	0.26	Shallow meteoric
68	-0.78	Na + SO <sub>4</sub>	-0.13	Shallow meteoric
69	-0.64	Na + SO <sub>4</sub>	3.60	Shallow meteoric
70	-0.49	Na + SO <sub>4</sub>	1.38	Shallow meteoric
71	-0.07	Na + SO <sub>4</sub>	0.52	Shallow meteoric
72	-2.30	Na + HCO <sub>3</sub>	1.22	Shallow meteoric
73	-0.01	Na + SO <sub>4</sub>	0.69	Shallow meteoric
74	-0.32	Na + SO <sub>4</sub>	0.54	Shallow meteoric
75	-0.11	Na + SO <sub>4</sub>	0.56	Shallow meteoric
76	-0.25	Na + SO <sub>4</sub>	0.18	Shallow meteoric
77	-0.22	Na + SO <sub>4</sub>	0.46	Shallow meteoric
78	-0.15	Na + SO <sub>4</sub>	0.26	Shallow meteoric
79	-0.01	Na + SO <sub>4</sub>	0.24	Shallow meteoric
80	-0.44	Na + SO <sub>4</sub>	0.31	Shallow meteoric



**Fig. 4** Cluster analysis of groundwater parameters

**Fig. 5** Cluster analysis of sampling sites



**Table 3** Physicochemical parameters of groundwater for six clusters

	pH	EC ( $\mu\text{S}/\text{cm}$ )	K <sup>+</sup> (mg/L)	Na <sup>+</sup> (mg/L)	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	Alkalinity (mg/L)	Hardness (mg/L)	TDS (mg/L)	Na (%)	SAR meq/L
<b>Cluster 1</b>															
Min	6.87	1354	191.1	82.8	46.6	76.8	341.6	127.8	4.8	4.48	336	480	866.5	26.4	1.61
Max	7.39	3900	460.2	285.2	94	260.4	427	653.2	1099.2	6.72	420	1320	2496	37.6	3.41
Mean	7.16	2449.2	301.8	182.9	73.3	153.6	397.7	332.2	403.2	5.04	391.2	824	1567.4	31.9	2.69
<b>Cluster 2</b>															
Min	6.88	1914	159.9	82.8	55	130.8	366	142	182.4	0.2	360	740	1224.9	18.36	1.27
Max	7.2	2000	296.4	103.5	83	156	427	284	398.4	6.16	420	800	1280	23.07	1.64
Mean	6.99	1958	212.9	94.8	69	143.5	402.6	224.3	305.2	3.22	396	772	1253.12	21.09	1.48
<b>Cluster 3</b>															
Min	6.83	2030	152.1	138	52.2	116.4	268.4	142	201.6	0.24	264	650	1299.2	28.5	2.19
Max	7.16	2150	331.5	185.1	84	130.8	427	397.6	465.6	6.16	420	750	1376	38.2	3.15
Mean	7.04	2107.5	239.8	166.6	66.4	121.9	370.5	250.2	351	4.26	364.5	675	1348.8	34.9	2.79
<b>Cluster 3</b>															
Min	6.92	2130	140.4	170.2	47	116.4	268.4	213	14.4	4.48	264	650	1363.2	30.83	2.56
Max	7.41	2770	928.2	218.5	76.4	177.6	427	710	475.2	6.72	420	920	1772.8	38.59	3.32
Mean	7.08	2442.5	343.6	196.8	67.02	146.8	349.2	481.02	228.6	5.6	343.5	780	1563.2	35.49	3.06
<b>Cluster 4</b>															
Min	6.95	601	39	9.43	40	38.4	244	42.6	52.8	0.16	240	270	384.6	5.25	0.21
Max	8.31	12,160	2952.3	963.7	134	874.8	427	2272	2457.6	7.3	420	3980	7782.4	36.15	6.64
Mean	7.20	2076.3	323.02	121.6	69.3	141.8	363.3	275.3	319.9	2.84	357.3	764.3	1328.8	20.83	1.59
<b>Cluster 5</b>															
Min	6.91	518	39	8.28	36.8	33.6	146.4	28.4	28.8	0.2	144	230	331.5	7.258	0.23
Max	8.31	2000	280.8	105.8	83	156	439.2	1136	398.4	7.3	432	800	1280	32.28	2.02
Mean	7.22	1459.5	170.13	74.5	54.4	101.2	343.8	221.4	192	4.735	338.2	558.1	934.08	21.71	1.34
<b>Cluster 6</b>															
Min	6.9	965	70.2	20.7	38.4	57.6	305	71	62.4	0.18	300	385	617.6	8.06	0.42
Max	7.42	2050	245.7	148.3	80.1	145.2	427	284	350.4	8.96	420	770	1312	32.17	2.47
Mean	7.13	1495.6	150.9	67.14	57.1	107.9	366	160.5	191.2	5.21	360	592.6	957.2	19.07	1.18

**Table 4** Principal component analysis of groundwater parameters

Component	Initial eigen values			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of Variance	Cumulative%	Total	% of Variance	Cumulative%	Total	% of Variance	Cumulative%
1	9.72	64.8	64.8	9.72	64.8	64.8	9.70	64.7	64.7
2	2.36	15.7	80.5	2.36	15.7	80.5	2.26	15.0	79.7
3	1.27	8.4	89.0	1.27	8.4	89.0	1.39	9.2	89.0
Variables	Component matrix			Variables	Rotated component matrix				
	PC1	PC2	PC3		PC1	PC2	PC3		
pH	0.027	<b>-0.571</b>	-0.367	pH	0.018	<b>-0.655</b>	0.176		
EC ( $\mu\text{S}/\text{cm}$ )	<b>0.997</b>	-0.007	0.039	EC ( $\mu\text{S}/\text{cm}$ )	<b>0.998</b>	0.004	0.008		
$\text{K}^+$ (mg/L)	<b>0.923</b>	-0.044	0.029	$\text{K}^+$ (mg/L)	<b>0.924</b>	-0.034	0.003		
$\text{Na}^+$ (mg/L)	<b>0.970</b>	-0.002	0.081	$\text{Na}^+$ (mg/L)	<b>0.973</b>	0.022	-0.032		
$\text{Ca}^{2+}$ (mg/L)	<b>0.693</b>	0.276	-0.544	$\text{Ca}^{2+}$ (mg/L)	<b>0.664</b>	0.096	0.635		
$\text{Mg}^{2+}$ (mg/L)	<b>0.982</b>	-0.037	0.069	$\text{Mg}^{2+}$ (mg/L)	<b>0.985</b>	-0.015	-0.030		
$\text{HCO}_3^-$ (mg/L)	0.008	<b>0.956</b>	0.128	$\text{HCO}_3^-$ (mg/L)	0.001	<b>0.950</b>	0.171		
$\text{Cl}^-$ (mg/L)	<b>0.858</b>	-0.007	0.064	$\text{Cl}^-$ (mg/L)	<b>0.860</b>	0.012	-0.022		
$\text{SO}_4^{2-}$ (mg/L)	<b>0.899</b>	-0.084	-0.072	$\text{SO}_4^{2-}$ (mg/L)	<b>0.896</b>	-0.103	0.086		
$\text{NO}_3^-$ (mg/L)	0.100	-0.344	<b>0.885</b>	$\text{NO}_3^-$ (mg/L)	0.145	-0.058	<b>-0.942</b>		
Alkalinity (mg/L)	0.008	<b>0.956</b>	0.128	Alkalinity (mg/L)	0.001	<b>0.950</b>	0.171		
Hardness (mg/L)	<b>0.989</b>	-0.005	0.008	Hardness (mg/L)	<b>0.989</b>	-0.004	0.037		
TDS (mg/L)	<b>0.997</b>	-0.007	0.039	TDS (mg/L)	<b>0.998</b>	0.004	0.008		

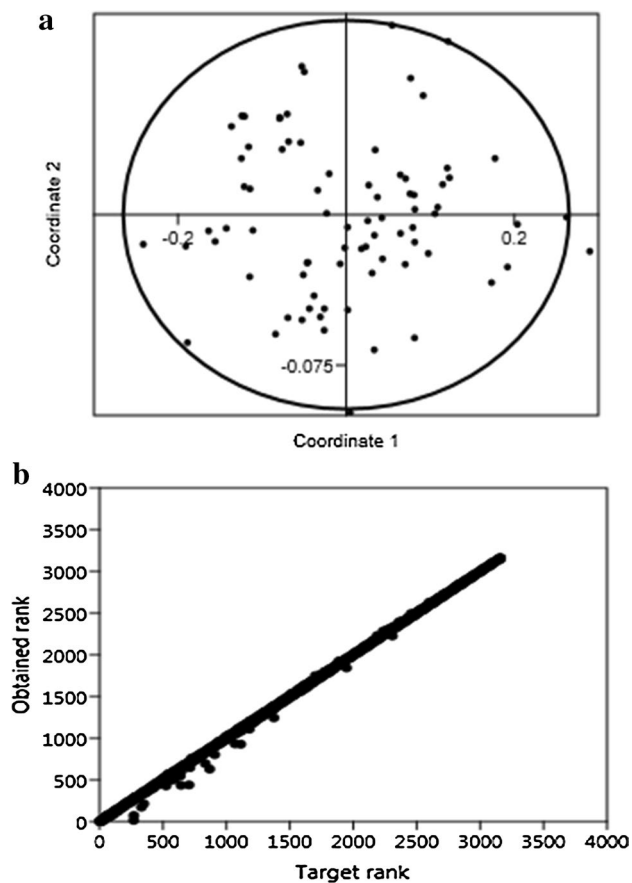
Bold letter indicates significant loadings in the PCs

40, 50, 80, 71, 7, 30, 50, 52, 64, 75, 73, 27, 41, 49, 55, 65, 70, 22, 69 and 62), (28, 58, 79, 43, 48, 44, 68, 46, 29, 51, 31, 37, 63, 34, 56 and 57), and (4, 32, 42, 33, 39, 66, 35, 54, 38, 47, 72, 61 and 67). From the results of CA, it was established that combined anthropogenic activities like cement factory, gas power plant, Rishmark factory and vegetable Oil Company, and natural processes like rock weathering are responsible for the source apportionment of groundwater parameters. The content of various physicochemical parameters of groundwater for six clusters are presented in Table 3. Cluster 1 showed high content of EC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and hardness. Cluster 2 is dominated by high content of alkalinity and  $\text{HCO}_3^-$ . Cluster 3 is contributed by high concentrations of  $\text{K}^+$ ,  $\text{Na}^+$ , Na (%) and SAR, while cluster 4 is dominated by  $\text{Cl}^-$  and  $\text{NO}_3^-$ . Among the entire parameters cluster 5 is controlled mainly by pH. Cluster 6 showed alterations in the content of all the parameters.

Principal component analysis (PCA) was applied to the groundwater parameters (Table 4). The first three PCs accounted for 89% of the total variation. Three components were extracted on the basis of eigenvalues of more than one [49]. The loadings of the PCs in the component matrix explained that PC1 had maximum loadings on EC,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , hardness and TDS, and accounted for 64.8% of the variation. EC and TDS loadings control the overall mineralization. Loading of Ca may be ascribed to its usage in the cement

factory located in the study area.  $\text{K}^+$  and  $\text{Na}^+$  are generally contributed by rocks and anthropogenic sources.  $\text{Cl}^-$  containing minerals contributes  $\text{Cl}^-$  content in the groundwater [50]. Atmospheric deposition and power plants contributes  $\text{SO}_4^{2-}$  content in the area [51]. Hardness occurs due to chemical and mining industry waste or high usage of lime. The PC1 is mainly contributed by anthropogenic activities, i.e., cement factory, gas power plant, Rishmark factory and vegetable Oil Company existed in the Shiraz city as well as natural processes. 15.7% of the variation explained by the PC2 and have maximum loadings on  $\text{HCO}_3^-$  and alkalinity. The  $\text{HCO}_3^-$  and alkalinity are contributed mainly by rock sources to this PC.  $\text{NO}_3^-$  had maximum loading on PC3 and accounted for 8.4% of the variance. The application of agricultural fertilizers contributes to this PC. The similar type of loadings was obtained for different groundwater parameters after varimax rotation. Selvakumar et al. [52] in their studies on groundwater in Tamil Nadu, India reported loadings of EC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  on PC1 which supports our results. Our results find support from Ravikumar and Somashekar [53] in their research on groundwater of Karnataka and reported loadings of EC, TDS, hardness,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  on PC1. Non-metric multidimensional scaling (NMDS) was done on 80 different sampling sites on the basis of groundwater parameters. Correlation was





**Fig. 6** **a** NMDS scatter plot (95% ellipse) of groundwater parameters using correlation, **b** NMDS Shepard 2-D plot of groundwater parameters

used as the similarity measure. NMDS is a nonparametric multivariate technique. The ranks were compressed in two dimensions. NMDS scatter plot and Shepard plot for the sampling sites are presented in Fig. 6a, b. Shepard plot indicated a stress level of 0.0078. A stress level less than 0.05 is a good fit of the data. The stress level formed in NMDS showed that levels of sampling points are maintained on data compression, indicating that differences in the sampling points are dependable on groundwater quality parameters.

## 4 Conclusion

The study area comprised of surface unconstrained to deep aquifers. Due to shallow water table groundwater may become susceptible to discharge of pollutants from the surface, and about 80 samples were collected and analyzed for various physiochemical parameters. The mean values of EC,  $K^+$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$  and TDS were found above

the permissible limits of WHO for drinking water. 97.5% samples for hardness were falls in the category of  $> 300$ , indicating very hard water. SAR and Na% results indicated that water is acceptable for irrigation as well as domestic purposes. The MGI results indicated that 83.75% sampling sites showed shallow meteoric percolation type, whereas 16.25% sampling sites showed deep meteoric percolation type. 83.75% sampling sites showed BEI values less than one, while 16.25% sampling sites showed BEI values greater than one showing Na +  $HCO_3$  water type. Multivariate statistical analysis (CA & PCA) showed that both anthropogenic activities such as cement factory, gas power plant, Rishmark factory and vegetable Oil Company, and natural processes like rock weathering are responsible for the contents of groundwater parameters.

## Compliance with ethical standards

**Conflict of interest** Authors declared that there is no conflict of interest.

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