

Evaluation of groundwater quality and assessment of pollution indices for heavy metals in North of Isfahan Province, Iran

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Received: 18 April 2017 / Accepted: 24 October 2017 / Published online: 7 November 2017
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Abstract Groundwater resources can be potentially a target for various sources of contaminations. One major step towards characterization of contamination sources and the associated parameters, is to conduct groundwater quality assessment through different methods. When dealing with heavy metals, calculation of pollution indices is among well-known techniques of contamination characterization. The objectives of this study include primary assessment of physicochemical parameters of the groundwater and heavy metal concentrations and finding distributions using multivariate statistical methods in the study area (i.e. north Isfahan province, Iran). Heavy metal pollution index (HPI) and metal index (MI) were the two indices evaluated for contamination assessment of heavy metals in 35 samples drawn within the study area. Generally, results indicated that the HPI of the groundwater in the study area was less than the critical value (< 100). Based on HPI values, 51% of samples were classified as having low pollution levels, 46% medium pollution levels and 3% high pollution levels. The MI results revealed that two samples in the study area were significantly polluted with heavy metals. Water-type classification according to dominant cations and anions was also conducted and the result identified four types of water: Na–Cl, Na–SO₄,

Na–HCO₃ and Ca–HCO₃. Multivariate statistical techniques [namely, correlation analysis and principal component analysis (PCA)] were applied for the evaluation of variations and interpretation of a large complex groundwater quality data set from the study area. The principal component analysis (PCA) extracted four components that control the groundwater chemistry. Findings of our study can be used in devising preventive measures to control pollution in the study area and similar regions where the groundwater resource would be relied upon for drinking purposes in the future.

Keywords Groundwater quality · Heavy metal pollution index · Physicochemical parameters · Isfahan, Iran

Introduction

Groundwater resources are among most important sources of fresh water. Similar to surface water resources, water quality is an important environmental issue in groundwater worldwide which largely depends on a number of physicochemical parameters (Kumar Tiwari et al. 2017). Characterization of water quality for groundwater resources should be carried out before making any decisions as how to allocate water for different purposes (drinking, irrigation, industry, etc.). In many regions of the world, groundwater chemistry has been utilized as a measure to determine water quality for drinking and irrigation purposes (Edmunds et al. 2002).

Complexity of geological formations and flow domains are widely observed in groundwater resources. Hydrogeological and geochemical studies are, therefore, warranted for groundwater quality assessment and groundwater resource management, particularly in an event when groundwater quality is potentially degraded by non-natural activities (Colak 2012; Tang et al. 2013; Jabbari et al.

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2016). Groundwater sampling and monitoring are also required on an ongoing basis to back up hydrogeological studies and to more accurately assess water quality and propose sustainable management strategies.

Heavy metals are carcinogenic compounds that are among the most common environmental pollutants with their occurrence in water and biota reflecting presence of natural or anthropogenic sources (Adaikpoh et al. 2005; Akoto et al. 2008). Heavy metals exist in water in colloidal, particulate and dissolved phases (Adepoju-Bello et al. 2009) with their occurrence in water bodies being either of natural origin (e.g. eroded minerals within sediments, leaching of ore deposits and volcanism extruded products) or of anthropogenic origin (i.e. solid waste disposal, industrial or domestic effluents) (Marcovecchio et al. 2007). Variations in natural and human activities reflect spatial variations of the aquifer and the hydrochemical parameters of the groundwater. Elevated heavy metal concentrations in water lead to environmental problems which make it necessary to center studies around potential water contamination from metals sources. Industrial, agricultural, and solid waste disposal practices are famous examples of human activities playing role in increasing levels of heavy metals in water, soil, and air (Adekunle et al. 2007; Nagajyoti et al. 2010; Jaishankar et al. 2014).

When studying heavy metals, pollution parameters are generally monitored for assessment of water quality and are then compared with allowable heavy metal concentrations recommended by water standards. Several water quality indices and corresponding applications of index methods have been proposed for estimation of water quality (Edet and Offiong 2002; Bhuiyan et al. 2010). Pollution indices are useful tools for water quality executives, environmental managers, and decision makers as measures which have combined influences of all parameters. In recent years, much attention has been given to evaluation of heavy metal pollution in groundwater using the heavy metal pollution index (HPI) (Rajkumar et al. 2015). The spatial study of heavy metals HPI can be helpful in identifying and quantifying trends in water quality (Mishra et al. 2017). Another index is the general metal index (MI) for drinking water, which takes into account possible additive effects of heavy metals on human health (Enaam Abdullah 2013). MI helps to quickly evaluate the overall quality of drinking water (Enaam Abdullah 2013).

Metals indices can be coupled with statistical methods to obtain more robust results when analyzing water quality data. Multivariate statistical techniques, such as correlation matrix and principal component analysis (PCA), are examples of statistical methods that have been broadly used by researchers around the world for the assessment of water quality (Arora and Mehra 2009; Vieira et al. 2012).

Application of multivariate statistical techniques facilitates interpretation of complex data matrices for a better understanding of water quality and a variety of environmental factors.

In this study, we are focused on assessing the prevailing water quality condition to identify the pollution status and probable sources of pollutants in the study area. This work is primarily aimed to assess physicochemical parameters of groundwater [i.e. pH, electrical conductivity (EC), temperature, and total dissolved solids (TDS)] and calculate HPI and MI indices. The indices are used as quantitative criteria to pinpoint areas with high degree of heavy metal pollution. Spatial frequencies and distributions of heavy metal concentration are then evaluated by applying multivariate statistical methods. Heavy metals of concern include arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn). The result of this research can help identifying segments of groundwater with suitable quality for drinking water purposes.

Study area

Similar to many other countries in arid and semi-arid regions of the world, groundwater is a major source of water supply for domestic, industrial and agricultural sectors in Iran (Rezaei and Hassani 2017). The area of study of this research is located in north of Isfahan province in Iran which is historically known for low annual precipitations and long droughts. More precisely, this area is located in northern part of the Sanandaj–Sirjan zone and southern part and middle division of central Iran tectonic zone. The study area lies between longitudes $52^{\circ}15'00''$ to $53^{\circ}15'00''$ E and latitudes $33^{\circ}20'05''$ to $33^{\circ}30'05''$ N, covering an estimated area of approximately 1500 km^2 (Fig. 1). Groundwater is an important water resource especially for drinking and agricultural uses in the study area.

Geological features and information of the study area are discussed in this section. The main lithology consists of Eocene volcanic and pyroclastic rocks (Fig. 2). In the Oligocene–Miocene, marl, limestone, sandstone, shale and gypsum units are known as Qom Formation. In the Late Miocene, deposition of sandstone, marl, conglomerate and evaporate rocks known as the upper red formation developed in a molasses-type condition of a sedimentary environment as a result of slow positive movement of the basin (Babaahmadi et al. 2010). Natural sources of heavy metals include volcanism, bedrock erosion, and atmospheric transport. The main sources of potential pollution are deemed to be related to activities in mining, agricultural, municipal and also in part to natural sources.

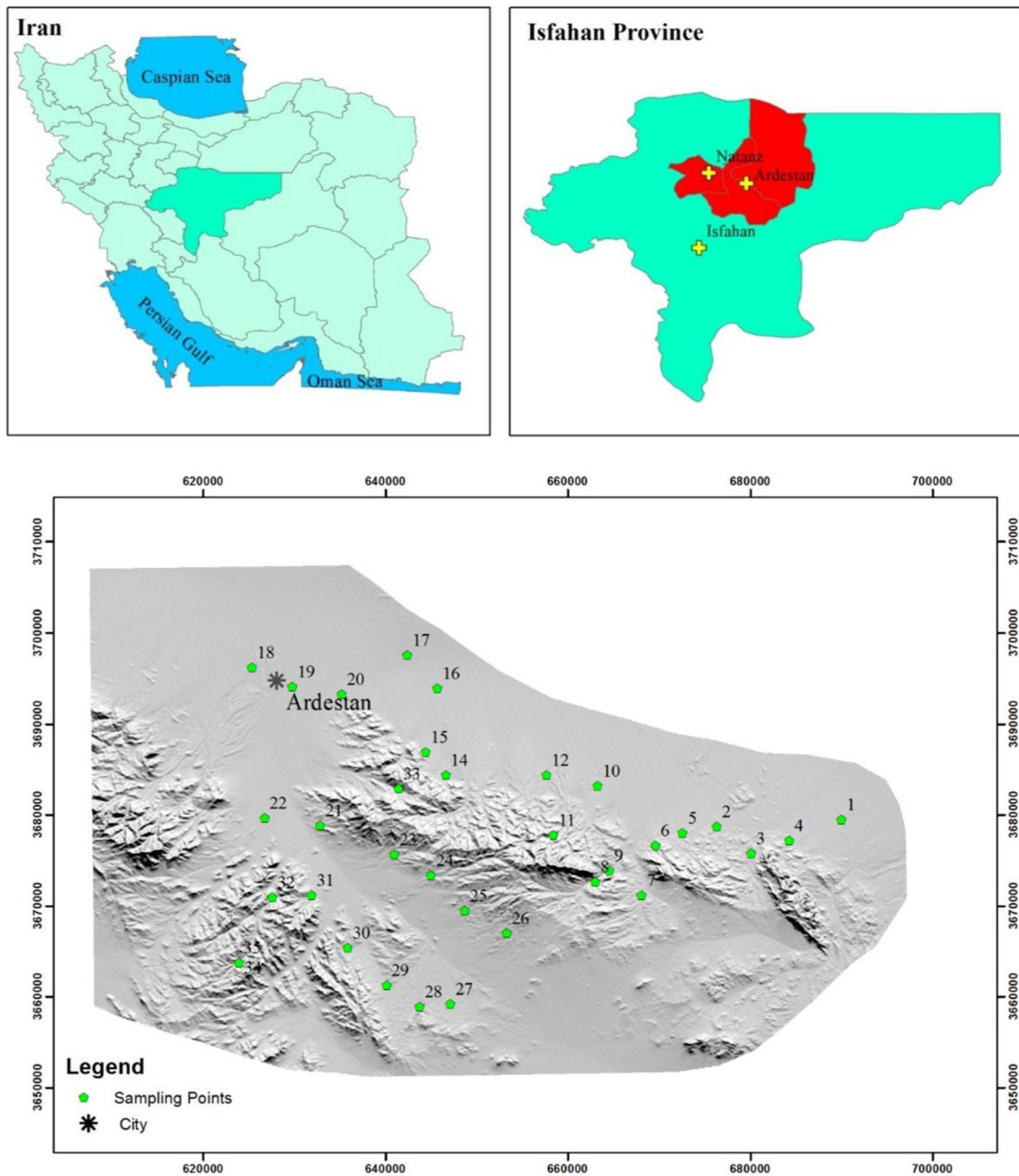


Fig. 1 Location map of the study area and sampling stations. Green dashed line is used on top right figure to show sampling area extension with respect to jurisdictional boundaries of Isfahan province

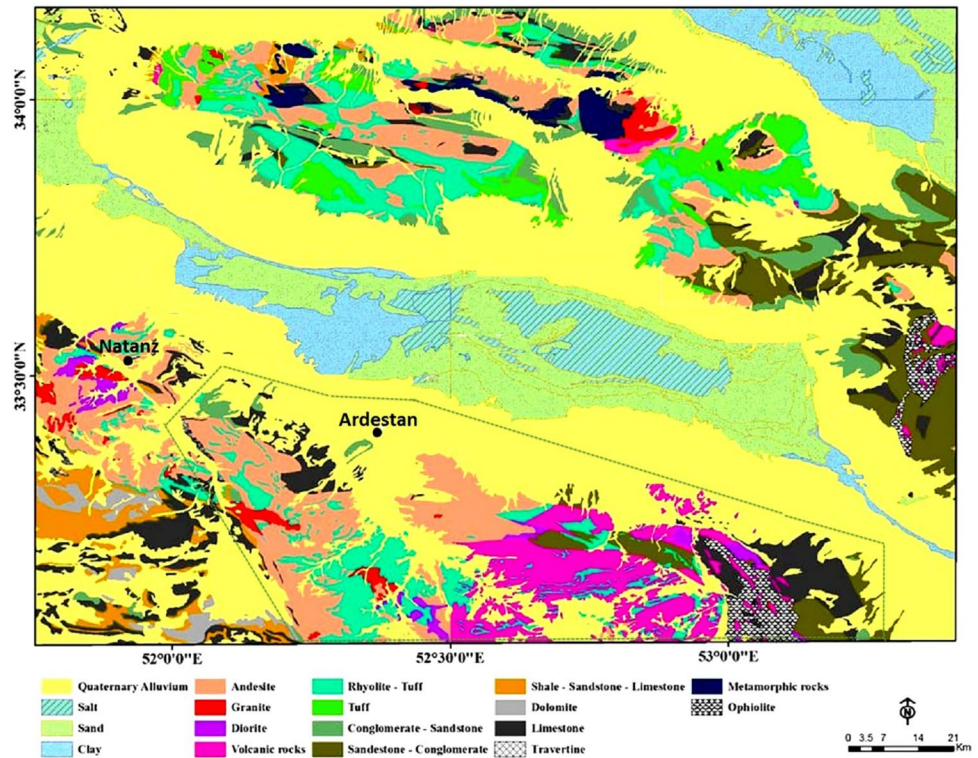
Materials and method

As the first step in investigation of heavy metals concentrations, samples were drawn from 35 monitoring wells in the area. Specifications and coordinates of sampling stations are listed in Table 1.

Water samples were collected from stations during April and May 2016. Location of sampling stations is demonstrated in Fig. 1 and Table 1. Physicochemical parameters including temperature, pH, electrical conductivity (EC), and

total dissolved solids (TDS) were measured in situ, using a multi-parameter portable meter (HATCH, Germany). Groundwater sample collection procedure included drying, cleaning and sterilizing in polyethylene bottles. Samples were, then, labeled, sealed and transported to the laboratory and preserved in the refrigerator at a temperature of about 4 °C until analysis time. Water samples were analyzed for major cations and anions using standard methods within 48 h after sampling. Quality control and analysis procedures for obtaining accurate data were performed, including probe

Fig. 2 Geological map of the study area (Amidi and Zahedi 1988)



calibration for the in situ parameters. The concentration of heavy metals (i.e. As, Cr, Cu, Ni, Pb, and Zn) was determined using inductively coupled plasma mass spectrometry (ICP-MS) method at the Lab West Laboratories, Australia. The accuracy and precision of the measurements were checked using duplicate samples.

Indexing approach

In this research, two indices, namely, heavy metal pollution index (HPI) and metal index (MI), are applied as quantitative measures of water quality.

Heavy metal pollution index (HPI)

Heavy metal pollution index (HPI) is defined as a quantity reflecting the composite influence of different dissolved heavy metals (Sirajudeen et al. 2014). HPI is a powerful tool for ranking amalgamated effects of individual heavy metals on the overall water quality and determining suitability of groundwater for human consumption with values below 100 safe for consumption (Rizwan et al. 2011). The HPI is a method of assigning a rating or weighting (W_i) for each selected parameter. The rating is a value between zero and one, reflecting the relative importance of individual quality considerations and defined as inversely proposal to the recommended standard for each heavy metal (Mishra et al. 2017). The rating value can also be

defined as inversely proportional to the recommended standard (S_i) for each parameter (Mohan et al. 1996; Prasad and Kumari 2008). The highest tolerance value for drinking water (S_i) refers to the maximum allowable concentration (MAC) in drinking water in the absence of any alternate water source. The desirable maximum value (I_i) indicates the standard limits for the same parameters in drinking water. The HPI index is calculated as follows (Mohan et al. 1996):

The first step involves computing the relative weight (W_i) of each parameter using Eq. 1.

$$W_i \propto \frac{1}{\text{MAC}} \rightarrow W_i = \frac{k}{\text{MAC}} \quad (1)$$

with k being the constant of proportionality.

In the second step, an individual quality rating (Q_i) is computed for each parameter using Eq. 2.

$$Q_i = \sum_{i=1}^n \frac{|M_i - I_i|}{S_i - M_i} \times 100 \quad (2)$$

where M_i is the monitored value of heavy metal of i th parameter in the water sample, I_i is the ideal value of the i th parameter, and S_i is the standard value of the i th parameter. Third, summing these sub-indices to compute the overall index:

$$\text{HPI} = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad (3)$$

Table 1 Specifications and coordinates of sampling stations in the study area

Sampling station number	X (UTM)	Y (UTM)	Elevation (m)	Type of well
1	690,052	3,679,491	1270	Open well
2	676,381	3,678,680	1573	Open well
3	680,129	3,675,753	1650	Open well
4	684,310	3,677,192	1520	Bore well
5	672,630	3,677,980	1651	Open well
6	669,644	3,676,658	1771	Open well
7	668,124	3,671,155	1189	Open well
8	663,060	3,672,645	1979	Open well
9	664,573	3,673,876	1890	Open well
10	663,285	3,683,198	1500	Open well
11	658,431	3,677,761	1910	Open well
12	657,710	3,684,362	1453	Open well
13	651,013	3,677,811	2055	Open well
14	646,648	3,684,338	1515	Open well
15	644,453	3,686,911	1355	Open well
16	645,718	3,693,900	1070	Bore well
17	642,450	3,697,588	990	Bore well
18	625,408	3,696,211	1150	Open well
19	629,812	3,694,117	1203	Open well
20	635,238	3,693,290	1180	Open well
21	632,901	3,678,846	1640	Bore well
22	626,781	3,679,662	1615	Bore well
23	641,005	3,675,614	1940	Open well
24	645,045	3,673,367	2062	Open well
25	648,736	3,669,479	2109	Open well
26	653,341	3,666,970	2229	Open well
27	647,161	3,659,192	2103	Bore well
28	643,808	3,658,907	2090	Open well
29	640,169	3,661,255	2062	Open well
30	635,897	3,665,412	1970	Bore well
31	631,953	3,671,184	1851	Open well
32	627,642	3,670,905	1874	Open well
33	641,452	3,682,874	1803	Open well
34	623,974	3,663,746	2213	Open well
35	623,964	3,663,707	2202	Open well

where, Q_i is the sub-index of the i th parameter, W_i is the unit weight for the i th parameter, and n is the number of parameters. Generally, the critical value is 100 for drinking water.

Metal index (MI)

The metal index (MI) was preliminarily defined by Tamasi and Cini (2004). This index can be expressed by Eq. 4, where MI is the metal index, C is the concentration of each element in the solution, MAC is the maximum allowed

concentration of each element, and the subscript i indicating the i th sample.

$$MI = \sum_{i=1}^n \frac{C_i}{(MAC)_i} \quad (4)$$

The higher the concentration of a metal compared to its respective MAC value, the worse the quality of the water. MI value > 1 is a threshold of warning (Bakan et al. 2010).

Statistical analyses

Multivariate statistical analyses are applied to identify the relationship between groundwater parameters in the study area. Correlation matrix of heavy metal concentrations and calculated indices was constructed to find relations among parameters. The bivariate correlation analysis method was applied to quantify the relation between hydrogeochemical parameters and heavy metals (As, Cr, Cu, Ni, Pb, and Zn). Also, Ca^{2+} , Mg^{2+} , K^+ , Na^+ and HCO_3^- and SO_4^{2-} were included in the matrix to capture their potential effect on redox and the metals mobility.

Spearman's correlation coefficient was utilized for displaying relationships among variables using SPSS 18.0 statistical package (SPSS Inc. 2017). Because the distribution of ions in groundwater samples is non-parametric, the Spearman's correlation analysis is appropriate to be considered here. A high correlation analysis [correlation coefficient (r) near $+1$ or -1] indicates a good relationship between two variables (either positively or negatively correlated) and a value around zero is reflective of no relationship. It should be noted that, if the r value is greater than 0.7, two parameters are considered to be strongly correlated; whereas an r value between 0.5 and 0.7, indicates a moderate correlation at 95% significance level (Guey-Shin et al. 2011).

Principal component analysis (PCA) was next performed to reduce the number of variables with meaningful relations. PCA is one of the multivariate statistical methods that can be used to reduce the complexity of the variable analysis and also a better interpretation of large volumes of information and data (Noori et al. 2010). This method allows us to display most of the original variability in a smaller number of dimensions and has been widely used in geochemical and hydrochemical studies (Razo et al. 2004). In this study, PCA with varimax normalized rotation (VNR) was carried out using SPSS 18.0 (Kaiser 1958).

All of the hydrochemical variables measured consisting of T, TDS, EC, pH, anions and cations, heavy metals (As, Cr, Cu, Ni, Pb and Zn), HPI and a MI were used in this statistical studies.

Discussion

Physiochemical parameters of groundwater samples

The physiochemical parameters and statistical summary for all of the 35 water samples are shown in Table 2.

The analytical results of physiochemical parameters were compared with the standard guideline values recommended by the World Health Organization (WHO) for drinking and public health purposes (WHO 2004). In the study area, pH values of groundwater samples vary from 7.05 to 8.76 with a mean of 7.78, indicating a neutral to slightly alkaline water (Fig. 3). TDS values range from 230 to 2200 mg/l, with a mean value of 640 mg/l. Groundwater with high TDS is not suitable for both drinking and irrigation purposes. The maximum allowable limit for the TDS in drinking water is 1000 mg/l (WHO 2004) (Fig. 4). EC and TDS are the most important parameters to demarcate salinity hazard and suitability of water for irrigation purposes. Water EC values vary from 480 to 4300 $\mu\text{S}/\text{cm}$ with an average of 1280 $\mu\text{S}/\text{cm}$

Table 2 Summary statistics of physicochemical parameters of groundwater samples of the study area

Parameters	Unit	Max	Min	Mean
pH	–	8.75	7.05	7.78
EC	$\mu\text{S}/\text{cm}$	4300	480	1280
TDS	mg/l	2200	230	640
T	$^{\circ}\text{C}$	30.1	17.20	21.25

cm. It should be noted that maximum allowable limit for EC in drinking water is 1500 $\mu\text{S}/\text{cm}$ according to WHO 2004 (Fig. 5). Also, water temperature (T) values vary from 17.2 to 30.1 $^{\circ}\text{C}$ with an average of 21.25 $^{\circ}\text{C}$ (Fig. 6).

Figures 3, 4, 5 and 6 show the spatial distribution of pH, TDS, EC and T values in the study area. The concentration gradient is calculated using the inverse distance weighting interpolation method.

Hydrogeochemical facies and classification (water types)

The Piper (1944) diagram was used to identify water types in the study area. The chemical composition of groundwater is dependent on the geology, especially lithology, and solution kinetics, flow patterns of the aquifer and anthropogenic activities which take place within the aquifer system. To find the dominant hydrochemical type and characterization of waters in the study area, groundwater samples are plotted onto trilinear Piper’s diagrams based on major ion concentrations in meq/l (Piper 1944). The Piper plot (Fig. 7) shows that groundwater in the study area consists of four water types: Na–Cl, Na– SO_4 , Na– HCO_3 and Ca– HCO_3 . This suggests that there might be a considerable number of different processes influencing the chemistry of groundwater in the study area and indicating the variable nature of the groundwater chemistry. Also, Fig. 8 shows the distribution of water types in groundwater of the study area. The results show that the majority of samples (17

Fig. 3 Spatial distribution of pH values of the groundwater samples in the study area

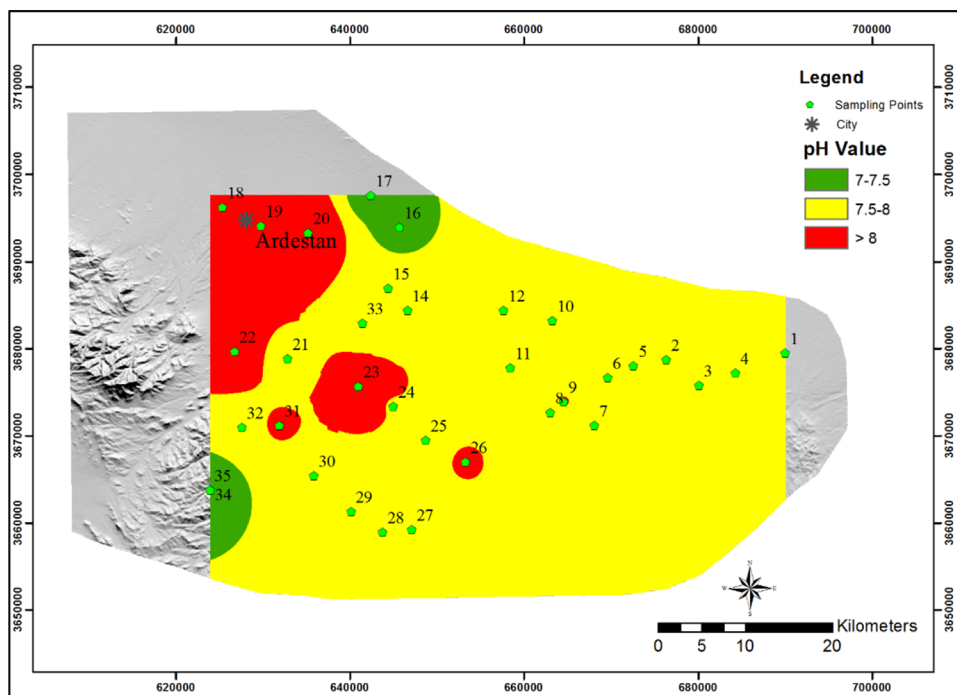


Fig. 4 Spatial distribution of TDS values of the groundwater samples in the study area

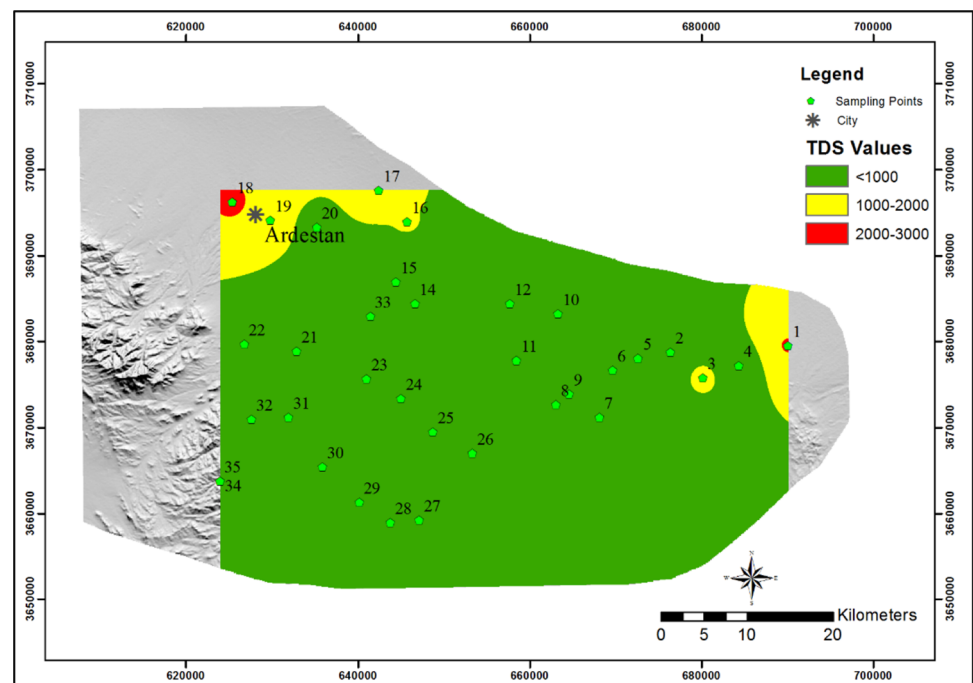
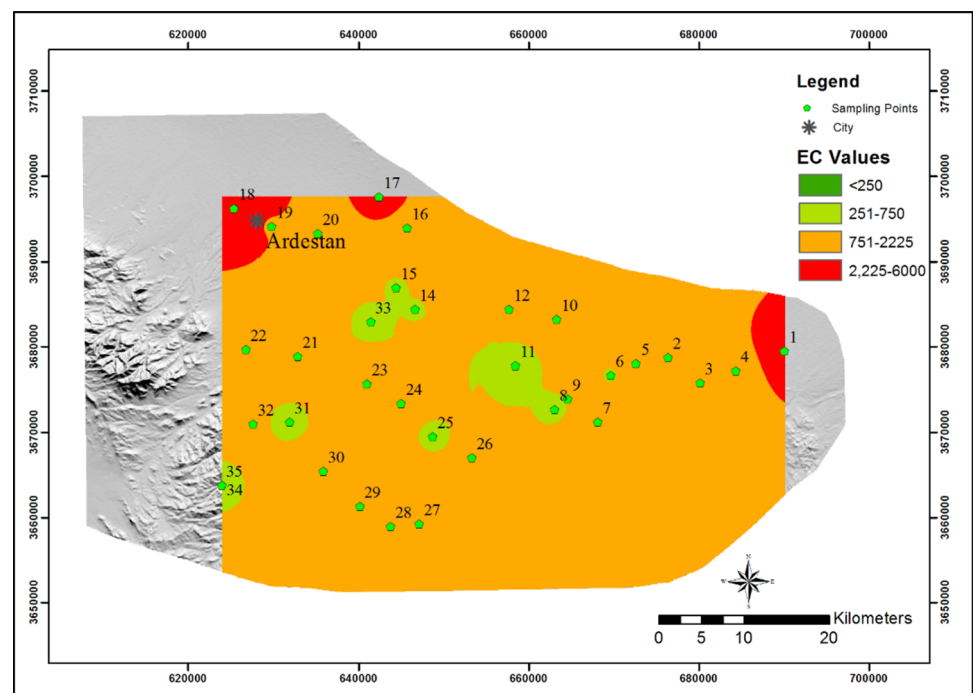


Fig. 5 Spatial distribution of EC values of the groundwater samples in the study area



samples, 49%) belong to the mixed Na–SO₄ water type. Ca–HCO₃ water type (one sample, 3%): this type indicates mineral dissolution (probably secondary carbonate and silicate minerals) with sufficient recharge from fresh water (Ako et al. 2012; Srinivasamoorthy et al. 2014). In Na–Cl water type (eight samples, 23%), the final stage of evolution of water types from recharge zone to discharge zone

(i.e. bicarbonate → sulfate → chloride) can be observed in water samples of the study area at the discharge zone. In addition, water–evaporitic mineral interactions can be other potential reasons for the presence of chloride type in this zone (Todd and Mays 2005; Merkel and Planer-Friedrich 2008). Na–HCO₃ (nine samples, 26%) is another water type which can be a result of ion exchange.

Fig. 6 Spatial distribution of $T^{\circ}\text{C}$ values of the groundwater samples in the study area

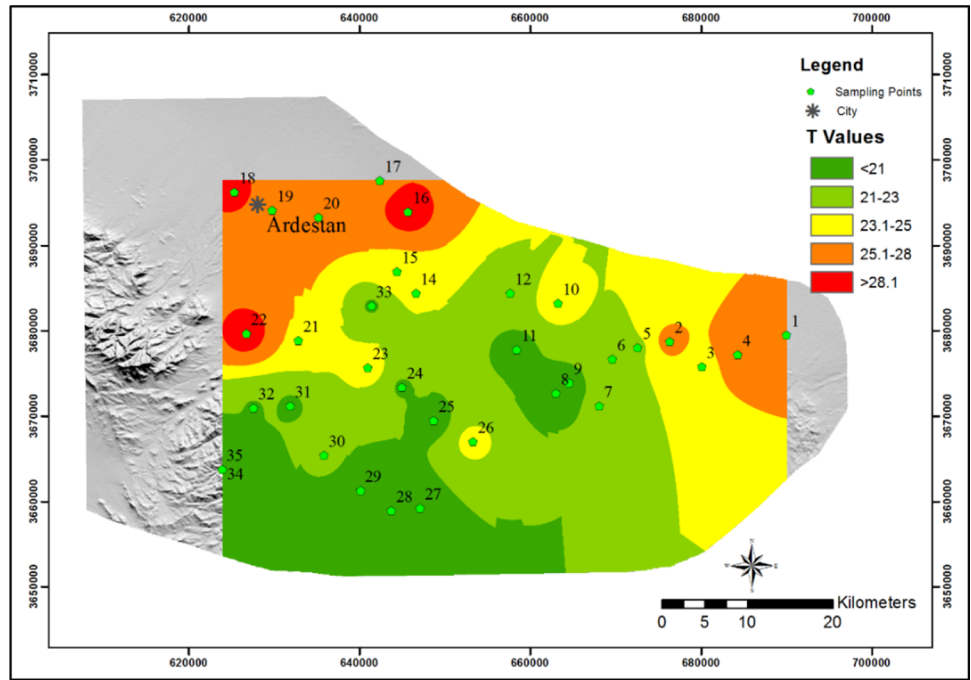


Fig. 7 Piper diagram illustrating the main hydrochemical features of the groundwater in the study area

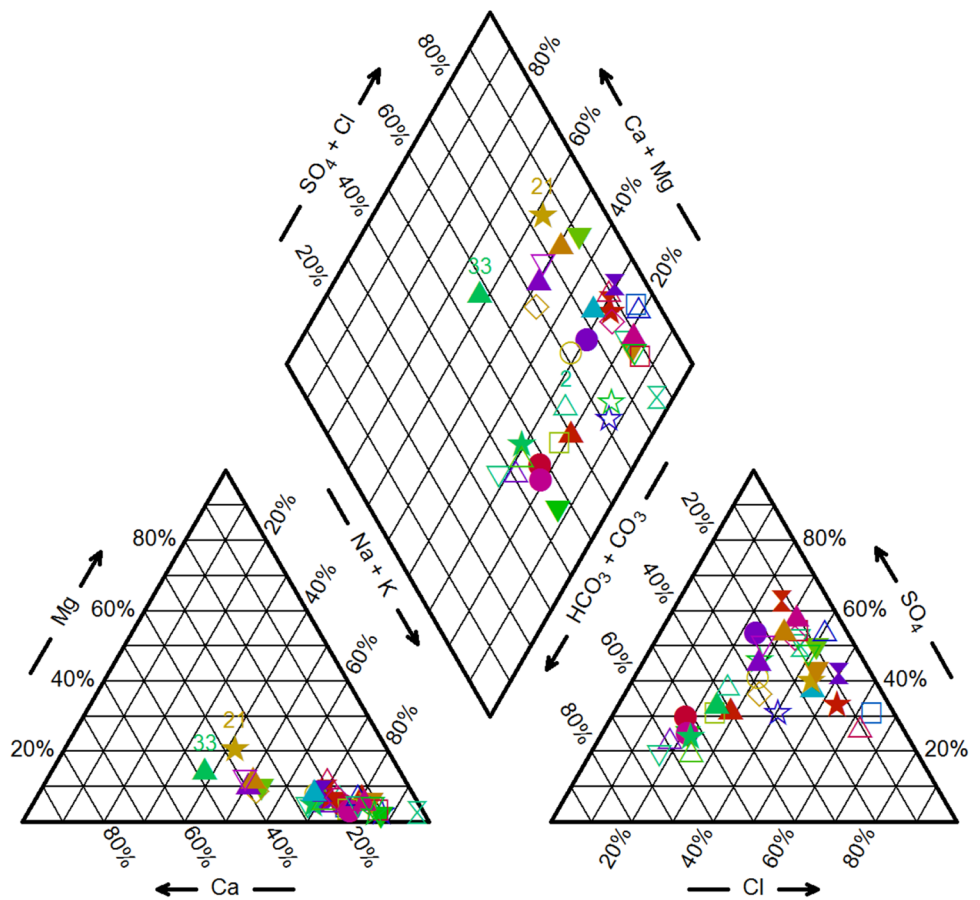


Fig. 8 Distribution of water types in the groundwater of the study area

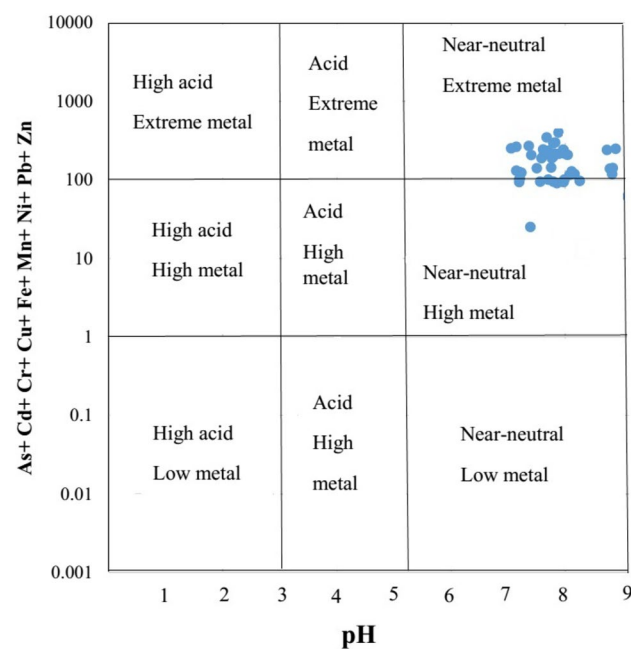
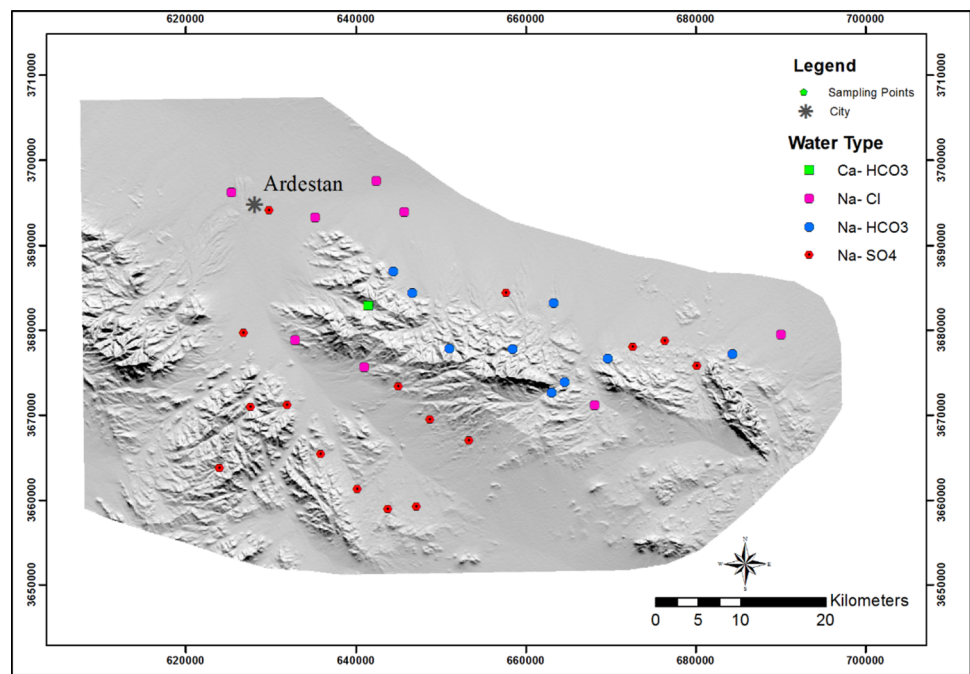


Fig. 9 Classification of water samples based on the plot of metal load and pH

Classification of water

To classify water samples of the study area, the relationship between pH and metal load (defined as As + Cd + Cr + Cu + Fe + Mn + Ni + Pb + Zn in mg/l) was employed (Ficklin et al. 1992; Caboi et al. 1999). Figure 9 shows the relationship between total metal contents (mg/l) and pH of the analyzed

samples. The results indicate that the majority of samples (86%, 30 samples) are classified as near neutral–extreme metal (stations 1–20, 22–23, 25–26, 28–31, 34–35), while five samples (14%) show near neutral–high metal (stations 21, 24, 27, 32, 33). The high metal contents of these stations can lead to serious threats for drinking water consumers.

Heavy metals concentrations

Quality of water in the study area, with regard to the concentration of heavy metals (As, Cu, Cr, Ni, Pb, and Zn) is assessed herein. The concentrations of heavy metals in water samples are listed in Table 3 and are compared with heavy metals MACs from WHO (2004). The variation of heavy metals in the study area water at different locations is also presented in Fig. 10. The average heavy metal concentration in the groundwater samples follows this series (in decreasing order): lead > nickel > zinc > copper > arsenic > chrome (Table 3).

Arsenic is a ubiquitous toxicant and a carcinogenic element associated with a wide range of adverse human health effects (WHO 2004; Tseng et al. 2002; Navas-Acien et al. 2006). Weathering and erosion of As-bearing minerals release As into surface water and groundwater resources (Wang and Mulligan 2006a, b; Armienta and Segovia 2008; Naidu and Bhattacharya 2009). The average Arsenic concentration in the study area was 0.023 mg/l, with a range of 0.0017–0.232 (Table 3). Higher concentrations of As at stations 1, 18, 19, 20 and 30 may be attributed to natural processes and anthropogenic sources. Natural processes in the study area consist of evaporation of water

Table 3 Heavy metal concentration (mg/l) in the study area

Station	As	Cr	Cu	Ni	Pb	Zn	Station	As	Cr	Cu	Ni	Pb	Zn
1	0.064	0.04	0.04	0.05	0.08	0.0005	19	0.04	0.0005	0.0005	0.01	0.01	0.06
2	0.04	0.0005	0.05	0.06	0.06	0.01	20	0.2	0.0005	0.0005	0.01	0.0005	0.0005
3	0.001	0.0005	0.05	0.06	0.05	0.01	21	0.01	0.0005	0.0005	0.01	0.0005	0.0005
4	0.002	0.0005	0.05	0.06	0.05	0.35	22	0.004	0.0005	0.0005	0.02	0.06	0.03
5	0.002	0.0005	0.05	0.06	0.05	0.03	23	0.009	0.0005	0.0005	0.01	0.1	0.04
6	0.002	0.0005	0.05	0.06	0.05	0.03	24	0.01	0.0005	0.0005	0.01	0.02	0.04
7	0.015	0.0005	0.05	0.06	0.05	0.02	25	0.02	0.0005	0.0005	0.01	0.02	0.03
8	0.006	0.0005	0.05	0.06	0.04	0.03	26	0.01	0.0005	0.0005	0.02	0.03	0.04
9	0.008	0.0005	0.05	0.06	0.06	0.01	7	0.01	0.0005	0.0005	0.02	0.02	0.03
10	0.018	0.0005	0.05	0.07	0.06	0.03	28	0.02	0.0005	0.0005	0.02	0.04	0.05
11	0.003	0.0005	0.06	0.07	0.07	0.01	29	0.01	0.0005	0.0005	0.02	0.03	0.07
12	0.002	0.0005	0.06	0.07	0.07	0.01	30	0.07	0.0005	0.0005	0.06	0.05	0.09
13	0.004	0.0005	0.06	0.07	0.07	0.02	31	0.009	0.0005	0.0005	0.02	0.05	0.04
14	0.007	0.0005	0.06	0.07	0.09	0.01	32	0.009	0.0005	0.0005	0.02	0.03	0.03
15	0.002	0.0005	0.07	0.07	0.06	0.02	33	0.0007	0.0005	0.0005	0.01	0.01	0.05
16	0.006	0.0005	0.06	0.07	0.07	0.05	34	0.02	0.0005	0.0005	0.01	0.01	0.04
17	0.018	0.01	0.05	0.07	0.08	0.01	35	0.01	0.002	0.006	0.001	0.006	0.03
18	0.115	0.0005	0.0005	0.01	0.0005	0.0005							
AVG	0.023	0.001	0.03	0.04	0.05	0.04							
MAC	0.01	0.05	2.0	0.07	0.1	5.0							

due to high temperature and low rate of rain falls in the last decade drought, which enhances a number of salts, trace, and toxic elements. Anthropogenic sources in the study area include the use of arsenical pesticides for protecting crops in the region, mainly. The As concentration at 17 stations is higher than the corresponding WHO values (Fig. 11). Also, transferring of As into the water system during water–acidic volcanic rock interactions are another source of arsenic in groundwater of the study area. The copper content in the water samples ranged from 0.0005 to 0.0709 mg/l with an average value of 0.0301 mg/l (Table 3). The higher level of Cu in some stations is attributed to runoff from farming areas (especially at stations 15 and 17) (Fig. 12). It is noteworthy to state that higher levels of Cu in some stations are due to existence of copper indices in the study area (natural processes). Nickel concentrations ranged from 0.011 to 0.078 mg/l with an average of 0.044 mg/l (Table 3). The Ni concentration at eight stations is higher than the corresponding WHO values (Fig. 13). Zinc concentrations ranged from 0.0005 to 0.035 mg/l with an average of 0.039 mg/l (Table 3). Zinc belongs to a group of trace metals, essential for growth in humans, animals, and plants and is potentially dangerous for the biosphere when present in high concentrations. High Zn concentrations were found at station 4, which can be attributed to the excessive use of zinc sulfate, an important constituent of fertilizers tremendously used in the region. Chromium is present in small quantities in nature. Chromium is extremely irritating and toxic to human body

tissue owing to its oxidizing potential and the permeability of biological membranes (Anderson et al. 1996). Chromium levels in the study area ranged from 0.0005 to 0.040 mg/l, with an average of 0.0019 mg/l (Table 3). Lead concentrations ranged from 0.0005 to 0.27 mg/l with an average of 0.056 mg/l (Table 3). It has been observed that sampling stations 23 and 25 have lead levels above the WHO standard of 10 µg/l (Fig. 14). The Pb concentration at two stations is higher than the corresponding WHO values. Lead contamination of the groundwater in the study area can be the result of entry from agricultural run-off containing phosphate fertilizers, and human and animal excreta.

Heavy metals indices

The descriptive summary statistics of heavy metals and MACs are shown in Table 4. The concentration of Cr, Cu, and Zn were below the MAC in drinking water. The concentration of As (11% samples), Ni (66% samples) and Pb (54% samples) are more than the MAC (Table 4).

For HPI calculation, the concentration limits (i.e. MAC, highest permissible value for drinking water (S_i) and the maximum desirable value (I_i) for each heavy metal) were retrieved from the World Health Organization standard (WHO 2004).

The unit weight (W_i) for various water quality parameters is assumed to be inversely proportional to the maximum

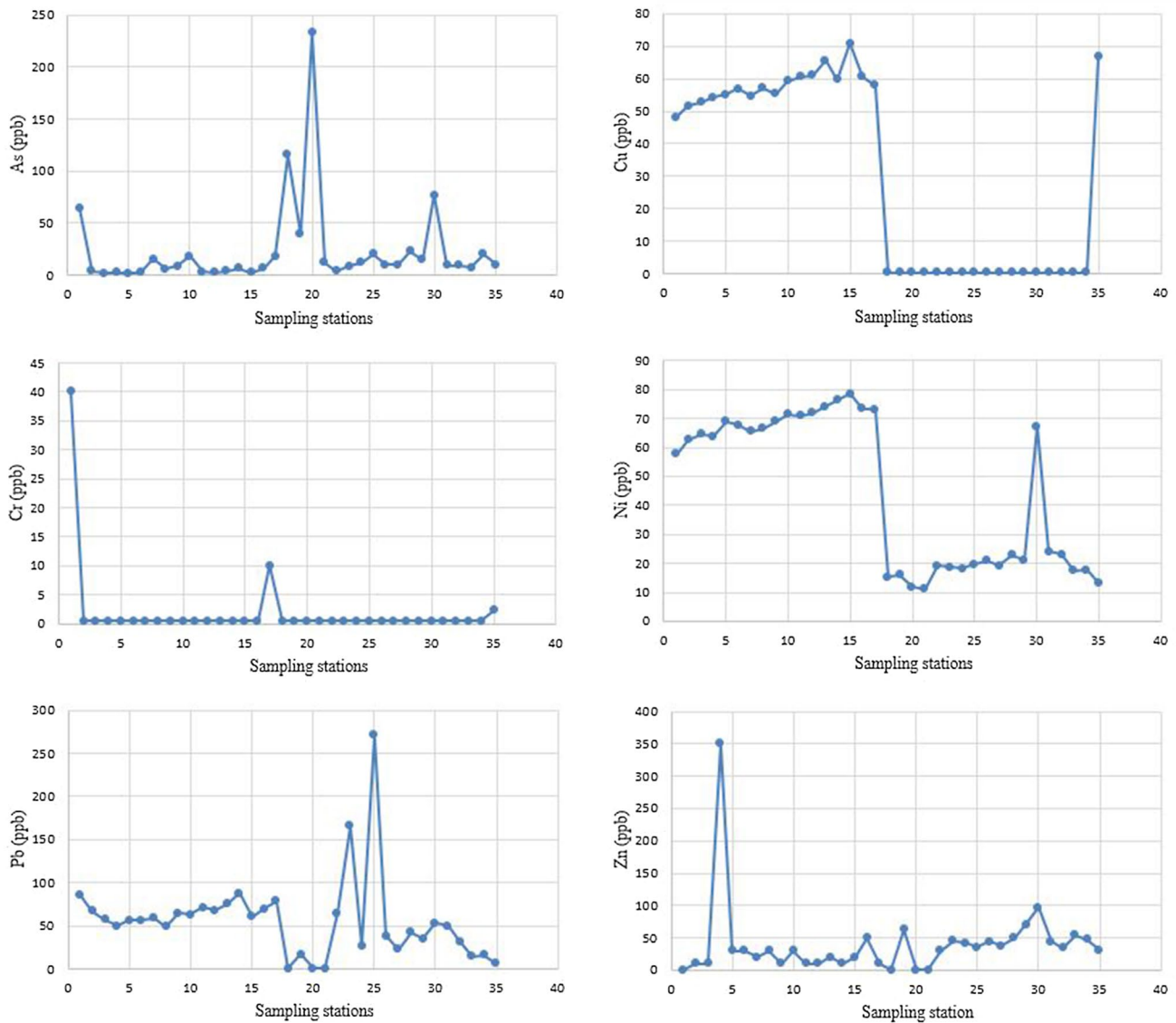


Fig. 10 Variation of heavy metals (As, Cu, Cr, Ni, Pb, and Zn) at groundwater samples of the study area

admissible concentration (MAC) for the corresponding parameter (Table 5).

$$\sum W_i Q_i = 3.7808; \quad \sum W_i = 0.1112$$

Mean HPI for all of the samples is calculated as $3.7808/0.1112=34$ (Table 6).

Similarly, the HPI values for 35 samples in the study area, As, Cu, Cr, Ni, Pb, and Zn, are calculated and the results are given in Table 7 (Fig. 16). Also, bar diagram of HPI values at sampling stations is shown in Fig. 15.

Maximum value of HPI is 129.75, which is associated to station 20 and is potentially due to leaching of heavy metals from industries, such as fertilizers, pigments etc.,

located within the study area. This sampling site is adjacent to the Ardestan city (7 km distance). The HPI in this station is higher than the threshold index value of 100, indicating critical contamination with heavy metals. The median deviation for the HPI indices was computed for each sampling station (Table 7). The median deviation on the more negative side indicates a slightly better quality with respect to heavy metals. To apply these HPI indices in the present study, the scales were slightly modified using multiples of the median as a criterion. For this purpose, the values are divided into three classes to demarcate the different levels of contamination as low, medium, and

Fig. 11 Spatial distribution of As values of groundwater samples of the study area

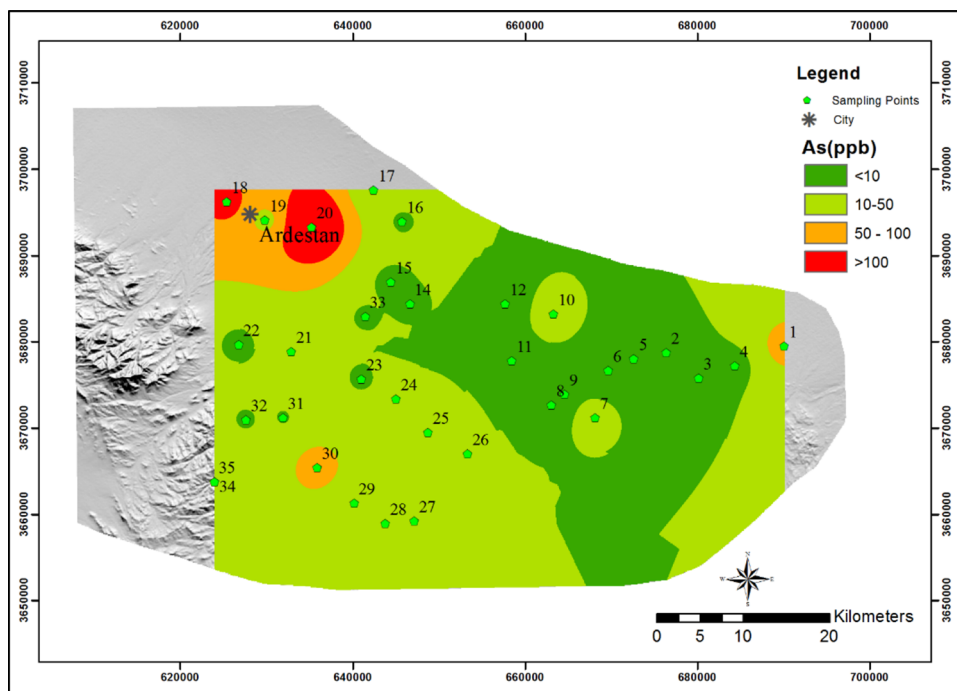
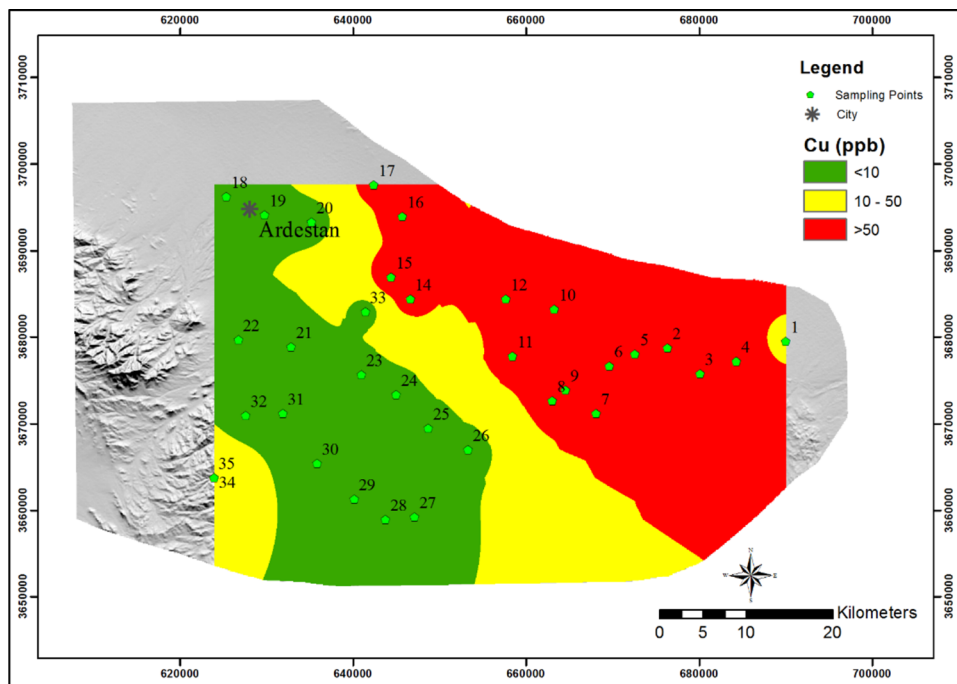


Fig. 12 Spatial distribution of Cu values of groundwater samples of the study area



high (Table 8). Using scaled HPI values, 51% of samples were classified as having low pollution levels, 46% with medium and 3% with high pollution levels (Fig. 16). Figure 17 shows the spatial distribution of MI values in the study area based on the inverse distance weighting interpolation method.

Computed MI values for groundwater samples are presented in Table 9. The mean MI value is 3.88. Water quality classification using MI has been conducted by Lyulko et al. (2001) and Caerio et al. (2005) (Table 10).

Water quality classification using MI (Table 11) was carried out (Fig. 18).

Fig. 13 Spatial distribution of Ni values of groundwater samples of the study area

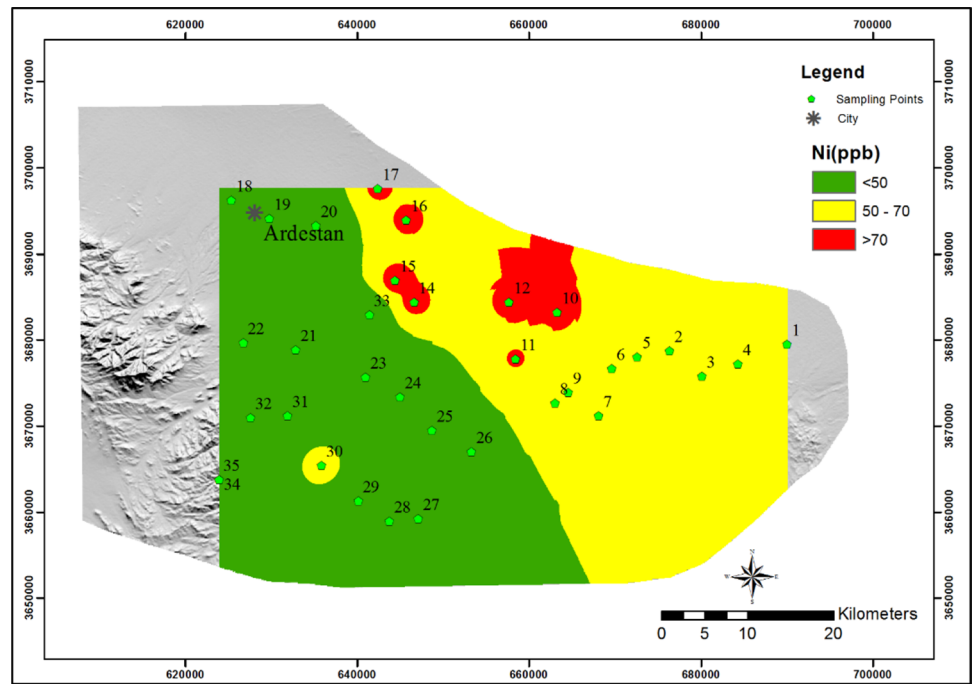
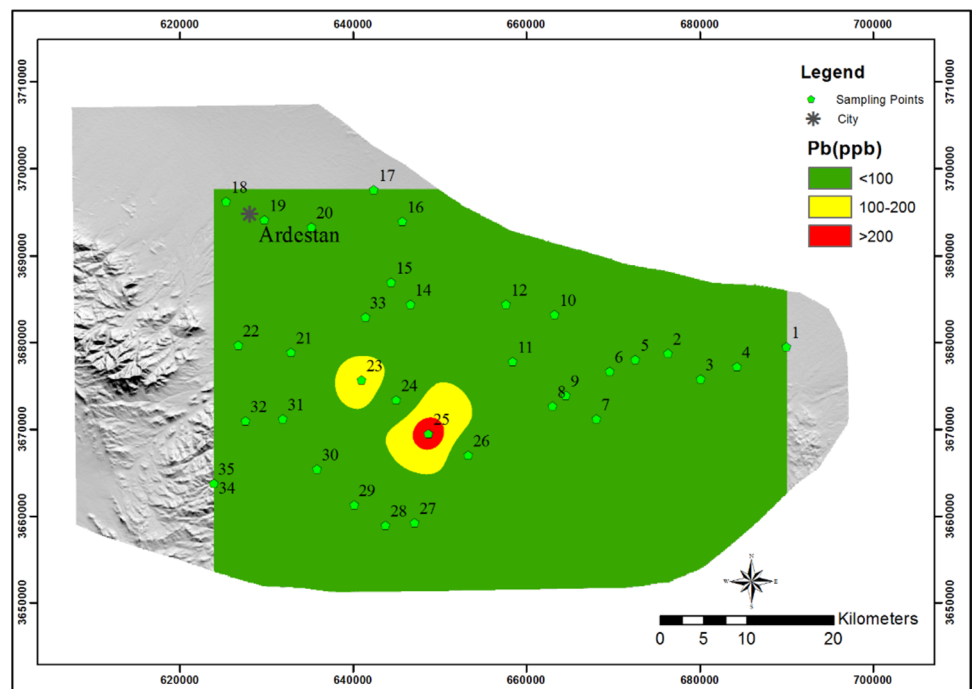


Fig. 14 Spatial distribution of Pb values of groundwater samples of the study area



The MI results show that two samples in the study area are significantly contaminated with heavy metals (sample numbers: 1 and 25). These sampling sites are located on Late Eocene (granodiorite, diorite, and gabbro) rock unit. The contamination may be due to the phenomenon of

volcanism and bedrock erosion in the study area. Nineteen samples were observed strongly polluted with heavy metals (sample numbers 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 20, 23 and 30). This can be attributed to the phenomenon of volcanism, bedrock erosion and mining

Table 4 Descriptive summary statistics for analyzed heavy metals in the study area (Adapted from Siegel 2002)

Parameter	Units	Minimum	Maximum	Mean	MAC	% > MAC
As	mg/l	0.0015	0.240	0.024	0.05	11.00
Cu	mg/l	0.0005	0.0700	0.030	1.0	0.00
Cr	mg/l	0.0005	0.045	0.0018	0.05	0.00
Ni	mg/l	0.010	0.75	0.045	0.02	66.00
Pb	mg/l	0.0005	0.290	0.055	0.05	54.00
Zn	mg/l	0.0005	0.036	0.040	5.0	0.00

MAC maximum admissible concentration

Table 5 Standard values used for the indices computation

Parameter	W	S	I	MAC
As	0.02	0.05	0.001	0.05
Cu	0.001	1.5	0.05	1.0
Cr	0.020	0.05	0.001	0.05
Ni	0.05	0.07	0.02	0.02
Pb	0.02	0.01	0.05	0.05
Zn	0.0002	15	5	5.0

W weightage (1/MAC) (adopted from Edet and Offiong 2002), S standard permissible in mg/l, I highest permissible in mg/l, MAC maximum admissible concentration/upper permissible

activities (often copper). Six samples were moderately polluted with heavy metals (sample numbers 18, 22, 26, 28, 29 and 31). Bedrock erosion in the study area can be a potential reason. Seven samples were slightly polluted with heavy metals (sample numbers 19, 24, 27, 32, 33, 34 and 35). This can be a result of agricultural activities in the region. One sample was clean with respect to heavy metal (sample number 21). This sampling site is near the Ardistan city and is located on a hillside with andesite–basalt rock unit. Figure 19 shows the spatial distribution of MI values in the study area based on the inverse distance weighting interpolation method.

Table 6 Mean HPI calculation for groundwater samples of study area

Parameter	Mean Value (mg/l) Mi	Standard permissible value (mg/l) Si	Highest desirable value (mg/l) Ii	Unit weighting W_i	Sub-index Q_i	$W_i \times Q_i$
As	0.023	0.05	0.01	0.02	33	0.66
Cu	0.030	1.5	0.050	0.001	1	0.001
Cr	0.0019	0.05	0.01	0.02	20	0.44
Ni	0.044	0.07	0.02	0.05	49	2.45
Pb	0.056	0.1	0.05	0.02	13	0.26
Zn	0.039	15.0	5.0	0.0002	49	0.0098

M median concentration value, $n=35$, S highest permissible value, I maximum desirable value, MAC maximum admissible concentration

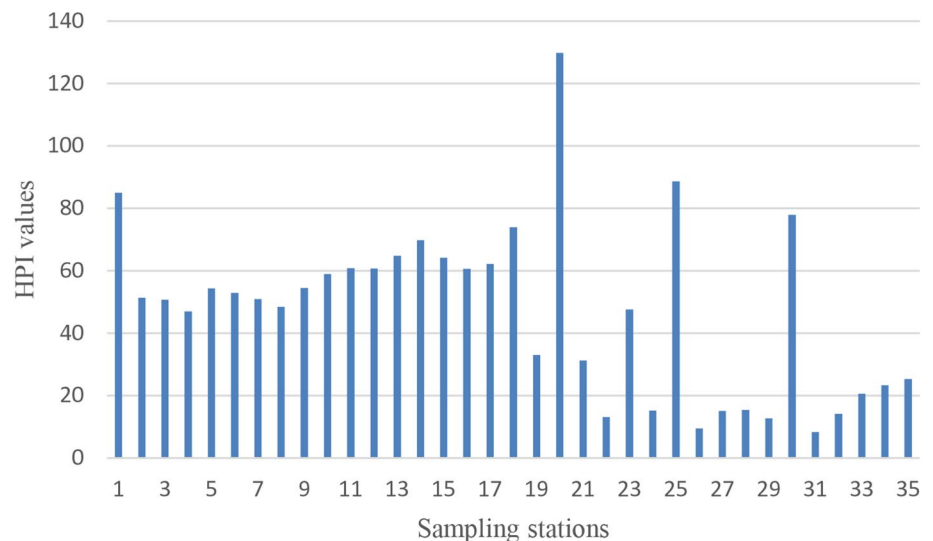
Statistical analyses

The correlation coefficient matrix for the hydrochemical parameters, anions and cations, and heavy metals are presented in Table 12.

The highest correlation exists between EC and TDS ($r=0.99$) because all of the dissolved components cause increased ionic concentration, as well as increased EC concentration. EC and TDS are moderately related to temperature ($r=0.678$ and 0.672 , respectively). A strong positive correlation was observed between TDS with Mg^{2+} , Na^+ , and SO_4^{2-} ($r=0.710$, 0.772 , and 0.942 , respectively) and also between HCO_3^- with Na^+ ($r=0.667$). Also, the strong positive correlation observed between K^+ with Ca^{2+} and Mg^{2+} ($r=0.818$ and 0.759 , respectively). This implies that these ions were derived from the common source. Ca^{2+} and Mg^{2+} presented a strong positive correlation ($r=0.855$), indicating a common source. The pH was negatively correlated with all metals with the exception of lead. The positive correlation between pH and Pb in this research is remarkable and consistent with the redox potential of the metal relative to hydrogen. The correlation relations show that there is a significant positive relation between nickel and copper ($r=0.757$, $p<0.01$), and also between nickel with lead and MI ($r=0.695$ and 0.714 , respectively). The correlation studies show that the relation between copper and nickel with arsenic is negative ($r=-0.550$ and $r=-0.506$, respectively)

Table 7 Heavy metal pollution index of study area at various sampling locations and median deviation

Station number	HPI	Median deviation	Class	Station number	HPI	Median deviation	Class
1	84.95	50.95	Medium	19	32.97	-1.03	Low
2	51.30	17.30	Medium	20	129.75	95.75	High
3	50.70	16.70	Low	21	31.28	-2.72	Low
4	46.91	12.91	Low	22	13.06	-20.94	Low
5	54.40	20.40	Medium	23	47.58	13.58	Low
6	52.90	18.90	Medium	24	15.24	-18.76	Low
7	50.94	16.94	Low	25	88.57	54.57	Medium
8	48.44	14.44	Low	26	9.49	-24.51	Low
9	54.45	20.45	Medium	27	15.06	-18.94	Low
10	58.97	24.97	Medium	28	15.43	-18.57	Low
11	60.84	26.84	Medium	29	12.74	-21.26	Low
12	60.75	26.75	Medium	30	77.93	43.93	Medium
13	64.74	30.74	Medium	31	8.34	-25.66	Low
14	69.78	35.78	Medium	32	14.13	-19.87	Low
15	64.19	30.19	Medium	33	20.61	-13.39	Low
16	60.64	26.64	Medium	34	23.27	-10.73	Low
17	62.19	28.19	Medium	35	25.26	-8.74	Low
18	73.95	39.95	Medium				

Fig. 15 Bar diagram of HPI values in the study area

and indicate one variable increases as the other decreases, and vice versa (Figs. 11, 12, 13). The correlation between HPI and MI is significant ($r=0.850$) and the results show the similar trends at various sampling locations. MI shows high positive correlation with Ni ($r=0.714$) and Pb (0.758). HPI has moderate negative relation with Zn ($r = -0.521$).

The rotated factor pattern after extraction using varimax rotation is given in Table 13. According to the results of the initial eigen values, five principal components extracted by

scree plot explained 85.3% of the total variance (Fig. 20), which is quite good and can be relied upon to identify the main sources of variation in the hydrochemistry. Principal component analysis of different parameters is presented in Table 13.

The first component (PC1), with 41.93% of the total variance, indicates that EC and TDS have high loading and reflecting the physicochemical characteristics of water quality while Temperature and Cr have moderate loading.

Fig. 16 HPI values of groundwater samples in the study area

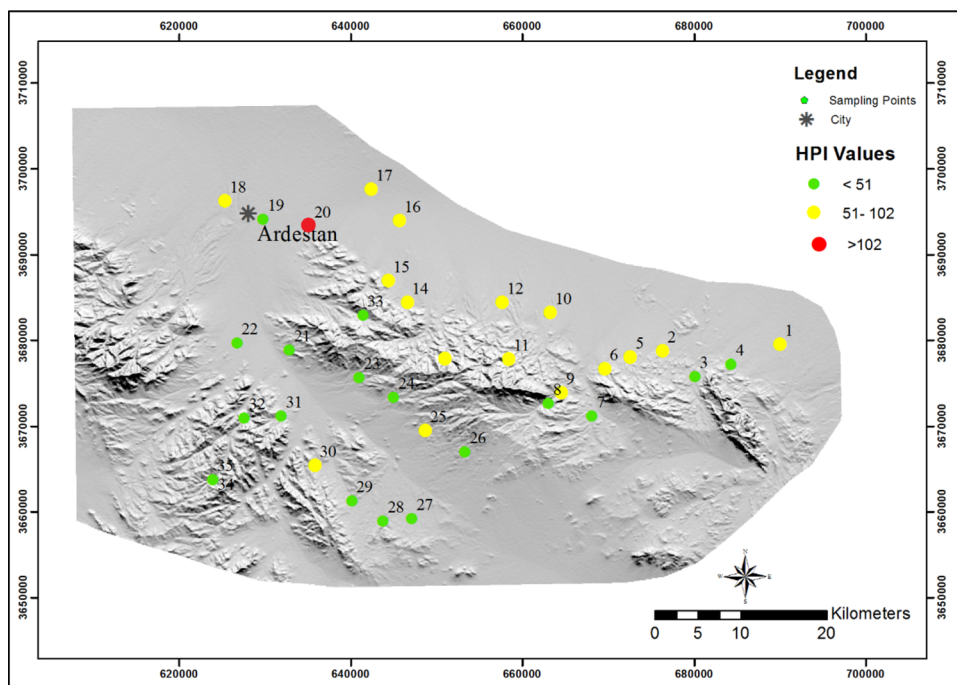


Table 8 Classification of groundwater water quality based on modified categories of HPI

ID	Index method	Class	Extent of pollution
1	HPI	<51	Low
		51–102	Medium
		>102	High

Also, there are high positive loadings of Ca^{2+} , Mg^{2+} , Na^+ , SO_4^{2-} and Cl^- , and probably shows the result of mineral water reactions in the study area.

The second component (PC2), with 19.39% of the total variance, contains high loadings for HCO_3^- , Cu and Ni. PC1 and PC2 are assumed to be indicative of the natural processes and water–rock interaction.

Fig. 17 Spatial distribution of HPI values of groundwater samples in the study area

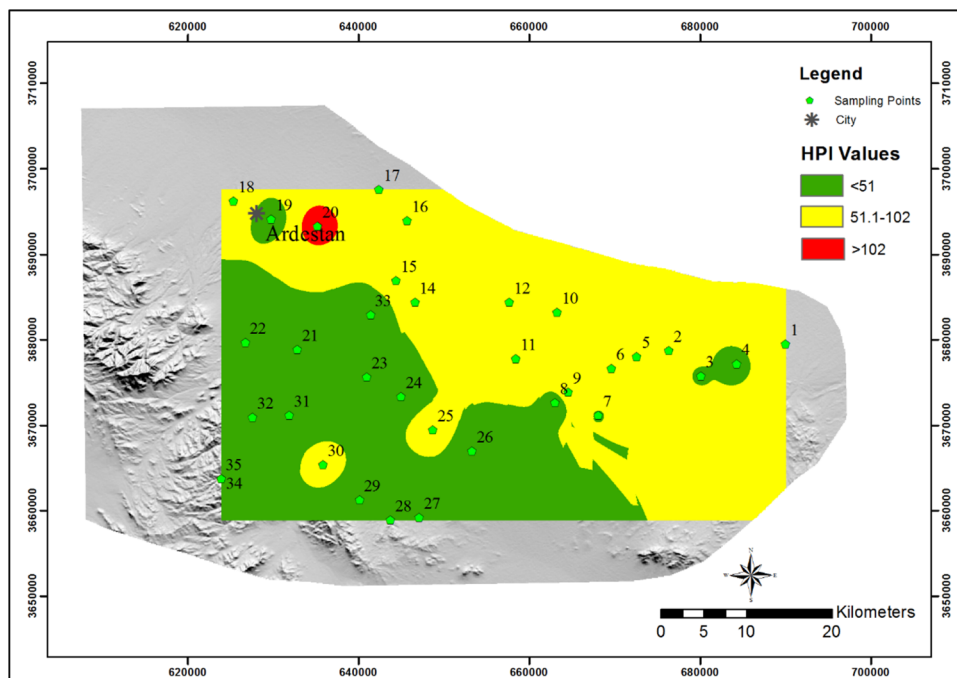


Table 9 The mean MI calculation for groundwater samples in the study area (Adapted from Siegel 2002)

Heavy metals	Concentration (C_i) (mg/l)	Maximum allowable concentration (MAC)	$MI = \sum_{i=1}^n \frac{C_i}{(MAC)_i}$
As	0.023	0.05	0.46
Cu	0.030	1.0	0.03
Cr	0.0019	0.05	0.039
Ni	0.044	0.02	2.21
Pb	0.056	0.05	1.13
Zn	0.039	5.0	0.0079

MAC maximum admissible concentration

Table 10 Water quality classification using MI

MI value	Characteristics	Class
<0.3	Very pure	I
0.3–1.0	Pure	II
1.0–2.0	Slightly affected	III
2.0–4.0	Moderately affected	IV
4.0–6.0	Strongly affected	V
> 6.0	Seriously affected	VI

The third component (PC3), with 10.1% of the total variance, indicates that K^+ and As have high loading while pH and HPI have moderate loading and can be ascribed to the natural hydrogeochemical evolution of groundwater by groundwater–geological interaction. Also, it reflects that the source of As in the groundwater is the weathering

process of minerals and anthropogenic sources (arsenical pesticides for protecting crops).

The fourth component (PC4) which contributes 7.8% of the total variance, indicates that Pb has high loading while MI has moderate loading and can be the result of entry from agricultural run-off.

The five component (PC5) contributes 6.1% of the total variance and is only associated with Zn. It can be attributed to the excessive use of zinc sulfate, which is an important constituent of fertilizers used in the region.

Conclusion

In this research, water quality and hydrogeochemistry characteristics of groundwater in north Isfahan of Iran have been investigated through analyzing samples from 35 stations. The quality of water in the study area, with regard to heavy metals (As, Cu, Cr, Ni, Pb, and Zn) has also been assessed. The Piper diagram showed that the groundwater in the study area has four types: Na–Cl, Na– SO_4 , Na– HCO_3 and Ca– HCO_3 . This result suggests that there might be a considerable number of different processes influencing the chemistry of groundwater in the study area and indicating the variable nature of the groundwater chemistry. A maximum HPI value of 129.75 was obtained for a sampling site adjacent to Ardestan City. The HPI in this location is higher than the critical index value of 100, indicating critical contamination with heavy metals. Using HPI index metric, 51% of samples were classified as having low pollution levels, 46% medium pollution levels and

Table 11 Results of water quality classification using MI in the study area

Sample no	MI	Median deviation	Class	Sample no	MI	Median deviation	Class
1	6.74	2.86	VI	19	1.95	–1.92	III
2	4.61	0.73	V	20	5.26	1.38	V
3	4.46	0.58	V	21	0.81	–3.06	II
4	4.36	0.48	V	22	2.34	–1.53	IV
5	4.69	0.81	V	23	4.45	0.57	V
6	4.64	0.76	V	24	1.69	–2.18	III
7	4.82	0.94	V	25	6.82	2.94	VI
8	4.50	0.62	V	26	2.02	–1.85	IV
9	4.98	1.10	V	27	1.63	–2.24	III
10	5.27	1.39	V	28	2.48	–1.39	IV
11	5.10	1.22	V	29	2.07	–1.80	IV
12	5.08	1.20	V	30	5.98	2.10	V
13	5.37	1.49	V	31	2.40	–1.47	IV
14	5.77	1.89	V	32	1.99	–1.88	III
15	5.27	1.39	V	33	1.33	–2.54	III
16	5.26	1.38	V	34	1.62	–2.25	III
17	5.86	1.98	V	35	1.11	–2.76	III
18	3.09	–0.78	IV				

Fig. 18 MI values of ground-water samples in the study area

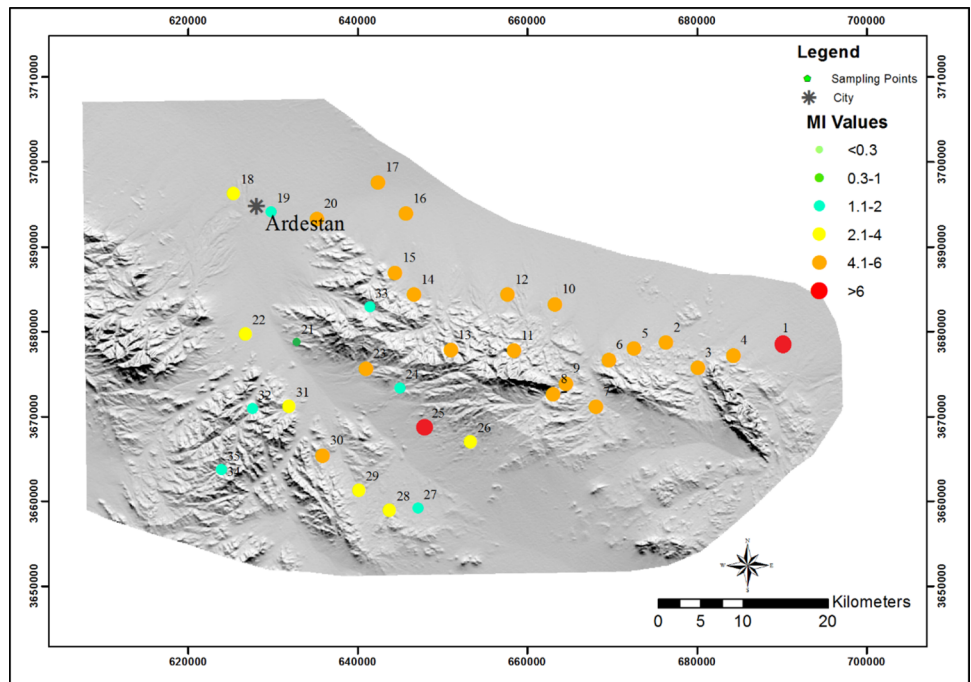
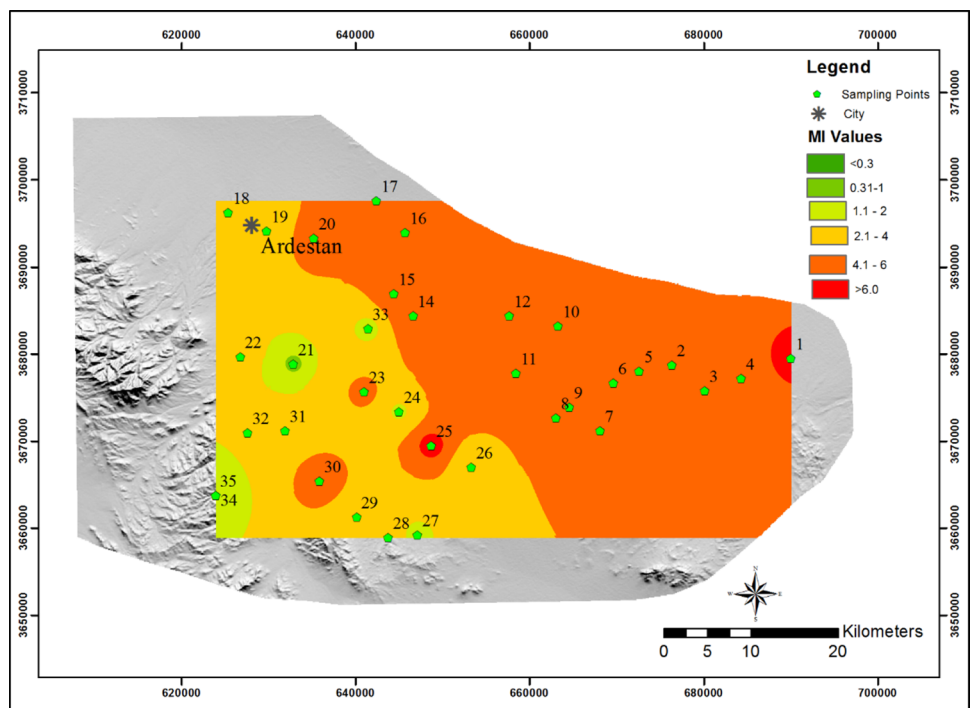


Fig. 19 Spatial distribution of MI values of groundwater samples in the study area



3% high pollution levels. Also, the MI results showed that two samples in the study area are significantly contaminated with a heavy metal.

Findings of the correlation analysis and PCA method show a strong impact of anthropogenic and agricultural sources for pollution load in the study area. Results indicate that there are water samples in the study area with

Table 12 Correlation matrix for physicochemical parameters, anions and cations, and heavy metals in the study area (Spearman's correlation)

	Ca	Mg	Na	K	HCO ₃ ⁻	SO ₄ (²⁻)	Cl ⁻	TDS	EC
Ca	1.000								
Mg	0.855**	1.000							
Na	0.573**	0.561**	1.000						
K	0.818**	0.759**	0.606**	1.000					
HCO ₃ ⁻	0.556**	0.309	0.667**	0.505**	1.000				
SO ₄ (²⁻)	0.406*	0.610**	0.712**	0.476**	0.063	1.000			
Cl ⁻	0.412*	0.618**	0.738**	0.472**	0.116	0.929**	1.000		
TDS	0.461**	0.710**	0.772**	0.555**	0.182	0.942**	0.953**	1.000	
EC	0.460**	0.654**	0.766**	0.555**	0.175	0.940**	0.954**	0.999**	1.000
pH	-0.028	-0.046	0.178	0.180	-0.015	0.242	0.284	0.208	0.206
T	0.481**	0.588**	0.630**	0.664**	0.374*	0.540**	0.688**	0.672**	0.678**
As	-0.002	0.085	-0.068	-0.025	-0.377*	0.291	0.289	0.338*	0.348*
Cr	0.245	0.291	0.170	0.239	-0.016	0.243	0.214	0.236	0.236
Cu	0.318	0.060	0.238	0.268	0.625**	-0.269	-0.226	-0.211	-0.218
Ni	0.218	-0.101	0.300	0.138	0.616**	-0.217	-0.140	-0.140	-0.152
Pb	0.088	-0.068	0.321	0.145	0.341*	-0.029	0.053	0.017	0.006
Zn	-0.458**	-0.281	-0.308	-0.397*	-0.375*	-0.061	-0.167	-0.153	-0.148
HPI	0.470**	0.226	0.366*	0.428*	0.479**	0.080	0.148	0.124	0.120
MI	0.289	0.015	0.408*	0.289	0.501**	0.027	0.110	0.093	0.084
	pH	T	As	Cr	Cu	Ni	Pb	Zn	
Ca									
Mg									
Na									
K									
HCO ₃ ⁻									
SO ₄ (²⁻)									
Cl ⁻									
TDS									
EC									
pH	1.000								
T	0.282	1.000							
As	-0.021	0.025	1.000						
Cr	-0.298	0.128	0.250	1.000					
Cu	-0.285	-0.015	-0.550**	0.258	1.000				
Ni	-0.160	0.039	-0.506**	-0.012	0.757**	1.000			
Pb	0.013	0.164	-0.326	0.147	0.480**	0.695**	1.000		
Zn	-0.114	-0.301	0.079	-0.249	-0.357*	-0.175	-0.228	1.000	
HPI	0.018	0.280	0.095	0.184	0.445**	0.434**	0.473**	-0.521**	
MI	0.006	0.232	-0.034	0.160	0.496**	0.714**	0.758**	-0.355*	

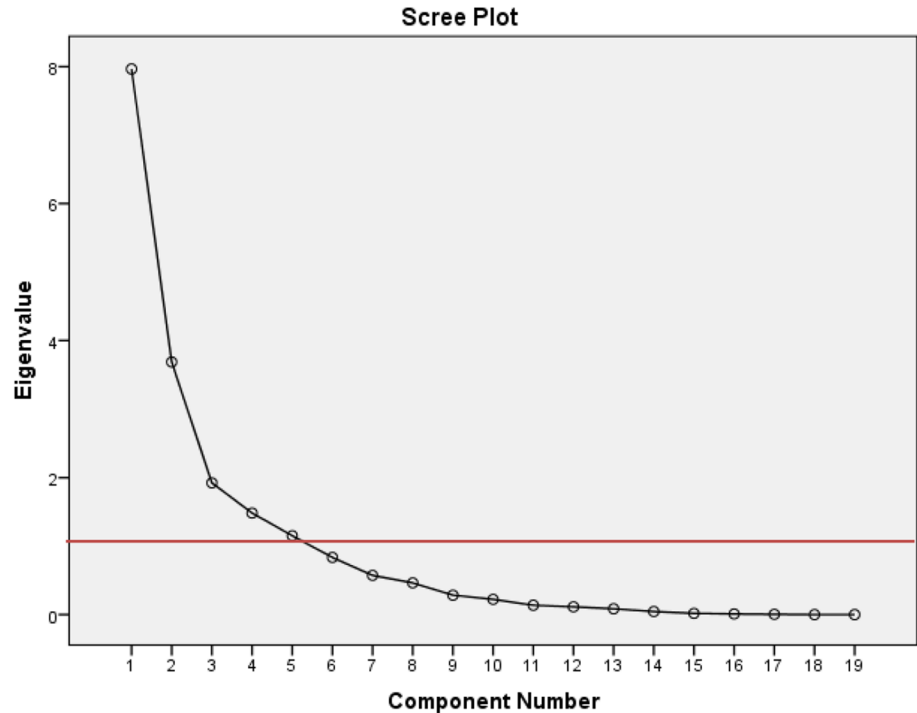
the best quality for irrigation and drinking purposes in the future (e.g., stations 21, 22, 24, 26, 27, 31, 32, 33, 34 and 35). Using the methodology proposed in this work, one

could perform similar analyses and nominate groundwater wells with suitable quality for different beneficial uses (drinking, industrial, agricultural, etc.).

Table 13 Principal component analysis (varimax with Kaiser normalization) for physicochemical parameters, heavy metals, HPI and MI in the study area

Parameters	Component				
	1	2	3	4	5
Ca ²⁺	0.836	0.240	0.227	-0.149	-0.125
Mg ²⁺	0.856	0.139	0.185	-0.205	0.003
Na ⁺	0.888	0.306	0.092	0.138	0.022
K ⁺	0.352	0.150	0.819	-0.183	-0.080
HCO ₃ ⁻	0.184	0.896	0.193	-0.060	0.149
SO ₄ ⁽²⁻⁾	0.888	-0.075	0.219	-0.104	0.038
Cl ⁻	0.947	-0.013	0.142	0.115	-0.142
TDS	0.969	-0.035	0.186	0.050	-0.045
EC	0.969	-0.037	0.180	0.051	-0.042
pH	0.177	-0.315	0.626	0.077	0.366
T	0.673	0.119	0.247	0.051	0.385
As	0.265	-0.177	0.853	-0.007	-0.196
Cr	0.613	0.001	-0.199	0.384	-0.360
Cu	0.031	0.918	-0.208	0.047	-0.101
Ni	0.015	0.925	-0.149	0.211	0.010
Pb	-0.091	0.080	-0.081	0.895	0.070
Zn	-0.089	0.013	-0.146	0.014	0.794
HPI	0.204	0.477	0.636	0.456	-0.198
MI	0.137	0.657	-0.245	0.680	-0.074
% of variance	41.925	19.39	10.1	7.8	6.1
Cumulative %	41.925	61.321	71.449	79.257	85.323

Fig. 20 PCA scree plot of the eigenvalues in the study area



Acknowledgements The authors would like to thank the Amirkabir University of Technology (Polytechnic Tehran) and Water Resources Management of Isfahan Province for supporting this research. The contribution of Adonis Fard Mousavi, Samira Rezaei and Bashir Shokouh Saljughy are highly appreciated.

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