

# Hydrochemistry and contamination of groundwater resources in the Behbahan plain, SW Iran

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**Abstract** The Behbahan plain with an area of 1320 km<sup>2</sup> is located in an arid to semi-arid zone. Since it has restricted water resources, the preservation of groundwater quality is of great importance. In order to investigate the contamination possibility which could be resulted from geogenic and anthropogenic sources, 30 wells were sampled during August 2014. The water samples were analyzed for heavy elements As, Cd, Fe, Mn, Zn, Sr, Pb, Se, Co, B and Cr, anions Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, cations Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>, and important quality parameters including pH, EC and TDS, using ICP-OES, FAES, OAS, titration, conductometry and drying methods. The concentration of major ions in most of the samples exceeds the allowed levels of WHO standard for drinking water. Geochemical data show that the water chemistry is influenced dominantly by weathering and dissolution of carbonate and evaporitic minerals, ion-exchange processes, and human activities. Groundwater in the Behbahan plain is mainly of calcium-sulfate facies, according to Piper diagram. The concentrations of nitrate and K show little correlation with that of major ions, suggesting unnatural sources for them. These components originated possibly from dissolution of nitrate- and K-bearing fertilizers used in farming. Geochemical maps indicate that concentration of toxic trace elements such as Pb, Cd, Cr, B, As and those of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and Na<sup>+</sup> ions have incremental trends. These high concentrations are caused probably by domestic and industrial waste waters leaked into the groundwater aquifer. The heavy metal pollution index

(HPI) in 29 samples is greater than 100, indicating that groundwater in the study area is highly polluted with heavy elements.

**Keywords** Groundwater · Hydrochemistry · Pollution · Heavy elements · Correlation coefficient

## Introduction

Groundwater is increasingly become an essential commodity throughout the world because of its incremental usage for various purposes. Quality and quantity of groundwater are equally important due to the suitability of water for drinking, irrigation and industrial uses (Singh et al. 2011a). Variation of groundwater quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities (Kumar and Singh 2015; Singh et al. 2011a). Geological formations such as carbonates and evaporites, which are relatively highly water soluble decreases the quality of groundwater. Human may causes contamination of groundwater by doing such activities as excess use of groundwater, developing agriculture and ranching, use of chemical fertilizers, and urban and industrial sewages disposal. Moreover, the composition and quality of groundwater is determined by the quality of surface water and soil characteristics. The chemical properties of groundwater also depend upon the chemistry of water in the recharge area as well as on the different geochemical processes that are occurring in the subsurface (Kumari et al. 2012; Singh et al. 2011b, c).

Heavy elements are of potential pollutants for environment. High amounts of heavy elements incorporated into nourishing resources may cause serious damage to human

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health. These elements are stable in environment and concentrate in herbaceous and animal tissues, resulting in toxic effects on living creatures (Bhaskar et al. 2010). Therefore, the heavy elements have come to focus of attention around the world, because of their toxic properties (Das 1990).

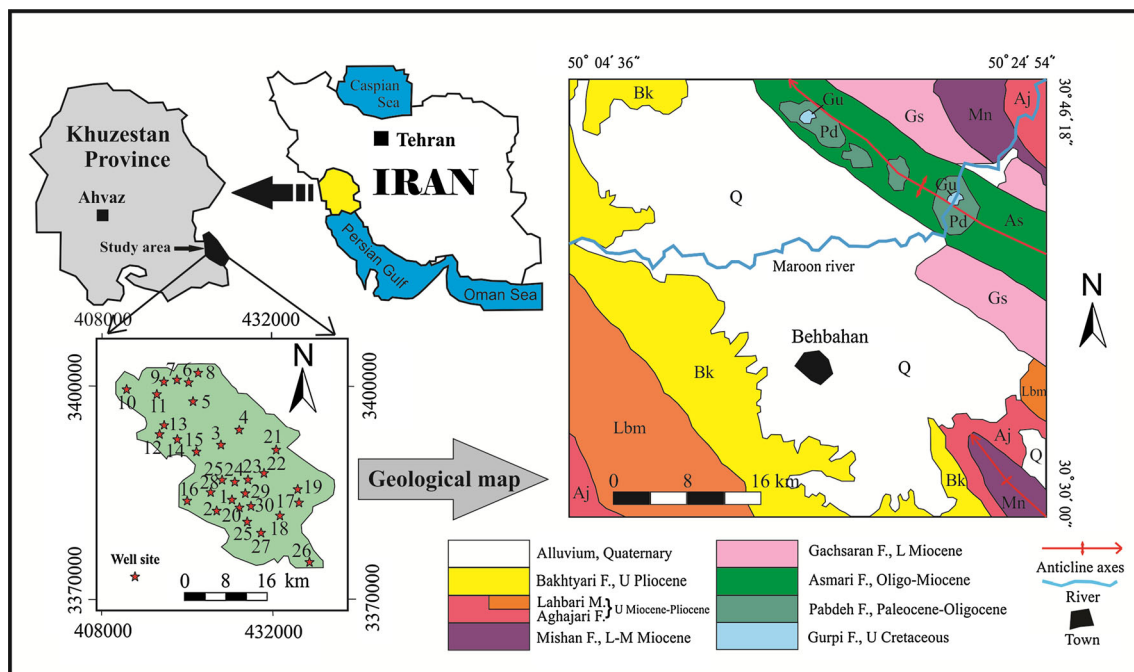
The possible heavy element contamination in groundwater from the Behbahan plain has not been evaluated so far. Taking into account the hydrogeological conditions, extensive agricultural activities, disregarding hygienic issues in urban and industrial sewages disposal, as well as burning of fossil fuels around oil wells near the study area, it is expected that the groundwater is contaminated with heavy elements, rendering its quality unsuitable for drinking purposes. This study was carried out with the objective to assess the hydrogeochemical processes that govern groundwater quality in the Behbahan plain and its suitability for drinking needs.

### Climatological and geological considerations

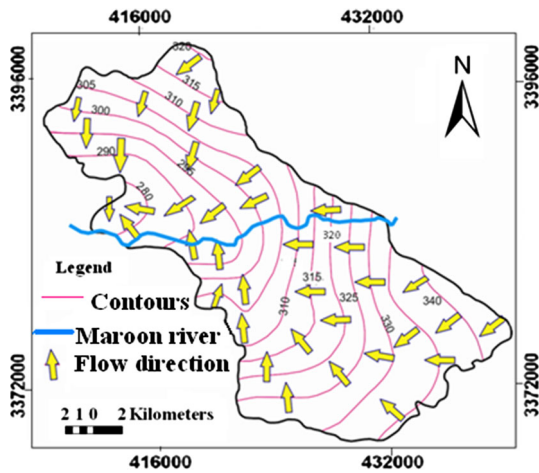
The Behbahan plain falls between north latitudes  $30^{\circ}31'$  and  $31^{\circ}00'$  and east longitudes  $50^{\circ}00'$  and  $50^{\circ}30'$  in southeastern Khuzestan Province of southwestern Iran (Fig. 1). This plain covers an area of  $1320 \text{ km}^2$  with an elliptical shape. Its long diameter is parallel to the main northwest-southeast directing trend of Zagros Mountain

Ranges. The mean elevation of the plain is 313 m above sea level. It is located in an arid to semi-arid area with an average annual precipitation of 336 mm, average annual moisture of 46 %, and average annual evaporation of 3401 mm. The absolute maximum temperature reaches up to  $50^{\circ}\text{C}$  in July and August and the minimum to less than  $0^{\circ}\text{C}$  in January and February.

Geologically, the study area is located in the Zagros Simply Folded Belt (Stöcklin 1968). Pazanan and Rag-e-Sefid anticlines lie down in south and southwest, and Khaviz and Bangestan anticlines in north and northwest of the Behbahan plain. The geological formations cropping out in the area are of upper cretaceous to recent ages (Fig. 1). From an older to younger order, marly Pabdeh and Gurpi Formations, limy Asmari Formation, evaporitic Gachsaran Formation, marly and limy Mishan Formation, red marly and sandy Aghajari Formation, silty and marly Lahbari Member, conglomeratic Bakhtyari Formation, and recent alluvial deposits crop out in the study area. Groundwater resources of the plain are contained in alluviums composed of clay, silt, marl, gravel and fine- to coarse-grained sand, and in Bakhtyari conglomerate. The overall direction of groundwater flow in the aquifer is from northern and eastern margins to the south of the Behbahan plain, toward the Maroon river (Fig. 2). The Maroon river drains the southern part of the plain. The draining action reaches to its maximum level in southwest of the plain.



**Fig. 1** Maps showing the geographic situation and geological map (modified from Macleod 1970) of the study area. Location of the sampled wells is also shown



**Fig. 2** Contour map (in meter) showing the depth of water table and the direction of groundwater flow in the aquifer of the Behbahan plain

## Materials and methods

### Sampling and analysis of the samples

A total of 30 wells supplying drinking and agricultural waters were sampled during August 2014, the driest season with respect to meteoritic precipitations. Geographical locations of the sampled wells were recorded using a Trimble GeoExplorer 2008 Series GPS apparatus. The samples were stored in 250 ml polypropylene bottles after rinsing with the water samples. Since the required parameters were measured separately in three laboratories (see below), three bottles of water were sampled in each well site. The sampling operation was done 15 min after pumping in order to stabilize pH and TDS (total dissolved solids) parameters at constant values, rendering the sampled water a good indication of water accumulated in the aquifer. All samples were kept in temperatures below 4 °C during sampling and analysis operations.

Values of pH and EC (electrical conductivity) were measured immediately after sampling on well site using a Hach-SensION5 conductivity meter (EC meter) and a Jenway pH meter. The nitrate concentration is measured using optical absorption spectroscopy (OAS) during a time span of maximum 24 h after sampling operation at the laboratory of Bid Boland Gas Refinery Company, Behbahan, Iran. The concentration of major anions and cations  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were measured using titration method. The concentration of  $\text{K}^+$  and  $\text{Na}^+$  cations determined using flame atomic emission spectrometry (FAES), and that of TDS using drying method. The concentration of major anions and cations, as well as TDS values were analyzed at the laboratory of Khuzestan Water and Power Authority, Ahvaz, Iran. The samples taken for heavy elements were passed through 0.45  $\mu\text{m}$  membranous

filters and acidified to below pH 2 by concentrated nitric acid, in order to avoid possible precipitation of cations, growth of micro-organisms, and to reach to a least surface absorption by container wall (Langmuir 1997). These samples were analyzed for elements As, Cd, Fe, Mn, Zn, Sr, Se, Co, B and Cr using inductively coupled plasma optical emission spectroscopy (ICP-OES) at the laboratory of Faculty of Sciences, Zanjan University, Zanjan, Iran.

### Preparation of geochemical maps and data analysis

The values of different water quality parameters are presented in Figs. 3, 4, 5, 6, 7 and 8 and Tables 1, 2, 3 and 4 compared to World Health Organization (WHO) standards. The values of different variables formed the attribute database for Inverse Distance Weighted interpolation maps using ArcGIS 9.2 software. The correlation coefficients between chemical components of groundwater were calculated using Microsoft Excel 2010 software, in order to estimate the source of chemical elements.

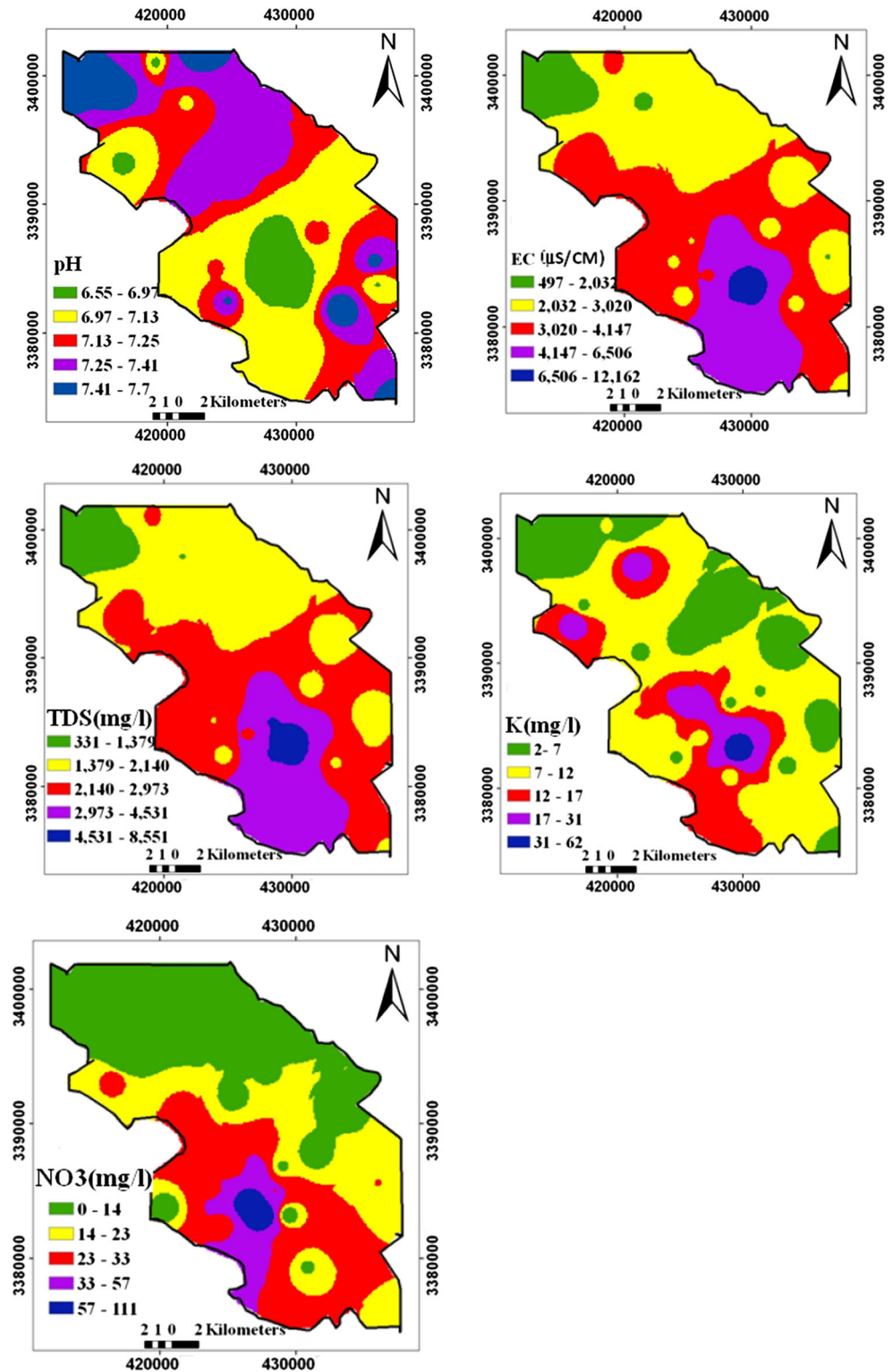
## Results and discussion

### Hydrochemistry of major components

Table 1 presents the statistical summary of hydrochemical parameters analyzed in groundwater samples from the study area. The pH values fall in the range of 6.55–7.71 with an average value of 7.18, indicating that groundwater in the Behbahan plain is neutral to alkaline. The alkaline character of groundwater may suggest semi-arid climatic influence on groundwater. This alkalinity also suggests that dissolution has been occurred due to interaction between soil and rainwater, giving groundwater alkaline character (Singh et al. 2013). The average values for TDS and EC are 2437.7 mg/l and 3221.6  $\mu\text{S}/\text{cm}$ , respectively. The TDS and EC values in more than 90 % of the samples are above the allowed level for drinking water according to WHO (2008) standard. However, in the northwestern part of the area, TDS and EC quantities fall in the prescribed levels of WHO (2008) standard for drinking water. Examining the distribution maps (Fig. 3), identical spatial variations are found for EC and TDS values. The positive correlation between concentration of chemical constituents and quality factors may clarify the source of these components (Hasanzadeh et al. 2010). The high value for correlation coefficients between TDS and  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  (Table 2) suggests that the source of dissolved salts in groundwater is the dissolution of carbonate and evaporitic minerals.

The nitrate values in groundwater from the study area range from 1.4 to 111.4 mg/l, with an average of 21.19 mg/l

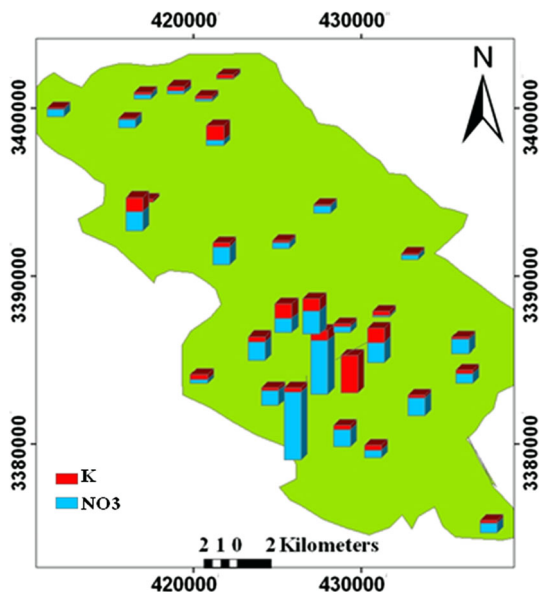
**Fig. 3** Variation of pH, EC, TDS, potassium and nitrate amounts in groundwater over the Behbahan plain



1. The nitrate concentration in wells no. 1 and 29 (87.5 and 111.4 mg/l, respectively) locating in the urban areas of the plain are above the permissible level for drinking water according to WHO (2008) standard. Geochemical maps (Fig. 3) show identical variations for nitrate and potassium

over the majority of the plain. The concentrations of nitrate and potassium represent little correlation with those of major ions, indicating an unnatural source for these constituents. It is fairly probable that they have been brought into groundwater through dissolution of chemical





**Fig. 4** Diagram comparing concentrations of nitrate and potassium in groundwater over the Behbahan plain

fertilizers. Vast areas in the Behbahan plain are under agricultural activities using ammonium nitrate- and potassium-bearing fertilizers. When rain and irrigation waters leach through the soil which has been extra-treated with nitrate- and potassium-bearing fertilizers, the natural waters are contaminated by nitrate and potassium (Mesa et al. 2003). On the other hand, Fig. 4 shows that concentration of nitrate is greater than that of potassium in most places of the plain. The higher concentration of nitrate than that of potassium, especially in urban areas is possibly due to nitrification process (Saha and Kumar 1990). Nitrogen-bearing compounds involved in the aquifer by urban and rural sewages are converted to nitrate through nitrification process. The high permeability of sandy aquifer provides favored conditions for vertical oxygen transfer into the deep parts of the aquifer (Hamilton and Helsel 1995; Kraft et al. 1999). The nitrification process occurred at the presence of abundant oxygen will result in the conversion of ammonium to nitrate (Lorite-Herrera and Jiménez-Espinosa, 2008):

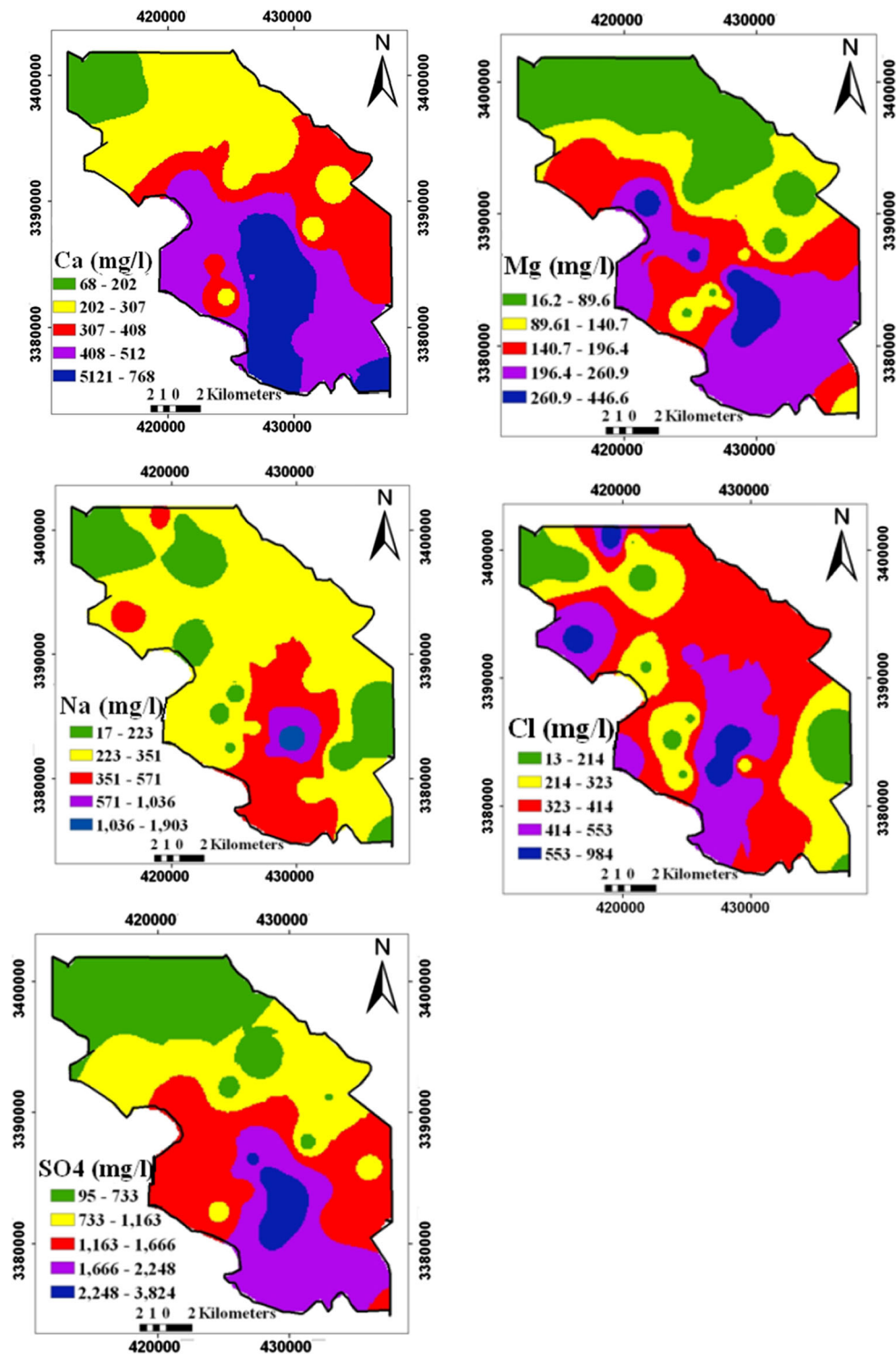


The identical spatial variations for calcium, sulfate and magnesium in the study area (Fig. 5) suggest a common source from which these components have been introduced into the groundwater. Extensive carbonate- and sulfate-rich rocks, such as limestone, dolomitic limestone, marl, and gypsum- and anhydrite-bearing evaporitic rocks are the major sources for carbonate and sulfate weathering in the study area. The carbonates and sulfates available in these rocks could have been dissolved during irrigation,

rainfall infiltration and groundwater movement, and added to the groundwater system with recharging water (Singh et al. 2013, 2014). The  $\text{Ca}^{2+} + \text{Mg}^{2+}$  to  $\text{TZ}^+$  (total major cations) ratio is equal to 0.6, indicating the abundance of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in groundwater. This abundance is due to the weathering of carbonate rocks. The variations of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus total major cations ( $\text{TZ}^+$ ) are a linear trend with a correlation coefficient of 0.6 (Fig. 6a). This linear relation also states that the dissolution of carbonate minerals in groundwater has been occurred (Avatar et al. 2013). In the  $\text{HCO}_3^- + \text{SO}_4^{2-}$  versus  $\text{Ca}^{2+} + \text{Mg}^{2+}$  diagram (Fig. 6b), the data points falling along the equiline ( $\text{HCO}_3^- + \text{SO}_4^{2-} = \text{Ca}^{2+} + \text{Mg}^{2+}$ ) indicate the dissolution of carbonate and sulfate (gypsum and anhydrite) minerals (Datta et al. 1996; Singh et al. 2014). Moreover, most of the data points are located in the  $\text{Ca}^{2+} + \text{Mg}^{2+}$  axis side, indicating that the source of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is not only the dissolution of carbonate rocks, but other processes such as ion-exchange are also involved (Singh et al. 2014). The variation extent for sulfate concentration is greater than those of calcium and magnesium (Fig. 5). So, an alternative source for sulfate must be considered in addition to dissolution of gypsum. The organic materials present in sewage contain sulfur which can be converted to sulfate due to oxidation (Langmuir 1997). Therefore, the sewages of absorptive wells have probably played an important role in the increase of sulfate concentration in groundwater from the study area.

The high concentration of calcium and bicarbonate is related to the presence of marl and limestone in the study area. The concentration of bicarbonate increases toward the urban areas of the plain, probably due to organic material-enriched urban sewages involved in the aquifer. Carbon dioxide produced as a result of organic material decomposition leads to the formation of bicarbonate in water. Dispersion of data points in  $\text{HCO}_3^-$  versus total major cations diagram (Fig. 6c) indicates the effects of anthropogenic activities (Rao and Rao 2010). In this diagram, most of the data points locate near the equiline, suggesting the weathering of carbonate rocks; however, the presence of some data points above the equiline and close to the bicarbonate axis reveals that the chemistry of groundwater is under the influence of human activities (Avatar et al. 2013).

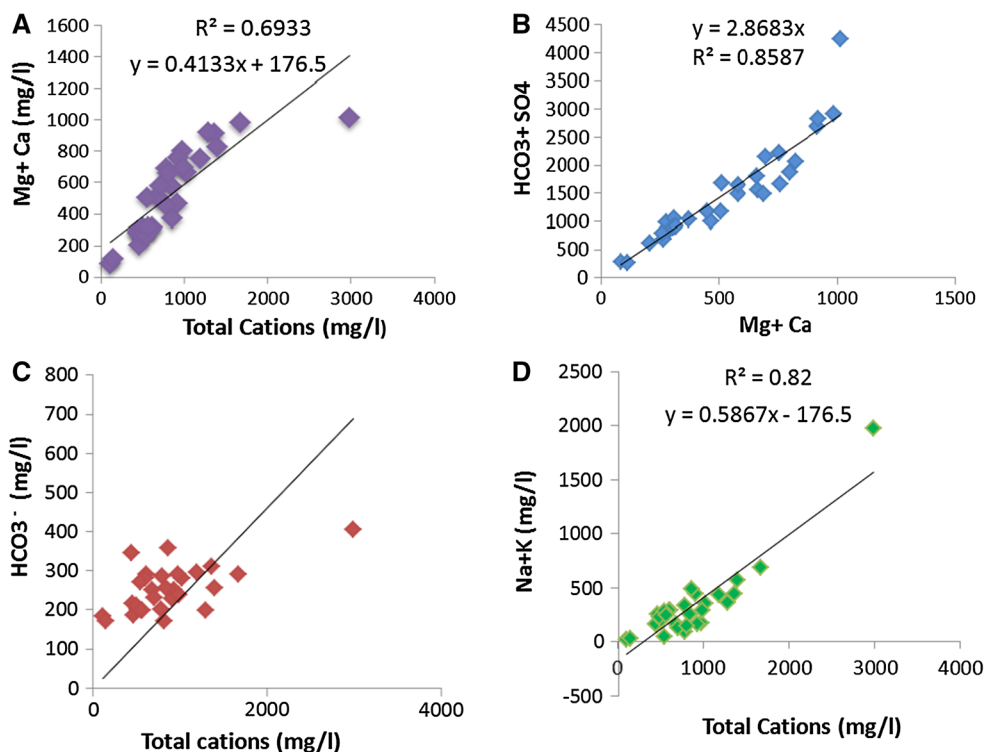
The similar spatial variations for sodium and chlorine state the dissolution of halite mineral (Fig. 5). The high values for sodium and chlorine concentrations are due to the homogeneous dissolution of halite in water, delivering directly  $\text{Na}^+$  and  $\text{Cl}^-$  into the groundwater. The source of halite in the Behbahan plain is evaporitic beds within Gachsaran and Aghajari Formations, as well as Lahbari Member. The high positive correlation between  $\text{Na}^+ + \text{K}^+$



**Fig. 5** Geochemical maps showing the variations of major cations and anions concentration in groundwater over the Behbahan plain

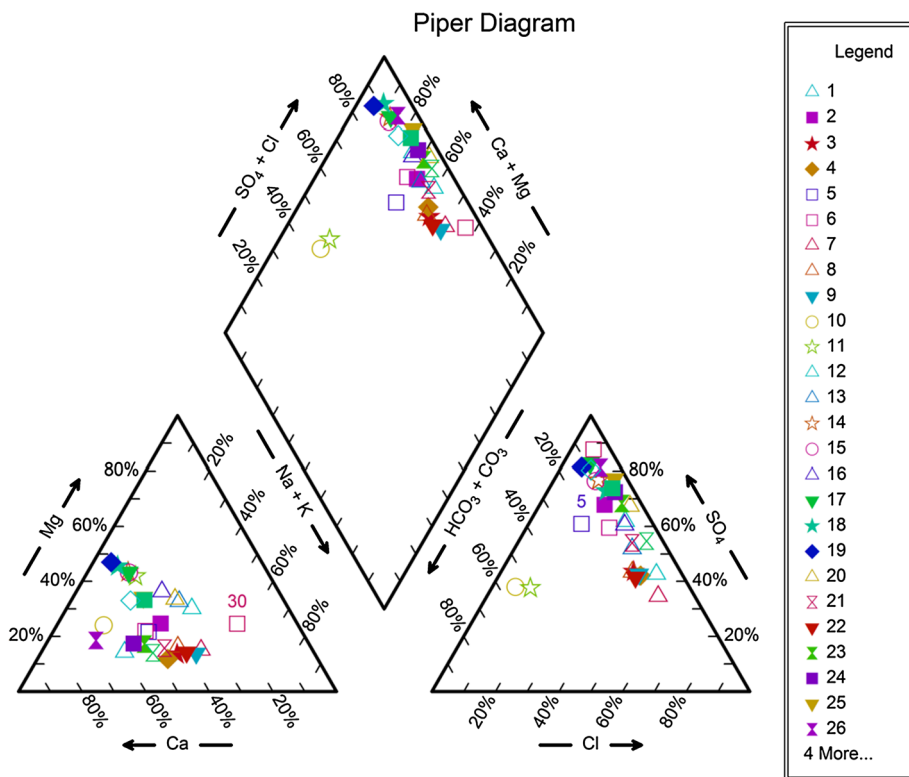
and total major cations ( $TZ^+$ ) (Fig. 6d) indicates that chemical weathering of clay minerals might have caused sodium and potassium to be involved into the groundwater (Sarin et al. 1989; Stallard and Edmond 1983). On the other

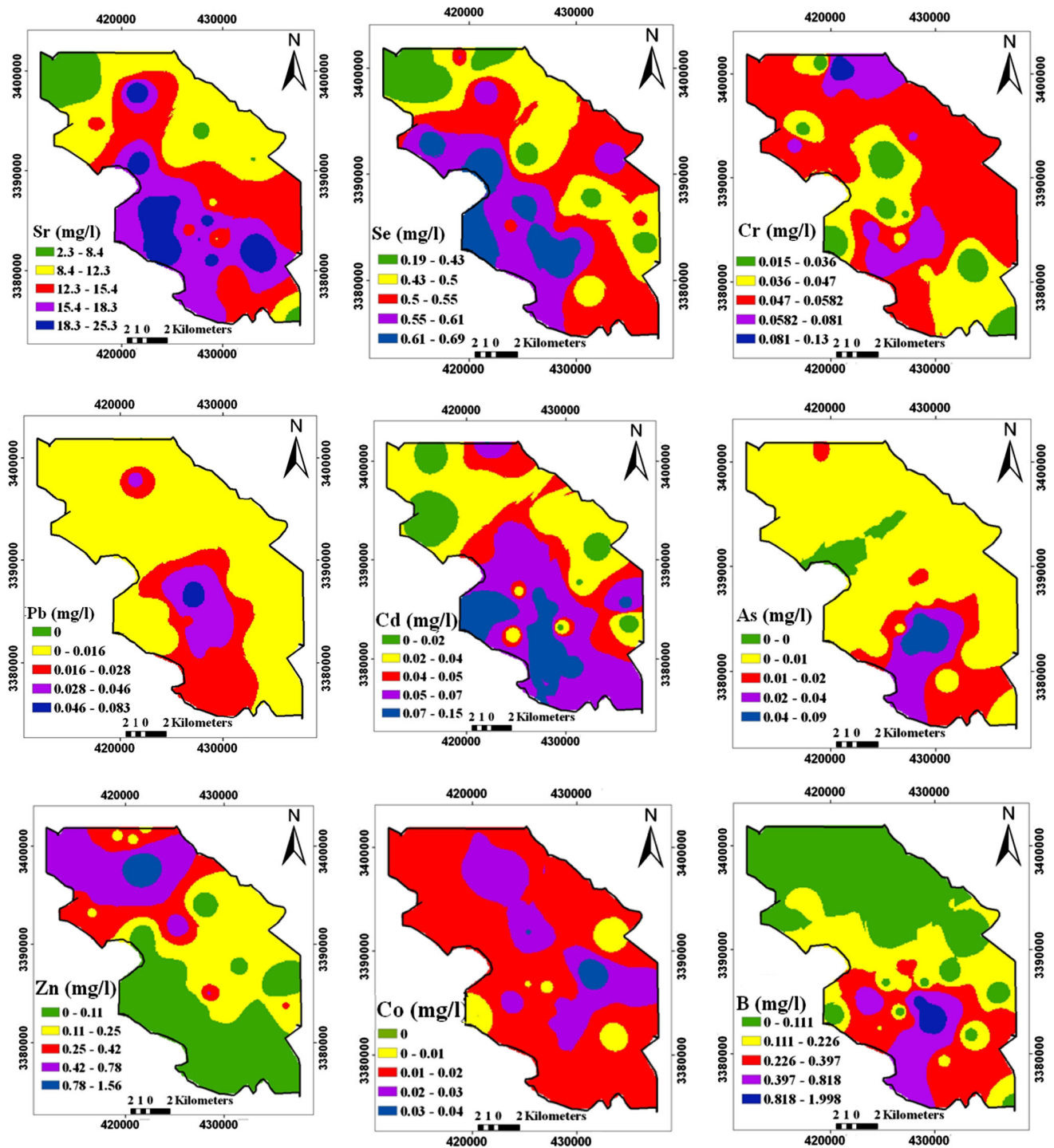
hand, the domestic sewage is characterized by high amounts of salt (Laws 2000). The leakage of these sewage into the groundwater causes the concentrations of sodium and chlorine to be increased.



**Fig. 6** a Scatter plot of  $Mg^{2+} + Ca^{2+}$  versus total major cations; b scatter plot of  $HCO_3^- + SO_4^{2-}$  versus  $Mg^{2+} + Ca^{2+}$ ; c scatter plot of  $HCO_3^-$  versus total major cations; and d scatter plot of  $Na^+ + K^+$  versus total major cations

**Fig. 7** Piper diagram for groundwater samples in the Behbahan plain





**Fig. 8** Geochemical maps showing the concentration of heavy elements in groundwater over the Behbahan plain

### Groundwater facies

The Piper (1944) diagram is commonly used to determine the type of water, hydrochemical facies, and hydrogeochemical evolution of the aquifers (Stober and Bucher 1999). The Piper diagram for groundwater in the Behbahan

plain indicates that 75 % of the samples are of calcium-sulfate ( $\text{Ca-SO}_4$ ) facies (Fig. 7). This is due to the dissolution of carbonate and evaporitic minerals such as gypsum, calcite and anhydrite in groundwater. About 24 % of the samples are of sodium-chloride ( $\text{Na-Cl}$ ) facies. This group of samples has been resulted from dissolution of



**Table 1** Statistical summary of hydrogeochemical parameters for groundwater samples

| Variable                             | Range        | Average ± SD    | Maximum desirable (WHO 1963, 2008) | Maximum allowable (WHO 1963, 2008) |
|--------------------------------------|--------------|-----------------|------------------------------------|------------------------------------|
| pH                                   | 6.55–7.71    | 7.18 ± 0.3      | 6.5–8.5                            | 9.2                                |
| EC (µS/cm)                           | 497–12,190   | 3421.6 ± 2082   | –                                  | 1500                               |
| TDS (mg/l)                           | 331–8570     | 2437.7 ± 1489   | 500                                | 1500                               |
| Na <sup>+</sup> (mg/l)               | 17.48–1909   | 269.5 ± 334     | 250                                | 450                                |
| K <sup>+</sup> (mg/l)                | 2.34–62.4    | 10.59 ± 11.9    | –                                  | –                                  |
| Ca <sup>2+</sup> (mg/l)              | 68–769       | 379.56 ± 181.65 | 75                                 | 200                                |
| Mg <sup>2+</sup> (mg/l)              | 16.2–447.6   | 150.16 ± 109.94 | 50                                 | 150                                |
| Cl <sup>−</sup> (mg/l)               | 13.68–405.65 | 360.13 ± 56.64  | 200                                | 600                                |
| HCO <sub>3</sub> <sup>−</sup> (mg/l) | 170.8–405.65 | 251.64 ± 57.61  | –                                  | –                                  |
| CO <sub>3</sub> <sup>2−</sup>        | 0.0          | 0.0             | –                                  | –                                  |
| SO <sub>4</sub> <sup>2−</sup> (mg/l) | 95.52–383.84 | 1249.05 ± 826   | 200                                | 400                                |
| NO <sub>3</sub> <sup>−</sup> (mg/l)  | 1.4–111.4    | 21.19 ± 6.43    | –                                  | 50                                 |

evaporitic minerals and leakage of domestic sewages into groundwater. Samples no. 10 and 11 from the northwestern part of the plain are of calcium-bicarbonate (Ca-HCO<sub>3</sub>) facies, which is probably due to proximity to recharge area. The groundwater in well no. 30 locating in the urban area is of sodium-sulfate (Na-SO<sub>4</sub>) facies, possibly due to involved urban sewages into the aquifer.

**Hydrochemistry of heavy elements**

One of the most important groundwater pollutants is toxic trace elements. These elements are incorporated into groundwater via meteoric processes, land erosion, and anthropogenic activities including industrial and domestic sewages, as well as mining operations (Laws 2000; Liu and Lipták 2000). Table 3 presents data regarding the concentration of heavy elements in analyzed samples, compared with WHO (1963) standard. The highest concentration value in groundwater is that of Sr with an average value of 13.59 mg/l. Strontium tends greatly to substitute in Ca-bearing minerals (Langmuir, 1997). So, the high concentration of Sr in groundwater is in line with the extensive occurrence of limestone and evaporitic formations in the study area. Considering the low correlation coefficients between Cr and Cd with major cations and anions (Table 2), the source of these heavy metals in groundwater is probably related to anthropogenic activities such as industrial sewages. Similarly, Se might have originated from anthropogenic sources including industrial sewerage and phosphate fertilizers (Kumar and Riyazuddin 2011). The low concentration of Fe, Mn, Zn and Co is in accordance with the geology of the area, because lithologies containing them are not found here. The wells containing higher concentrations of Pb, B and As than other wells locate in urban areas of the Behbahan plain

(Fig. 1). The industrial and urban sewages permeated into the aquifer through absorptive wells can cause the concentration of toxic trace elements to be increased in groundwater (Singh et al. 2014). Figure 8 shows the distribution patterns for heavy element concentrations over the study area.

**Heavy metal pollution index**

In order to evaluate the effect of heavy metals on the quality of water, it is useful to calculate the heavy metal pollution index (HPI). The HPI is formulated as (Kumari et al. 2013; Mohan et al. 1996):

$$HPI = \frac{\sum_i^n W_i Q_i}{\sum_i^n W_i}$$

where  $W_i$  is the unit weightage of the  $i$ th parameter considered, and is defined as a value inversely proportional to the recommended standard ( $S_i$ ) of the corresponding parameter ( $W_i = 1/S_i$ ) (Prasad and Bose 2001);  $n$  is the number of parameters considered; and  $Q_i$  is the sub-index of  $i$ th parameter. The sub-index ( $Q_i$ ) of the parameter is calculated separately as the following equation:

$$Q_i = \sum_i^n \frac{|M_i - I_i|}{S_i - I_i} \times 100$$

where  $M_i$ ,  $I_i$  and  $S_i$  are the monitored, ideal and standard values for the  $i$ th heavy metal considered, respectively. The quantity  $|M_i - I_i|$  indicates numerical difference of the two values, ignoring the algebraic sign; that is the absolute value (Yankey et al. 2013). According to indexing given by Prasad and Bose (2001), if the HPI value is greater than 100, water is polluted with heavy metals; if HPI = 100, water is at threshold of pollution risk; and if HPI is below 100, water lacks heavy metals pollution.

**Table 2** Pearson's correlation matrix of element concentrations in groundwater samples

|                               | pH   | TDS  | EC   | K <sup>+</sup> | Na <sup>+</sup> | Mg <sup>2+</sup> | Ca <sup>2+</sup> | HCO <sub>3</sub> <sup>-</sup> | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | As  | Cd  | Cr  | Co  | Mn  | Fe  | Pb   | Zn   | Sr   | Se   | B |  |
|-------------------------------|------|------|------|----------------|-----------------|------------------|------------------|-------------------------------|-----------------|-------------------------------|------------------------------|-----|-----|-----|-----|-----|-----|------|------|------|------|---|--|
| pH                            | 1    |      |      |                |                 |                  |                  |                               |                 |                               |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| TDS                           | 0.05 | 1    |      |                |                 |                  |                  |                               |                 |                               |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| EC                            | 0.45 | 0.9  | 1    |                |                 |                  |                  |                               |                 |                               |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| K <sup>+</sup>                | 0.32 | 0.64 | 0.65 | 1              |                 |                  |                  |                               |                 |                               |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| Na <sup>+</sup>               | 0.35 | 0.84 | 0.88 | 0.7            | 1               |                  |                  |                               |                 |                               |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| Mg <sup>2+</sup>              | 0.22 | 0.53 | 0.49 | 0.38           | 0.3             | 1                |                  |                               |                 |                               |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| Ca <sup>2+</sup>              | 0.31 | 0.48 | 0.48 | 0.15           | 0.17            | 0.35             | 1                |                               |                 |                               |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| HCO <sub>3</sub> <sup>-</sup> | 0.34 | 0.36 | 0.38 | 0.04           | 0.43            | 0.12             | 0.1              | 1                             |                 |                               |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| Cl <sup>-</sup>               | 0.31 | 0.16 | 0.18 | 0.01           | 0.11            | 0.0              | 0.21             | 0.12                          | 1               |                               |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| SO <sub>4</sub> <sup>2-</sup> | 0.37 | 0.82 | 0.76 | 0.44           | 0.5             | 0.66             | 0.73             | 0.18                          | 0.06            | 1                             |                              |     |     |     |     |     |     |      |      |      |      |   |  |
| NO <sub>3</sub> <sup>-</sup>  | 0.04 | 0.02 | 0.25 | 0.0            | 0.0             | 0.01             | 0.22             | 0.0                           | 0.11            | 0.04                          | 1                            |     |     |     |     |     |     |      |      |      |      |   |  |
| As                            | 0.23 | 0.69 | 0.7  | 0.48           | 0.64            | 0.24             | 0.22             | 0.19                          | 0.2             | 0.42                          | 0.06                         | 1   |     |     |     |     |     |      |      |      |      |   |  |
| Cd                            | 0.0  | 0.05 | 0.04 | 0.0            | 0.0             | 0.0              | 0.33             | 0.0                           | 0.18            | 0.11                          | 0.22                         | 0.1 | 1   |     |     |     |     |      |      |      |      |   |  |
| Cr                            | 0.0  | 0.01 | 0.01 | 0.01           | 0.02            | 0.0              | 0.0              | 0.03                          | 0.0             | 0.0                           | 0.0                          | 0.0 | 0.1 | 1   |     |     |     |      |      |      |      |   |  |
| Co                            | 0.0  | 0.0  | 0.0  | 0.0            | 0.02            | 0.1              | 0.0              | 0.03                          | 0.0             | 0.0                           | 0.01                         | 0.0 | 0.0 | 0.1 | 1   |     |     |      |      |      |      |   |  |
| Mn                            | 0.02 | 0.07 | 0.07 | 0.04           | 0.08            | 0.09             | 0.0              | 0.06                          | 0.0             | 0.03                          | 0.03                         | 0.0 | 0.0 | 0.0 | 0.1 | 1   |     |      |      |      |      |   |  |
| Fe                            | 0.1  | 0.0  | 0.0  | 0.0            | 0.02            | 0.03             | 0.0              | 0.02                          | 0.0             | 0.0                           | 0.0                          | 0.0 | 0.0 | 0.1 | 0.1 | 0.0 | 1   |      |      |      |      |   |  |
| Pb                            | 0.3  | 0.3  | 0.27 | 0.2            | 0.16            | 0.09             | 0.53             | 0.19                          | 0.12            | 0.4                           | 0.14                         | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 1    |      |      |      |   |  |
| Zn                            | 0.0  | 0.03 | 0.02 | 0.2            | 0.0             | 0.06             | 0.14             | 0.08                          | 0.02            | 0.07                          | 0.08                         | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0  | 1    |      |      |   |  |
| Sr                            | 0.07 | 0.0  | 0.06 | 0.06           | 0.0             | 0.21             | 0.22             | 0.09                          | 0.01            | 0.3                           | 0.09                         | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.1 | 0.11 | 0.0  | 1    |      |   |  |
| Se                            | 0.21 | 0.05 | 0.2  | 0.2            | 0.01            | 0.21             | 0.39             | 0.09                          | 0.08            | 0.21                          | 0.2                          | 0.1 | 0.0 | 0.0 | 0.0 | 0.1 | 0.1 | 0.0  | 0.04 | 0.28 | 1    |   |  |
| B                             | 0.24 | 0.72 | 0.71 | 0.63           | 0.71            | 0.49             | 0.14             | 0.22                          | 0.0             | 0.58                          | 0.0                          | 0.6 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.08 | 0.0  | 0.05 | 0.06 | 1 |  |

**Table 3** Basic statistical parameters for heavy elements in groundwater samples

| Heavy metals | Range (mg/l) | Average ± SD | Maximum desirable (WHO 1963) | Maximum allowable (WHO 1963) | Samples below WHO                         | Samples above WHO                           |
|--------------|--------------|--------------|------------------------------|------------------------------|---|---|
| Fe           | 0.0–0.90     | 0.03 ± 0.02  | 0.3                          | 1.0                          | All samples                               | –   |
| Mn           | 0.0–0.51     | 0.02 ± 0.09  | 0.1                          | 0.5                          | All samples                               | –   |
| Zn           | 0.0–1.56     | 0.21 ± 0.31  | 5.0                          | 15                           | All samples                               | –   |
| Co           | 0.02–0.05    | 0.17 ± 0.01  | No standard limit defined    |                              |   |   |
| Cd           | 0.0–0.02     | 0.01 ± 0.03  | –                            | 0.01                         | Nos. 1–28, 30                             | No. 29                                      |
| Cr           | 0.02–0.13    | 0.05 ± 0.02  | –                            | 0.05                         | Nos. 1, 3, 7, 9, 10, 13–16, 18, 20, 24–27 | Nos. 2, 4–6, 8, 11,12, 17, 19, 21–23, 28–30 |
| Pb           | 0.0–0.84     | 0.12 ± 0.02  | –                            | 0.05                         | Nos. 1–23, 25–30                          | No. 24                                      |
| As           | 0.0–0.09     | 0.01 ± 0.02  | –                            | 0.005                        | Nos. 1–19, 21–29                          | Nos. 20, 30                                 |
| B            | 0.0–2.01     | 0.09 ± 0.4   | –                            | 1.0                          | Nos. 1–19, 21–28                          | Nos. 20, 29, 30                             |
| Se           | 0.1–0.49     | 0.32 ± 0.12  | –                            | 0.01                         | –   | All samples                                 |
| Sr           | 2.33–25.32   | 13.59 ± 5.8  | No standard limit defined    |                              |   |   |

**Table 4** Calculated values for heavy metal pollution index (HPI) based on the standard amounts of WHO (1963)

| Well no. | Heavy metal pollution index (HPI) | Well no. | Heavy metal pollution index (HPI) |
|----------|-----------------------------------|----------|-----------------------------------|
| 1        | 378.5                             | 16       | 408.4                             |
| 2        | 311.5                             | 17       | 142.6                             |
| 3        | 138                               | 18       | 198                               |
| 4        | 233.3                             | 19       | 253.3                             |
| 5        | 170.5                             | 20       | 260.6                             |
| 6        | 173.4                             | 21       | 309.4                             |
| 7        | 267                               | 22       | 177                               |
| 8        | 135.7                             | 23       | 202.3                             |
| 9        | 190.8                             | 24       | 332.5                             |
| 10       | 174                               | 25       | 358.9                             |
| 11       | 82                                | 26       | 276                               |
| 12       | 389.9                             | 27       | 191                               |
| 13       | 248.5                             | 28       | 265.7                             |
| 14       | 370.6                             | 29       | 368.8                             |
| 15       | 155.9                             | 30       | 368                               |

In this study, WHO (1963) standard was considered as criterion and the HPI values were calculated for all samples, considering nine heavy elements Fe, Zn, Mn, Se, Cd, Cr, Pb, As and B (Table 4). The HPI values are greater than 100 in 29 samples (Table 4), indicating that groundwater in the study area is highly polluted with heavy elements. The high HPI values in samples could be related to high concentrations of Se. The highest HPI value (408.8) belongs to well no. 16 that contains the highest concentration of Se among samples. Most of the wells locating within and around the urban area have HPI values greater than 300. This could be resulted from combustion of fossil fuels, consumption of plague killers and chemical fertilizers, and leakage of urban and industrial sewages into the groundwater (Ahmad et al. 2009). The well no. 11 in the

northwest of the study area lacks pollution with heavy elements (HPI = 82), but it is at the risk of being polluted with these elements.

**Conclusions**

Chemical analysis of the selected samples from groundwater in the Behbahan plain reveal that concentration of major constituents is above the permitted levels of WHO standard for drinking water in most of the samples. The concentration of anions and cations follow the orders  $SO_4^{2-} > Cl^- > HCO_3^- > NO_3^-$  and  $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ , respectively. The linearly related  $Ca^{2+} + Mg^{2+}$  concentrations to total major cations ( $TZ^+$ ) indicates

the dissolution of carbonate and evaporitic minerals in groundwater. The similar spatial variation for sodium and chlorine concentrations suggests the dissolution of halite in groundwater.

The dominant groundwater facies in the Behbahan plain is calcium-sulfate one. The domestic sewages leaked into the aquifer have increased the concentrations of sulfate, sodium and chloride. The dispersion of data points in bicarbonate versus total major cations diagram also indicates the effect of anthropogenic activities on the chemistry of groundwater. The concentrations of nitrate and potassium have little correlation with major ions, reflecting the unnatural source of these components. They have been probably brought into the groundwater through dissolution of chemical fertilizers. The extent in which concentration of nitrate varies is greater than that of potassium, owing to nitrification process acting on nitrogen-bearing compounds present in involved urban and rural sewages into the aquifer.

The concentration of heavy elements As, Cd, Cr, Pb and B in some samples, and that of Se in all samples are above the allowed levels of WHO standard for drinking water. The concentration of these elements follow the order  $Se > B > Pb > Cr > Cd > As$ . The concentrations of Fe, Mn, Zn and Co are very low and below the standard limit of WHO for drinking water. According to geochemical maps, groundwater pollution is least at the northwestern part, and is the maximum at the south and southwestern parts of the plain. The high concentration of heavy elements in the urban segment is obviously due to the leakage of urban and industrial sewages from absorptive wells. The calculated HPI values for selected samples based on the WHO standard for drinking water are greater than the permissive levels. The prolonged use of groundwater in this area, therefore, will bring about injurious results for inhabitants.

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