

# Controls on the distribution of arsenic and rare earth elements in groundwaters of the Bafgh city area, central Iran

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## ABSTRACT

High arsenic (As) contents in groundwater were found in the Bafgh area in central Iran and chosen for hydrogeochemical study. A total of 20 groundwater samples were collected from existing tube wells in the study areas in 2013 and analyzed. The water chemistry is predominantly of Na–Cl type, with concentrations of dissolved As in the range between 0.9 and 74.7  $\mu\text{g/L}$ . The chondrite-normalized rare earth elements patterns exhibited a flat profile, positive Gd anomaly with a predominance of light rare earth elements (LREEs) over heavy rare earth elements (HREEs), suggest that they originated from the same source. The metals in the groundwater of the region have a geological origin.

**Key words** | arsenic, Bafgh, hydrogeochemical, REEs

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## INTRODUCTION

Groundwater is generally considered to be a high quality ubiquitous resource, which constitutes approximately 97% of global freshwater and supports the supply of 25–40% of the world's drinking water (Kim *et al.* 2011; Taylor *et al.* 2013; Radic *et al.* 2016). Groundwater with high concentrations of As in drinking-water, which exceeds the World Health Organization (WHO) guideline (10 mg/L) (WHO 2011), receives global attention. This problem is experienced all over the world (Guo *et al.* 2010; Mahanta *et al.* 2015; Bondu *et al.* 2016). In Iran, the use of groundwater is increased owing to the increased water demand and the decline in surface water availability under climate conditions. Although arsenic contamination of groundwater has been reported in some parts of Iran (Mosaferi *et al.* 2008; Chitsazan *et al.* 2009; Keshavarzi *et al.* 2011), no comprehensive study has been conducted to identify groundwater contamination, especially in central Iran, which is facing a greater shortage of water.

However, a few of these studies attempted detailed hydrogeochemical investigations to understand the nature of its source, distribution, and the mechanism of As release in groundwater. Because of similar physical or chemical properties but slight differences, rare earth elements (REEs) have

been extensively applied as tracers for studying groundwater–aquifer rock interactions because of their generally coherent and predictable behavior (Guo *et al.* 2010; Shouyang *et al.* 2011; Chevis *et al.* 2015; Omonona & Okogbue 2017).

The aim of this study was to determine the chemical composition of the water and the main geochemical reactions that control the groundwater composition in an arid aquifer in central Iran where the arsenic concentration is high. Major ions and REEs to characterize geochemical behavior were used to understand the geochemical characteristics, the processes shaping the chemistry and quality of the groundwater of the area, and discuss and evaluate possible controls on their geochemical behavior; and implications of the REE patterns on mechanisms of As mobilization.

## STUDY AREA

The study area is situated in central Iran, in Yazd province, and has a hot temperate with dry desert climate, with mean maximum summer temperatures (July and August) of about 50 °C and minimum winter temperatures (January) of 10 °C,

with the annual precipitation being approximately 40–50 mm. Because of the water shortage, groundwater is the main resource of drinking water. The study area has a low population and the natural vegetation has been reduced to low bushes. Cultivation is limited to small fields of corn, wheat and palm trees (Torab 2008). The study area is part of Bafgh district that is considered as a part of the central Iran zone, and has conserved its characteristics as a platform since the Triassic period, but it has been affected by folds and thrusts since the Jurassic (Hossein Mirzaee 2015). The Bafgh district is the most important Fe metallogenic province in the region and a significant district on a worldwide basis, and is one of the greatest iron mining regions in Iran with 750 million tones of reserves (Jami 2005; Rajabzadeh *et al.* 2014). Some of these deposits have apatite and REE mineralization, and represent important resources (Torab 2008). Most of the study area is formed by recent

alluvium that consists of sand dunes, recent alluvium, young terraces, clay and salt flat. Volcanic Rocks consisting of basic to intermediate in the Paleozoic period affected by diorite intrusions, have an outcrop in the northeastern part of study area. The central part of the area consists of Paleozoic carbonate rocks. The conglomerate and gypsum-bearing marly clastic sediment (Miocene) overlaps the oldest rocks (Amini *et al.* 2005). The central and eastern basin is characterized by sand dunes (Figure 1).

## WATER SAMPLING AND ANALYTICAL METHODS

A total of 20 groundwater samples from wells were collected during the period of June 2013 to July 2013 in the study area. The geographical location of the sampling sites is shown in Figure 1. The selected wells are used for agricultural and

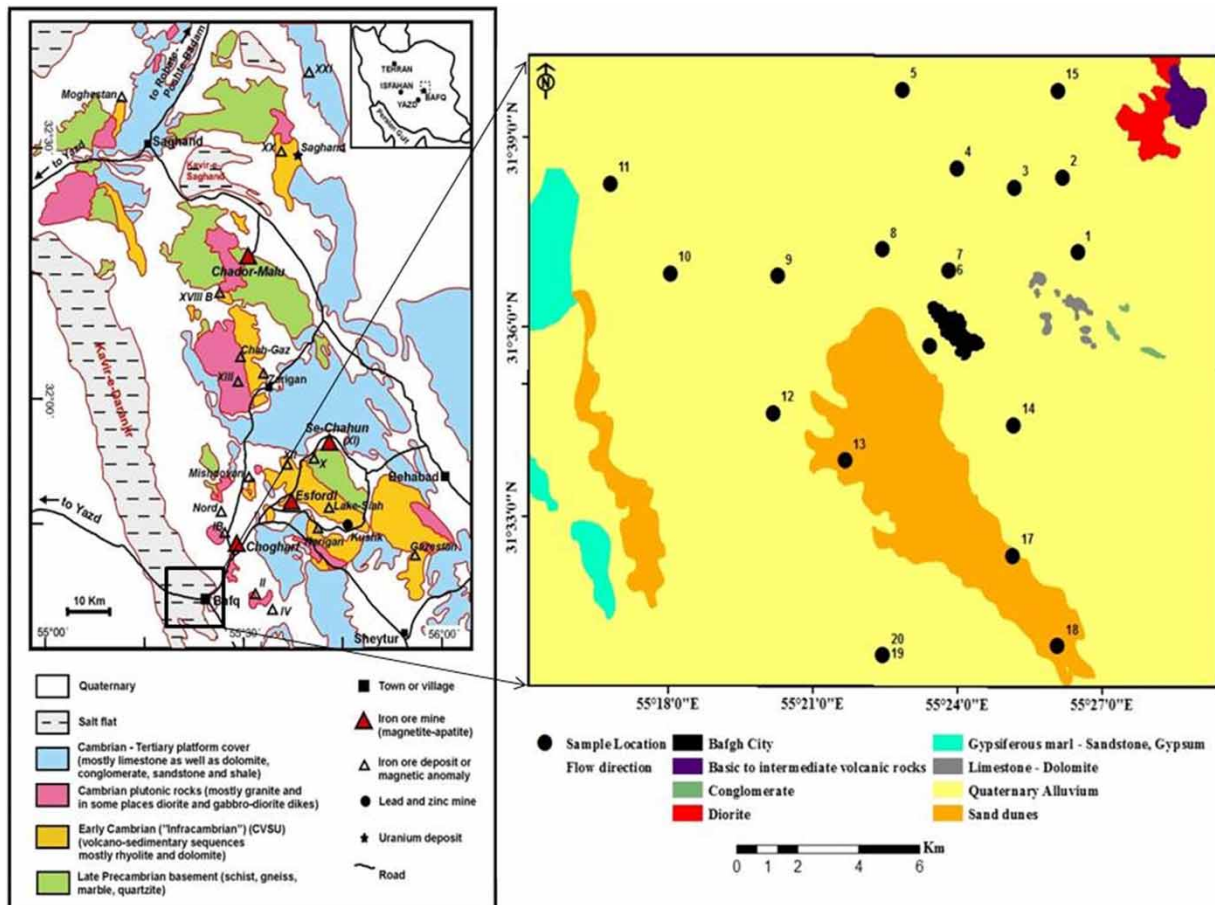


Figure 1 | Geology map of Bafgh district (Torab 2008) and a simplified geological map of the study area (modified from Amini *et al.* 2005).

domestic purposes. The samples were collected and stored in 100 ml polyethylene bottles. The bottles were rinsed several times with deionized water followed by rinsing three times with the groundwater to be sampled prior to their filling with groundwater samples to minimize the chance of any contamination. The water samples from bore wells were collected after pumping out water for about 10 min to remove stagnant water from the well. Immediately after sampling, pH, Eh, dissolved oxygen concentration, electrical conductivity (EC), and total dissolved solids (TDS) were measured in the field using a multi-parameter portable meter (HACH, Germany). At each site, the pH electrode was calibrated using two buffers (Merck, Germany). The samples for the determination of metals were vacuum filtered through a 0.45 µm pore size membrane, acidified to a final concentration of about 1% nitric acid. Titration techniques with HCl were used to analyze total alkalinity (HCO<sub>3</sub><sup>-</sup> + minor CO<sub>3</sub><sup>2-</sup>). Chloride (Cl<sup>-</sup>) was determined by the standard AgNO<sub>3</sub> titration method and sulfate (SO<sub>4</sub><sup>2-</sup>) by spectrophotometric turbidimetry. Cations and other major and trace elements were measured by inductively coupled plasma and mass spectrometry (ICP-MS) in the filtered and acidified water samples within 2 weeks of sampling at the Labwest Laboratory, Australia. The analytical precision for the measurement of ions was determined by the ionic balances, calculated as 100 × (cations – anions) / (cations + anions), which is generally within ±5%.

## RESULTS AND DISCUSSION

### General chemistry

Chemical analysis of samples is presented in Table 1. Groundwater samples have pH values ranging from 7.32 to 8.26 (median value of 7.76) which is considered slightly alkaline. Field measured Eh values ranged from –54.4 to –1.4 mV, indicating reducing conditions. EC varied in a wide range from 2,550 to 14,590 mS/cm and averaged 7,988 mS/cm, showing a high salinity content of the groundwater, with dissolved oxygen concentrations in the range of 5.04–7.58 mg/L. TDS in the Bafgh area vary between 1,238 and 8,160 mg/L. Groundwater samples would be classified as brackish when the TDS is between 1,000 mg/L and 10,000 mg/L. Such water is not

Table 1 | Hydrochemical data of groundwaters from the study area

Parameter	EC	Eh	pH	TDS	O <sub>2</sub>	Cl <sup>-</sup>	SO <sub>4</sub>	HCO <sub>3</sub>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Fe	P	Sr	S	As	Ba	Cd	Co	Cu	Li
Maximum	14,590	-1.4	8.26	8,160	7.58	6,913	17,172	180	727	403	5,300	57.4	0.13	0.05	50	1,350	74.7	38	1.05	0.87	6.3	465
Minimum	2,550	-54.4	7.32	1,238	5.04	691	417	65	111	75.6	779	8.48	<0.01	0.02	3.59	265	0.9	15.5	<0.05	0.18	2.1	65.5
Average	7,988	-26.1	7.7685	4,328	6.43	2,932	2242.8	102.8	398	269.8	2,526	27.9	0.043	0.04	13.2	847.6	20.6	20.08	0.298	0.469	3.975	233.4
Standard deviations	2836.7	13.99	0.238	1,617	0.65	1,357	3572.8	25.83	158	99.85	1,072	14.1	0.032	0.01	5.81	309.4	27	5.199	0.316	0.173	1.14	116
Parameter	Mo	Pb	Si	Mn	V	Y	Zn	Ni	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Maximum	12.9	6.1	15,300	8.95	31.2	0.14	403	11.1	0.78	1.03	0.15	0.36	0.03	0.02	0.12	0.01	0.04	0.01	0.02	0.01	0.02	0.01
Minimum	2.4	<0.1	4,250	1.27	6.4	0.03	2.1	1.1	0.01	<0.01	<0.01	0.01	<0.01	0.01	0.04	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01
Average	9.135	2.132	7,950	4.093	19.6	0.08	42.775	5.565	0.07	0.122	0.021	0.06	0.011	0.01	0.07	0.01	0.02	0.01	0.013	0.01	0.015	0.01
Standard deviations	3.4027	1.139	3030.8	2.002	7.58	0.028	95.765	2.674	0.17	0.219	0.032	0.07	0.006	0	0.02	0.002	0.01	0.003	0.004	0.002	0.007	0.004

suitable as drinking water. The TDS as a function of the mineralization characteristics of the groundwater values is influenced by climate, the interaction between groundwater and host rock, and the residence time of the groundwater in the geological matrix. Due to low rainfall and the intensity of evaporation, the area tends to be arid/semi-arid (Pazand & Javanshir 2014; Hussin *et al.* 2016; AlSuhaimi *et al.* 2017). The order of abundance of the major cations is  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$  with value ranges 779–5,300 mg/L, 111–727 mg/L, 75.6–403 mg/L and 8.48–57.4 mg/L, respectively. The trend for anions was  $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$  with concentrations varying between 691–6,913 mg/L, 417–17,172 mg/L and 65–180 mg/L, respectively. Anion and cation concentrations in the majority of samples were not within WHO recommended limits (WHO 2011).

A scatter distribution of groundwater samples on a Piper diagram reveal that the dominant cation is  $\text{Na}^+$  and the

anion is  $\text{Cl}^-$ , and shows the major hydro facies identified in the study area is the Na-Cl type (Figure 2).

Sodium and chloride show a positive correlation ( $r = 0.94$ ), suggesting the dissolution of evaporate minerals and water-rock interaction controlled groundwater chemistry (Figure 3). In the plot of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus  $\text{SO}_4^{2-} + \text{HCO}_3^-$  most of the points lie close to the 1:1 line, suggesting that the dissolutions of calcite, dolomite, and gypsum are the dominant reactions in a system (Munzo *et al.* 2016).

### Arsenic concentrations

The concentration of arsenic for each well water sample is presented in Table 1. Arsenic concentrations in the groundwater range between 0.9 and 74.7  $\mu\text{g/L}$ , with 35% of the selected samples exceeding the World

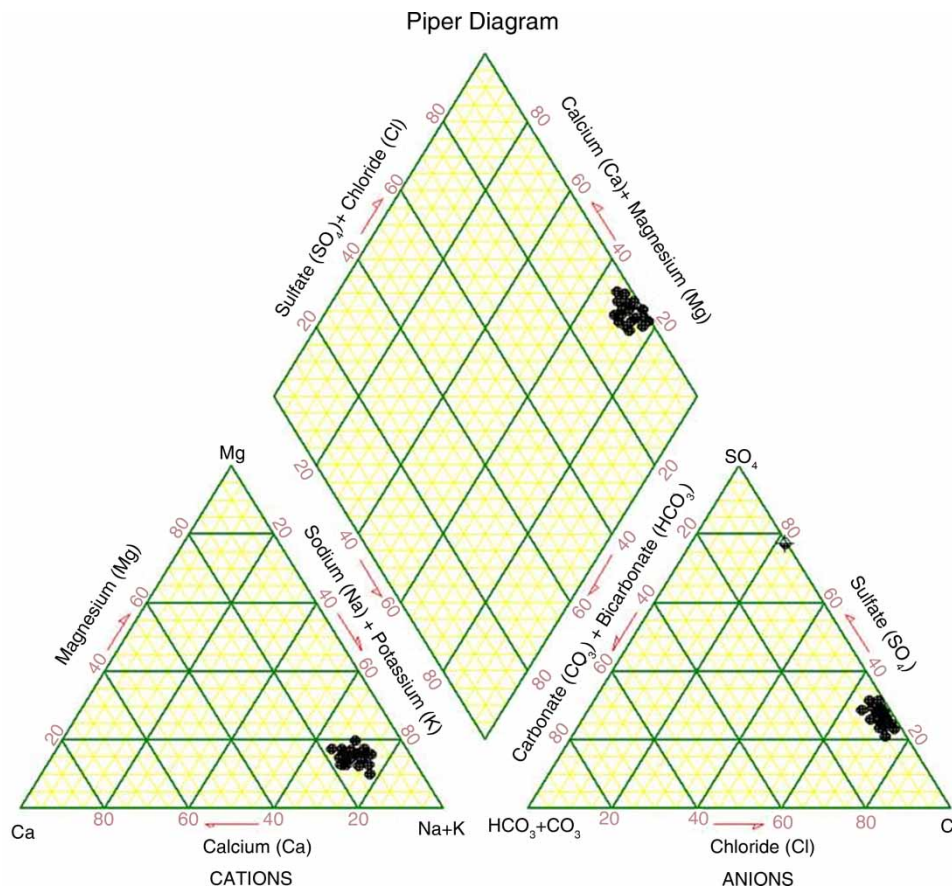
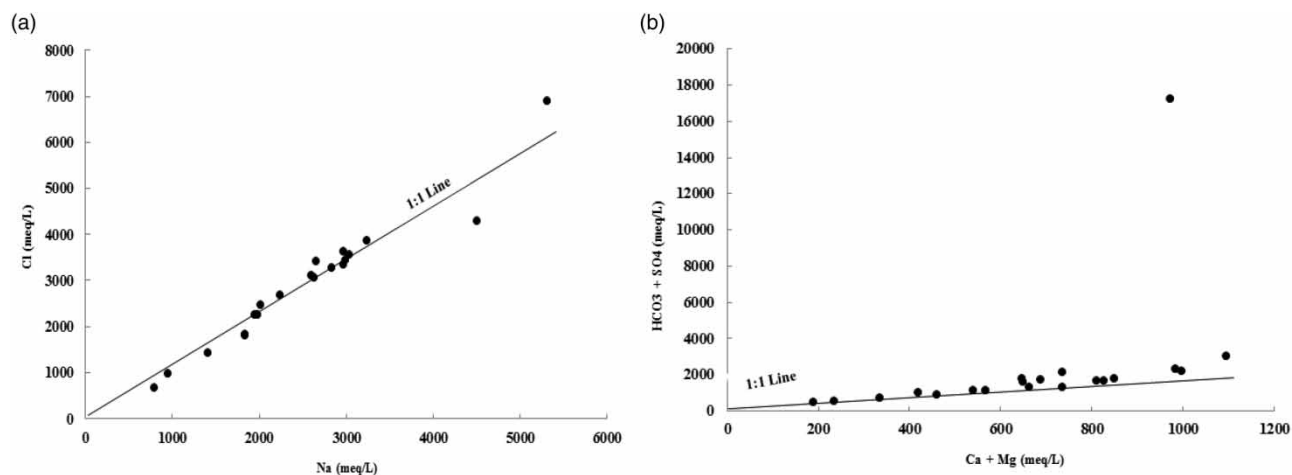


Figure 2 | The Piper diagram for the groundwater samples.



**Figure 3** | Bivariate plots for groundwater samples: (a) Na vs Cl and (b) Ca + Mg Vs HCO<sub>3</sub> + SO<sub>4</sub>.

Health Organization standard of 10 µg/L (WHO 2011). Weak correlation was observed between As and Fe, including As and Mn (Figure 4). The geographical trends of As concentrations were apparent. Figure 4 indicates that there are two distinct trends of As versus the concentrations of Fe and Mn in the eastern and western part of the study area. Low As concentration (<8 µg/L) appears in the Eastern part, and high As concentration (>28 µg/L) in the Western part. No strong correlation between As and Fe-Mn indicates that the adsorption/desorption from Mn-Fe oxides/hydroxides play a minor role in controlling the mobility of As in the aquifer (Mahanta *et al.* 2015). Mobilization of As into the groundwater is controlled by redox reactions in the aquifers (Mukherjee *et al.* 2009; Pazand & Javanshir 2013), and Eh in the study area ranged from -54.4 to -1.4 mv, which indicated reducing conditions prevail in the study area.

It can be seen that the arsenic concentration increases with the decrease in concentration of bicarbonate in the study area (Figure 4). This could be because As is readily adsorbed and co-precipitated by calcite (Roman-Ross *et al.* 2006). Arsenic occurrence is plausibly associated with the presence of silicic rocks and their weathering products. Studies have also shown that the mining and activity of Bafgh iron ore processing mines (Figure 1) is one of the sources of arsenic in the region (Rezapoorbaghedar *et al.* 2016).

### REE concentrations in groundwater

REE concentrations in the study area vary, with the total REE concentration ranging from 0.12 µg/L (sample 20) to 2.53 µg/L (sample 10) (Table 1), with Ce varying from <0.01 to 1.03 µg/L and La from 0.01 to 0.78 µg/L. There are no notable variations in concentrations of the REEs within aquifers, which could be explained in terms of similarity in rock forming processes, hydrothermal processes, and discrepancies in the degree of weathering processes (Omonona & Okogbue 2017). Chondrite-normalized REE fractionation patterns (Anders & Grevesse 1989) for Bafgh aquifer groundwaters are presented in Figure 5.

Apart from sample 10, the Bafgh groundwaters have strikingly similar chondrite-normalized REEs patterns and show a flat profile with a predominance of LREEs over HREEs, suggest that they originated from the same source. The groundwater samples show positive Gd anomaly (Figure 5). Gadolinium anomalies are known in groundwater, but these are small and appear to be restricted, resulting from natural REE fractionation (Kualaksi & Bau 2007). Presence of positive Gd vs. other REEs may be indicative of greater mobility of Gd.

Many studies have shown the potential of REEs in the Bafgh region, and REEs originated from a continental margin rhyolitic magma in this area (Sabet-Mobarhan-Talab *et al.* 2014; Khoshnoodi *et al.* 2017). The distribution of REEs in several area in Bafgh region demonstrates the

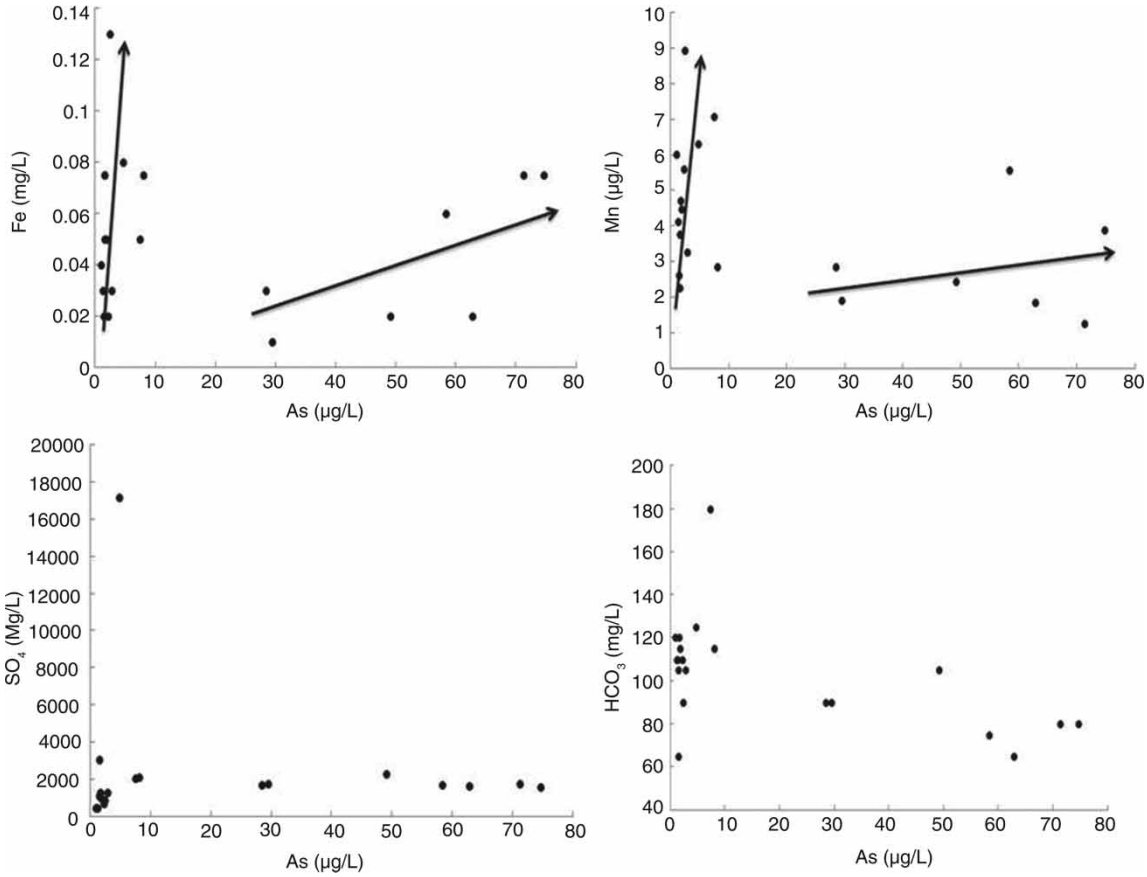


Figure 4 | Plots of relations between As and other elements for the 20 groundwater samples.

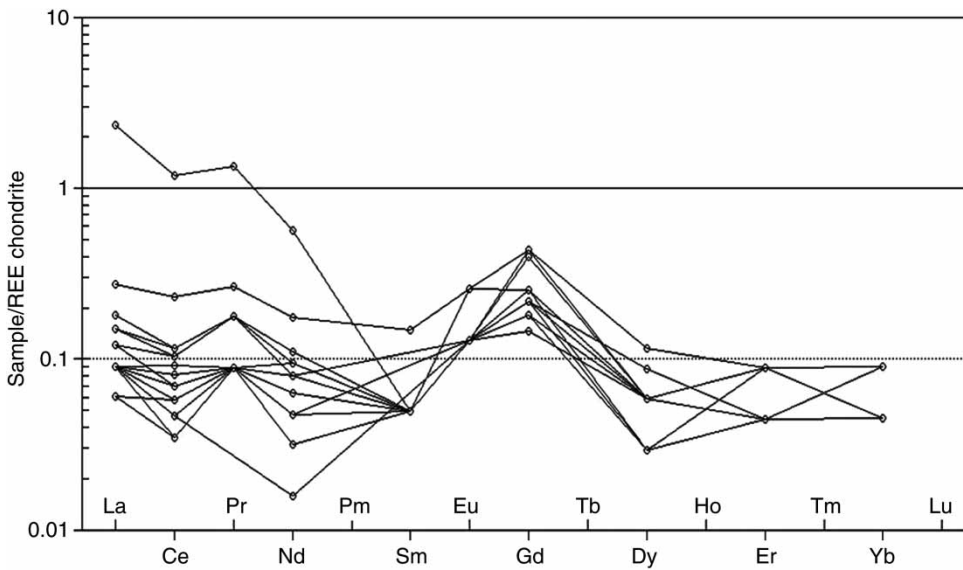


Figure 5 | The chondrite-normalized distribution patterns in different groundwater.

enrichment of light to heavy REEs (Rahimi *et al.* 2016; Shekarian *et al.* 2017).

## CONCLUSIONS

The following conclusions can be drawn from the REE data derived from this study:

- Groundwater is mostly Na–Cl type for the study area, with  $\text{Cl}^-$  and  $\text{Na}^+$  as the dominant anion and cation, respectively.
- Assessment of water samples according to exceedance of the permissible limits prescribed by WHO for drinking purposes indicated that groundwater in the Bafgh area is chemically not suitable for drinking uses.
- The concentrations of rare-earth elements in the groundwater are low in the study area, and the chondrite-normalize REE patterns show a flat profile, slight LEE enrichment as compared with HREE, positive Gd anomalies.
- Arsenic concentrations are high in the Bafgh area, with 35% of our groundwater samples exceeding the WHO guideline of 10  $\mu\text{g}/\text{L}$ .
- In the vicinity of the study area, there are mining/ore processing activities reported to be potential sources of arsenic contamination of groundwater.

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