



Hydrogeochemical and isotopic evaluation of arsenic contaminated waters in an argillic alteration zone



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ABSTRACT

Mineralization of sulfidic minerals including realgar, orpiment and pyrite occurs in argillic alteration zones in northeastern Iran, which affects water quality and health in these semi-arid localities. Geochemical source of ions in surface and ground waters was examined to evaluate potential effects of sulfidic mineralization on water quality. The surface and groundwater samples were analyzed to determine the major ions (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , HCO_3^- , SO_4^{2-} , Cl^-) and trace elements (such as As, B, Br). Water-rock interactions and evaporation defined as the key phenomena on groundwater chemistry using Gibbs diagram. Concentrations of arsenic (As) varied from 16 to 606 $\mu\text{g/L}$, which was higher than the WHO (2011). Calculated ionic ratios revealed that anions and cations in surface and ground waters originated from partial leaching through ion exchange in alteration zones. We postulate that the primary source of As resulted from oxidation of As-bearing sulfide minerals such as orpiment, realgar and arsenopyrite in argillic-pyrite alteration zone. High pH (>8) could provide the alkalinity to increase sulfide oxidation and release As into the water. The stable isotope data ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) indicated the origin of the waters, which is mainly meteoric precipitation with partial effects from evaporation processes and exchanging ions with surrounding rocks. This confirms the notion that the source of all analyzed ions including the toxic As is geogenic. Hydrogeochemical process, which affected the water chemistry and thus environmental public health are likely to be water-rock interactions and evaporation.

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1. Introduction

Widespread arsenic (As) accumulation, mobility in sediments, water and air (dust) is a critical environmental public health issue, worldwide (Ravenscroft et al., 2009; Rodríguez-Lado et al., 2013; Taheri et al., 2016a). As a result of geological phenomena and environmental changes, high levels of geochemically dispersed As can be found in feed, foods, water, soil and air in both organic and inorganic forms (Hall et al., 2006; Fillol et al., 2010) reaching toxic levels to surrounding human and animal populations and adversely affecting biochemical processes of cells and organs. International Agency for Research on Cancer (IARC) has classified As as a Class I carcinogen (IARC, 2004). Owing to its carcinogenic properties, the maximum allowable concentration (MAC) value of As in drinking water is 10 $\mu\text{g/L}$ (Tamasi and Cini, 2004). The Environmental Protection Agency (EPA) and the National Research Council

(NRC) stated that chronic effects on humans may be caused by prolonged consumption of water with a concentration of As as low as 5 $\mu\text{g/L}$ (EPA) or even 3 $\mu\text{g/L}$ (NRC) (Hogue, 2001a, 2001b; Tamasi and Cini, 2004).

Water-rock interaction is one of the main factors controlling geochemical characteristics of the water. Indeed, one of the crucial areas of research in chemical geology is groundwater chemistry (Hounslow, 1995); application of groundwater hydrochemistry and how rocks/sediments physicochemically interacts with the water would multidisciplinary broaden our knowledge about environmental and public health. Although evaporation-based concentration and precipitation-related dilution could change the chemical compositions of groundwaters, rock/sediment-water interaction is nonetheless the major process because solid phases (inorganic and organic matter) are the primary sources and sinks of dissolved constituents in groundwater. The chemical reactions that are responsible for the water-rock interaction vary spatially and temporally, depending on the chemistry of the initial waters and dynamics of geological formations and residence time (Sarkar

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et al., 2007). The resulting concentrations of major ions of groundwater can be used to identify the intensity of water-rock interactions and chemical reactions.

Distinctive chemical composition of ground waters has been due to association with hydrothermal systems within fault zones, where interaction of hydrothermal fluids with the wall rocks and atmospheric water and subsurface brine occurs (Aiuppa et al., 2006). Chemical characteristics of spring water and hydrothermal alteration zones have been studied to evaluate their relationship. For example, oxidation of sulfide boosts SO_4^{2-} level, thus leading to precipitation of sulfate minerals such as gypsum (Karakaya et al., 2007). Hydrothermal activity and volcanic systems are typically associated with As release to the groundwater (Nriagu, 1989; Aiuppa et al., 2006). In addition to naturally occurring As, oxidation of arsenides and arsenosulfides such as orpiment (As_2S_3), realgar (As_4S_4) and arsenopyrite (AsFeS) in mine tailings are related anthropogenic As to the ground and surface waters.

Considering the broad hazardous effects of As on the natural environment and animal/public health (Argos et al., 2006; Banerjee et al., 2009; Taheri et al., 2016a), geochemical studies related to geogenic As contamination in vital water resources from this agro-ecologically important arid northeastern Iran, is warranted. We therefore intend to evaluate the geochemical source of As with other related major ions, and saturation parameters affecting the quality of surface and ground water resources in the highly mineralized region of Chelpu-Koohsorkh in northeastern Iran to rediscover a new window to understanding the geochemical mechanisms and functional consequences of As in inducing environmental health risks in As-exposed inhabitants.

2. Location and geological setting

Chelpu is located along the east longitude of $58^\circ 29' 44''$ to $58^\circ 36' 07''$ and north latitude of $35^\circ 33' 12''$ to $35^\circ 37' 77''$ (Fig. 1). This mountainous area demonstrates a semi-arid climate. Its dominant lithology consists of shale, limestone, sandstone, conglomerate and evaporites (gypsum and halite), from the Paleogene age.

There are numerous tectonic forms of anticline, syncline, and folded beds and in particular several faults in Chelpu. East-west trending strike slip “Doruneh fault” is the main fault accompanied by N-W to S-E oblique-slip and normal faulting system in the region (Aghanabati, 2004). Resulting fractures were filled by hydrothermal solutions leading to hydrothermal mineralization along the fractures. Epithermal mineralization of As, Sb and Au elements at temperatures $< 300^\circ\text{C}$ has been reported in stoke framework of veins in this area (Mazloumi Bajestani, 1992). Jarosite [$\text{KFe}(\text{SO}_4)_2\text{OH}_6$] and alunite [$\text{KAl}_3(\text{SO}_4)_3\text{OH}_6$] minerals together with montmorillonite and kaolinite (clay minerals) are hydrothermal alteration-minerals, present in this location that indicate hydrothermal activities in this region. Mineralization of sulfides such as realgar, orpiment, arsenopyrite, pyrite, and stibnite are accompanied with calcite and gypsum within the alteration zones, also known as argillic-pyrite alteration zones (Mazloumi Bajestani, 1992; Karakaya et al., 2007). In fact, the As-bearing sulfides (orpiment, realgar, pyrite and arsenopyrite) were hosted in the sedimentary rocks of shale, marly limestone, sandstone, conglomerate (Mazloumi Bajestani, 1992).

Stages of mineralization in the host rock are as following: 1) creation of fractures and hydrothermal fluid ascent through fractures, 2) stibnite

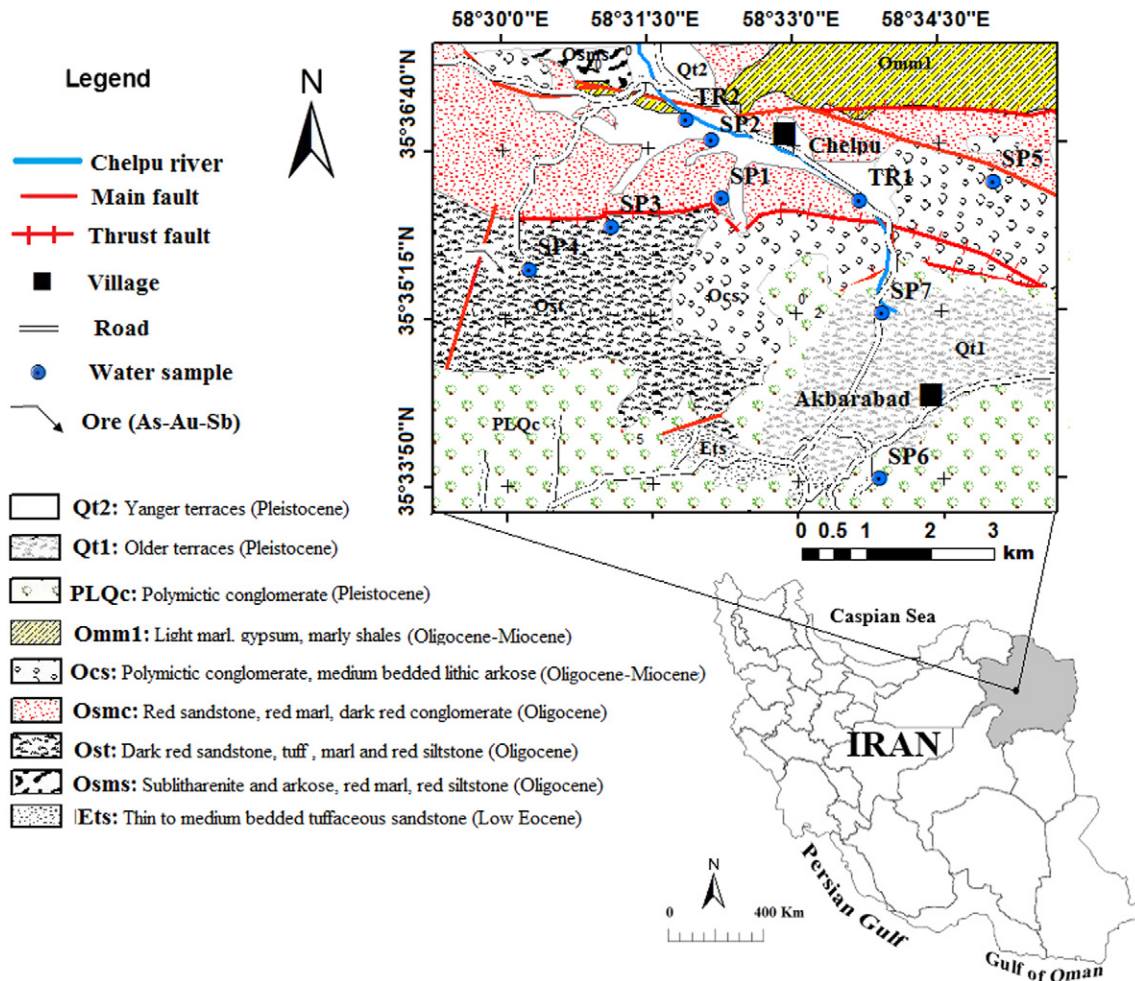


Fig. 1. Simplified Geological Map of Chelpu area (with slight modifications in drawing of 1:100,000 Shamkan and Kadkan map, Persian report of Geological Survey of Iran, N. Naderi Mighan, 1999a,b, #7661).

mineralization, 3) realgar and orpiment mineralization associated with stibnite, 4) fault reactivation and creation of joints and fractures, 5) gang intrusion that is associated with pyrite mineralization, 6) realgar and orpiment mineralization being associated with arsenopyrite (As rich) and finally 7) gypsum and quartz gang intrusion (Mazloumi Bajestani, 1992).

3. Materials and methods

All surface and ground waters resources including streams, springs, tap waters were sampled in Chelpu and Akbarabad (Fig. 1). Because of aired to semi aired conditions of the study area, there were not many water resources, and we could thus hardly found more than ten water samples for analyses.

Location of the water samples were presented/shown in Table 1 and Fig. 1. All water resources (except TR-1 and TR-2 used only for irrigation purpose) were routinely used for both drinking and irrigation purposes. The samples TR-1 and TR-2 were taken on Chelpu river as surface water samples. The springs water samples were collected from alteration zone or their host sedimentary rocks. One sample (Chelpu tap water) were pumped from wells to storage tanks. However, well depth was around 25–30 m. So, it seems the aquifer is relatively shallow. Tap water samples were allowed to flow freely for 5 min prior to sample collection from the well, allowing us to consider as wells waters.

Hydrochemical parameters including water temperature, pH and EC were measured in situ using portable pH meter (AZ-8686) and EC (AZ-8351) in field, which were calibrated before use. During water sampling all samples were filtered through 0.45 µm filter discs on-site. Water samples were stored in 500 mL high density polyethylene (HDPE) bottles for laboratory analyses. Pure nitric acid (69%, Merck) was added to the water samples to adjust the pH to ≤2 for the cations. Stable isotope samples were taken in 50 mL HDPE bottles screw-capped and sealed tightly to prevent evaporation. All water samples were kept at 4 °C until analyses. Cations of calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), iron (Fe), arsenic (As) and boron (B) were analyzed using Perkin-Elmer ICP-OES 8000 at geochemistry laboratory in department of geology in Kent University (Kent, Ohio, USA). Major anions as sulfate (SO₄²⁻), chloride (Cl⁻) and bromide (Br⁻), were

measured by ion chromatography (IC; Dionex ICS-2000). Bicarbonate (HCO₃⁻) was measured by titration at geochemistry laboratory of Ferdowsi university of Mashhad at the same day after sampling. Stable isotopes of δ²H and δ¹⁸O were analyzed in Stable Isotope Lab, INSTAAR, University of Colorado. The isotopic values are reported using the standard notations relative to the NIST/IAEA reference materials V-SMOW. The analytical precision is ±0.1‰ and ±0.3‰ for δ¹⁸O and δD, respectively.

Aq.QA, AquaChem (Version: 2010.1) and PHREEQC Interactive (Version: 2.14.3.2411, USGS) softwares were applied to determine hydrogeochemical characteristics of water samples and calculation of saturation indices (SI) of minerals respectively.

4. Results

4.1. Field parameters

Results from field measured parameters are presented in Table 1. Median pH of these samples varied within an alkaline range of 7.8–9.0. Among them, 20% showed higher pH levels in comparison to the acceptable range of 7.0 to 8.5 for drinking waters (DW) (WHO, 2011). Median (min–max) EC and total dissolved solids (TDS) in waters were 700 (240 to 3160) µS/cm and 627 (246–3101) mg/L respectively. Among them, 40% were within the range of brackish water (1000 to 10,000) mg/L (Todd and Mays, 2005) (Table 1; samples include SP1, SP4, SP5, and TR-2).

4.2. Ions and elements concentration

Summary of ionic concentration and stable isotope (δ²H and δ¹⁸O) values are presented in Table 1. Cl⁻ concentration in water varied from 8.0 to 722.6 mg/L with a median 93.7 mg/L. Thirty percent of the samples exceeded the permitted chloride level of 250 mg/L in DW (WHO, 2011). SO₄²⁻ concentration ranged 11.0 to 2052 mg/L with a median 119.8 mg/L. Among these samples, 40% comprised of higher than the permissible limit of SO₄²⁻ (250 mg/L, WHO). Both SO₄²⁻ and Cl⁻ ions have shown major effects on the EC and also water type (Fig. 2). In spring water samples, the maximum EC was 3160 µS/cm with

Table 1

Coordinates of sample location points, with locations of water sources and in-field measurements. Results of major ions, trace elements and stable isotope values (δ¹⁸O and δ²H) in Chelpu water samples. Except for items marked (*) which are in the µg/L, all the other components are expressed as mg/L. *TDS_c (calculated total dissolved solids).

Sample ID	Geographic coordinates	T (°C)	pH	EC (µS/cm)	TDS _c (mg/L)	Ca	Mg	Na	K	Fe*	B*	As*	HCO ₃	Cl	SO ₄	Br	δ ² H (‰)	¹⁸ O (‰)δ	D-Excess
SP-1	35°36'13.2"N 58°32'15.7"E	14.8	9	320	307	4.90	0.80	92.3	0.32	16	680	16	103.4	61.6	30.1	13.9	-41.2	-7.02	15.0
SP-2	35°36'41.8"N 58°32'8.5"E	17.9	8	1020	1248	64.35	11.26	156.7	1.02	16	1570	35	61.8	125.9	307.5	50.4	-47.8	-7.86	15.1
SP-3	35°35'37"N 58°31'13.8"E	14.2	8.9	490	586	7.81	8.40	152.4	1.33	27	7970	606	206.5	20.1	182.1	36.3	51.0	-8.28	15.3
SP-4	35°35'38.2"N 58°30'16.3"E	16	8.2	3160	3101	451	66.77	380	17	2	7990	48	34.2	99.8	2052	n.d	-49.5	-7.73	12.3
SP-5	35°36'17.08"N 58°35'2.34"E	18.6	8.5	1590	18,847	17.52	1.43	425	1.72	251	2800	29	79.7	370.4	370.8	42.9	-48.4	-7.40	10.7
SP-6	35°33'57.1"N 58°33'51.4"E	12.7	8.5	240	2467	8.2	1.07	52.8	0.52	4	50	66	144	8.0	11	21	-55.5	-8.56	13.0
SP-7	35°35'13.6"N 58°33'53.9"E	15.8	7.8	910	6677	36.13	8.65	164	0.91	13	390	21	187	191.9	57.5	21.4	-51.1	-8.48	16.7
TR-1	35°36'12.5"N 58°33'41.77"E	16	8.5	960	9117	42.91	14.2	236.4	1.25	60	650	18	251	276.6	74.5	14.4	-47.5	-7.52	12.7
TR-2	35°36'55.9"N 58°31'57.2"E	18.2	8.2	2400	1417	103.7	45.41	569	4.42	20	2480	34	111	722.6	553.9	n.d	-42.8	-6.84	11.9
TAP	35°36'47.3"N 58°32'34.1"E	12.4	8	950	781.7	67.6	14.9	186.4	1.2	n.d	n.d	29	203	114.8	194	n.d	n.d	n.d	n.d
Min		12.4	7.8	240	246	4.9	0.8	52.8	0.32	2	50	16	34.2	8.00	11	13.9	-55.5	-8.56	10.70
Max		18.6	9	3160	3101	451	66.8	568.9	17	251	7990	606	251.2	722.6	2052	50.4	-41.20	-6.84	16.70
Mean		15.66	8.36	1204	1115	80.41	17.28	241.5	2.96	45.44	2731	90.2	138.1	199.2	383.3	28.6	-48.31	-7.74	13.63
Median		15.30	8.5	700	627	12.85	4.91	154.55	0.96	16	1125	32	123.7	93.7	119.8	28.9	-49.70	-8.07	15.05
±SD		2.17	0.39	935.1	861.8	134.1	21.7	164.01	5.05	78.9	3117	181.8	71.5	215.8	611.1	14.5	4.32	0.61	1.96

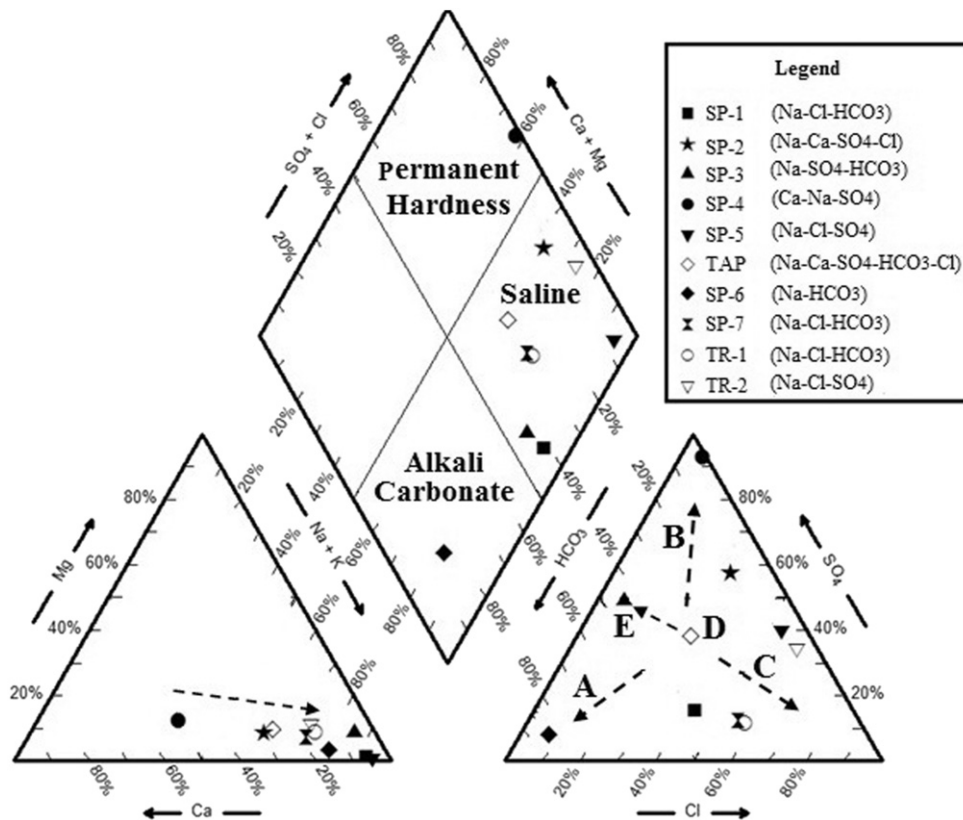


Fig. 2. Piper diagram of the Chelpu water samples: the Piper diagram shows non-mixing trends as demonstrated by letters A, B, C, D and E. A implies calcite dissolution and ion exchange, B: gypsum dissolution and ion exchange, C: dissolve halite, D: ion-exchange and E: oxidation of such minerals as pyrite, and neutralization by calcite.

dominant SO_4^{2-} of 2052 mg/L (SP-4 as in Fig. 1 and Table 1), which was collected from argillic alteration zones.

Also, EC and dominant chloride ions were 2400 $\mu\text{S}/\text{cm}$ and 722.6 mg/L in sample TR-2 from Chelpu streams (Fig. 1 and Fig. 2). HCO_3^- and Br^- concentrations varied from 34.2 to 251 mg/L with a median of 123.7 and from 13.9 to 50.4 mg/L with a median of 28.9, respectively (Table 1). Br^- and Cl^- concentrations exhibit increasing trends to the north, where is farther distance from recharge area of the water (Fig. 1 and Table 1).

In addition, concentrations of Ca^{2+} , Mg^{2+} , Na^+ and K^+ ranged from 4.9 to 451 mg/L, 0.8 to 66.8 mg/L, 52.8 to 568.9 mg/L and 0.32 to 17 mg/L, respectively (Table 1), most of which exceeded the permissible amount of (WHO, 2011). For example, 20% and 40% levels of Ca^{2+} and Na^+ in drinking water (DW) were observed to be above the permitted levels of 75 and 200 mg/L (WHO, 2011).

Fe concentration ranged from 2 $\mu\text{g}/\text{L}$ to 251 $\mu\text{g}/\text{L}$ (Table 1). No health-based guideline is proposed for iron. There is usually no noticeable taste at iron concentrations below 300 $\mu\text{g}/\text{L}$, although turbidity and color may develop (WHO, 2011). All samples were under the limit of 300 $\mu\text{g}/\text{L}$ for DW (WHO, 2011). As and B concentrations ranged from 16 to 606 $\mu\text{g}/\text{L}$ and 50 to 7990 $\mu\text{g}/\text{L}$, respectively (with a median of 32 and 1125 $\mu\text{g}/\text{L}$, respectively). In this study 100% and 70% of water samples exceeded the standard limits of As and B in DW of 10 $\mu\text{g}/\text{L}$ and 500 $\mu\text{g}/\text{L}$, respectively (WHO, 2011) (Table 1). Long-term exposure of even <3 $\mu\text{g}/\text{L}$ As-contaminated water causes various diseases especially cancer in humans (Kozul et al., 2009; Taheri et al., 2016a).

4.3. Stable isotope compositions

Stable oxygen and hydrogen isotopes are useful tracers in water quality studies. Their initial isotope ratio has originated from meteoric rainfalls, but the ratio is changed through physicochemical process

such as evaporation and water-rock interactions (Sharp, 2007). Median value of $\delta^2\text{H}$ for surface and ground waters was -49.70‰ , ranging from -55.5‰ to -41.2‰ (SMOW). $\delta^{18}\text{O}$ values ranged from -8.56‰ to -6.84‰ with a median of -8.07‰ (SMOW). The D-excess with a mean 13.63%, ranged from 10.7% to 16.7% (Table 1). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values spanned in close proximity to the local meteoric waters, which have been reported previously for the region in Mohammadzadeh (2010). The local meteoric water line (LMWL) was drawn based on equation of $\delta^2\text{H} = 11.22\text{‰} + 7.17 \times \delta^{18}\text{O}$ (Fig. 3), which represents a lower slope (of 7.17) than GMWL (8). Compared to the LMWL, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the groundwater samples indicate that the studied waters originated from meteoric waters precipitated in the area (Yin et al., 2011) (Fig. 3). Deviations in isotopic compositions away from the LMWL may result from various processes, e.g., evaporation, mineral hydration, precipitation and water-rock interactions (Karakaya et al., 2007; Clark, 2015).

5. Discussion

Groundwater chemical composition largely depends on the water-rock interactions and duration of contact with subsurface rocks or sediments and other physicochemical parameters such as temperature, pH, redox potential and ionic strength. Evaporation can also change the chemical composition and reduce quality of groundwater (Sarkar et al., 2007). Saturation Index (SI) are used to examine the quality of water and hydrochemical evolution, respectively. The major ions variety in the water and determination of their origin may help evaluate the phenomena, which affects the water quality. The examined correlations between dissolved major ions and As concentration smoothen our understanding of primary source and mobilization of As in the Chelpu ground and surface waters.

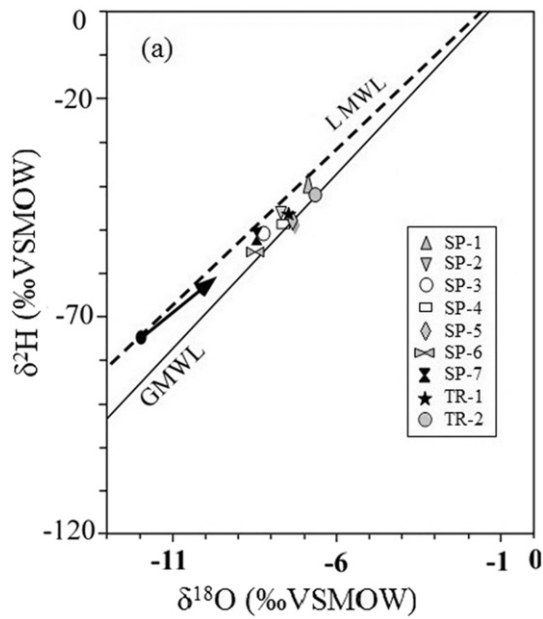


Fig. 3. Relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for surface and groundwater samples collected from Chelpu; GMWL and LMWL are the global and local meteoric water lines, respectively.

5.1. Determination of hydrogeochemical facies

The chemical composition of water is controlled by major ions (SO_4^{2-} , HCO_3^- , Cl^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+}) and water type-facies can be determined based on the ions plotted on Piper diagram (Piper, 1994) (Fig. 2). The various hydrochemical facies types were Na- Cl - HCO_3 , Na- SO_4 - HCO_3 , Ca-Na- SO_4 , Na- Cl - SO_4 and Na- HCO_3 (Fig. 2).

5.2. Water-rock interactions and source of major ions

Chemical processes including dissolution, ion exchange, oxidation and reduction occurs during water-rock interaction (Sarkar et al., 2007). Gibbs (1970) diagram has been used to determine the mechanisms controlling water chemistry by plotting the TDS vs. $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ and TDS vs. $\text{Na}/(\text{Na} + \text{Ca})$ as shown in Fig. 4. According to Gibbs diagram, the studied water samples are in the water-rock interaction zone (Fig. 4). Based on alteration type (Karakaya et al., 2007), water-rock interactions in alteration zone could likely increase various ions in sampled waters. Considering the dominant argillic alteration zone as associated with jarosite ($\text{KFe}(\text{SO}_4)_2 \cdot \text{OH}_6$), K^+ and SO_4^{2-} ions are likely to be increased in the water. Binary diagrams of K^+ vs. SO_4^{2-}

and Ca^{2+} vs. SO_4 showed a significant positive trend in surface and ground waters that can be related to simultaneous release of ions from jarosite and gypsum (Mazloumi Bajestani, 1992) in the alteration zone (as shown in Fig. 5a and b). Ionic ratios $\text{Na}/(\text{Na} + \text{Cl})$, $\text{Mg}/(\text{Mg} + \text{Ca})$, $\text{Ca}/(\text{Ca} + \text{SO}_4)$ and HCO_3^- were examined to determine the probable source of major anions, cations, and processes affecting water chemistry (Hounslow, 1995).

Ion ratios were calculated in terms of equivalent per liter, which is represented in Table 2 associated with probable sources of ions in the water samples. Whenever the concentration of Na and Cl is increased with the equal ratio (1:1), dissolution of halite (NaCl) can be the source of Na in water, or due to evaporative concentration. Otherwise, in the case of Na/Cl increasing, it is considered to have different origin of such processes as in silicate minerals dissolution or occurrence of ion exchange (Gomes et al., 2006; Sarkar et al., 2007). Considering the presence of halite minerals in sedimentary outcrops, and the ratio of sodium to chlorine (Table 2), source of sodium in water could primarily be sodium dissolution of halite or by increasing Na through ion-exchange with Na bearing clay minerals (Fig. 5c and Table 2).

Cl^- and bromide (Br^-) in the groundwater have different sources of atmospheric and dissolution of evaporites such as halite (NaCl) and d'ansite ($\text{MgNa}_{21}(\text{Cl}_3\text{SO}_4)(\text{SO}_4)_9$) (Davis et al., 1998). Most evaporites contain high concentrations of both Cl^- and Br^- , and high Cl/Br ratio. Regarding the geochemical characteristics of Br^- are similar to Cl^- , both elements have high solubility and tendency to ionize in water, but Br^- compounds are more soluble. Cl^- can be replaced by Br^- in halite structure (Warren, 2006 & Davis et al., 1998). The amount of Br^- in the studied waters varies from 13.9 to 50.4 mg/L. Though the coupling diagram Cl/Br vs. Cl indicates the likely effective impact of halite dissolution process (Fig. 6), but in most ground water samples it seems evapotranspiration (Fig. 6) is more important contributing factor for such process, partly causing decreased Cl^- and increased Br^- in water of the studied area (Xie et al., 2012 & Deng et al., 2009). Some samples were plotted between these two cases, illustrating their combined effect. If evapotranspirative concentration were the only factor, the molar Cl/Br ratio would not change as Cl concentration increased (Hogan et al., 2007).

Weathering of limestone cause Ca to increase (or a decrease in the ratio of $\text{Mg}/(\text{Mg} + \text{Ca})$ in water (Table 2). Sodium bearing silicate minerals (e.g. plagioclase and clay minerals) may also affect the calcium ratio when sodium releases into water during ion exchange, to increase Na/Ca ratio (Table 2). Calcium removal ion exchange or its deposition may decrease Ca/ CaSO_4 ratio to <0.5 in water.

When the ratio of bicarbonate to all anions is >0.8 it will likely indicate weathering of silicate and carbonate minerals. However, if this ratio is <0.8 with high sulfate contents, it will be an indication of gypsum dissolution that lessens the Ca/ CaSO_4 ratio (Hounslow, 1995). As seen in Table 2, low ratio of bicarbonate to anions can be the result of leaching and dissolution of gypsum in the altered zone.

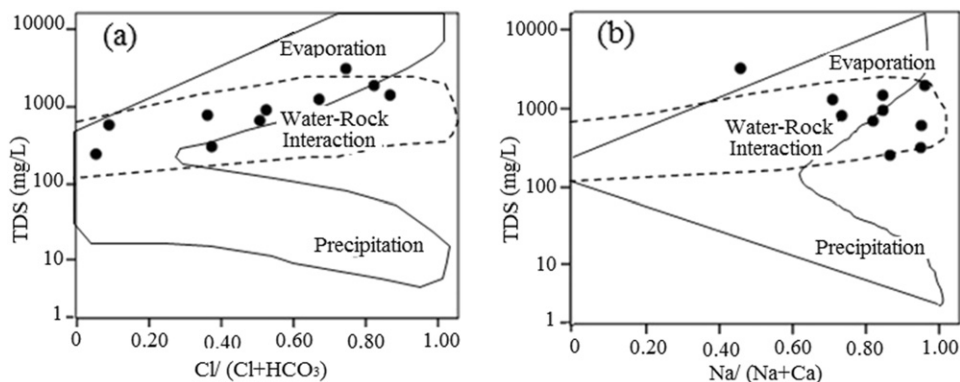


Fig. 4. Gibbs diagram interpretation of TDS measurements of Chelpu waters (as in Gibbs, 1970).

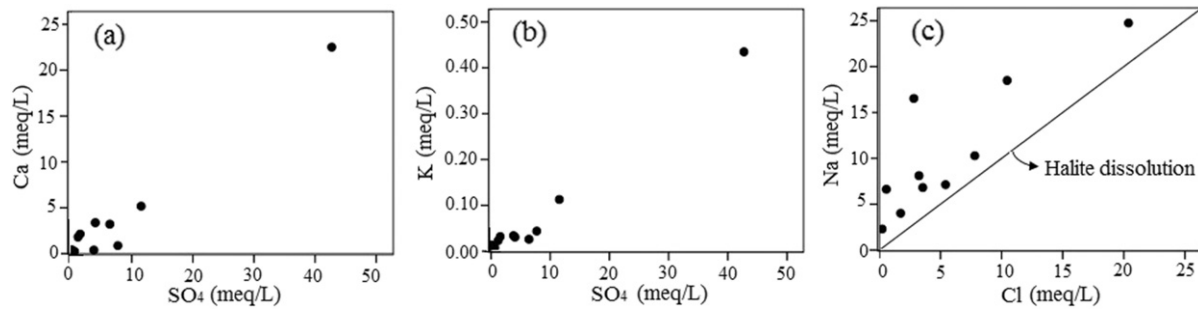


Fig. 5. Coupled ionic concentration diagrams of (a) Ca-SO_4^{2-} , (b) K-SO_4^{2-} and (c) Na-Cl .

Elements transfer between bedrock and groundwater occurs during water-rock interaction process such as dissolution and precipitation of minerals. Dissolution starts when groundwater tends to move towards equilibrium. This process continues until groundwater is saturated with those particular mineral components. At equilibrium concentration values, the mineral may continue to dissolve, and excess mineral components may combine in the solution to form precipitates of that particular mineral, and this reaction is called precipitation (Deutsch, 1997). Chemical equilibrium of groundwater for a particular mineral can be identified by calculating saturation indices. If the SI values are less than zero, it will take more mineral into the solution, which is called dissolution (i.e., $\text{SI} = \text{Log IAP}/K_s$, where IAP is ion activity product and K_s is solubility product of the mineral (Yin et al., 2011; Deutsch, 1997); indeed, the use of SI is best limited for simple soluble salts like carbonate minerals.

The SI of minerals (Table 3) show that SI in the samples SP-4, SP-3, TR-1 and TR-2 is greater than zero for the minerals calcite, dolomite, aragonite, and to some extent (samples, TR-1 and SP-3) for hardly soluble magnesite (Table 3). SI values for gypsum, anhydrite and halite were negative in all water samples, indicating a tendency towards rock dissolution.

Plotting data on Piper diagram leads to the same interpretation as provided above. The Piper diagram is a better indication of non-mixing trends tendency (as shown in Fig. 2 by codes A, B, C, D and E). Tendency of A implies to calcite dissolution and ion exchange, B to gypsum dissolution and ion exchange, C to dissolve halite, D to ion-exchange and E to oxidation of sulfide minerals, and neutralization by calcite (Hounslow, 1995).

5.3. Source of arsenic and its mobilization

There are a number of possible geochemical triggers which releases As from solid phase into the ground water in an aquifer. In mineralized areas such as Chelpu, oxidation of As bearing sulfides may be triggered by influxes of oxygen or other oxidizing agents (i.e., Smedley and

Kinniburgh, 2002). Under high pH conditions, oxidation of the minerals such as orpiment and realgar leads to release of As in waters (Lengke et al., 2009; Henke, 2009).

The correlation between As concentration and Fe, SO_4 and pH are shown in Fig. 7a, b and c. It is indicated that there is a positive correlation between As and pH in the water samples (Fig. 7a). In carbonate-hosted deposits, dissolution of carbonate minerals usually increases pH, and at higher carbonate levels, the oxidation rates of As-bearing sulfides increase (Lengke and Tempel, 2001, 2005; Lengke et al., 2009; Henke, 2009). It is also assumed that sulfide minerals dissolve faster at low pH; however, the evidence here shows that the oxidation rates of pyrite and arsenic sulfides by dissolved oxygen are enhanced by higher pH values (also as seen in Lengke and Tempel, 2001, 2003). Therefore, As contamination in water could be more problematic if As-bearing sulfides oxidize under alkaline conditions and later associate with environmental weathering.

Desorption from metal oxides (especially of Fe) at high pH is another mechanism for the development of groundwater-As problems under the oxidizing conditions and would account for the observed positive correlation of As concentrations with increasing pH (e.g. Robertson, 1989; Smedley et al., 2002). Under aerobic and acidic to near-neutral conditions (typical of many natural environments) As is very strongly adsorbed onto oxide minerals as arsenate ion (Smedley et al., 2002). As pH increases, especially above pH 8, As desorbs from the oxide surfaces (Xie et al., 2008), thereby increasing the concentration of As in the water.

Since the Fe oxy-hydroxides are not soluble, concentration of As does not increase with Fe concentration (Fig. 7b). It should be noted that because of various chemical and biogeochemical reactions during groundwater evolution there is no significant correlation between As and Fe (Nath et al., 2008).

Weathering of carbonate rocks and sediments (limestone as host rocks) in studied area could increase the pH. Though the increase of pH in the present context is multifactorial, nevertheless the most

Table 2
Chelpu water samples: ionic ratio and possible origins.

Sample ID	Na/Cl	Na/Na + Cl	Mg/Mg + Ca	Ca/Ca + SO_4	$\text{HCO}_3/\Sigma\text{anion}$	Na/(Cl + SO_4)
SP-1	2.31	0.698	0.212	0.28	0.418	1.7
SP-2	1.92	0.657	0.224	0.334	0.113	0.68
SP-3	11.67	0.921	0.64	0.093	0.437	1.52
SP-4	5.87	0.845	0.196	0.345	0.012	0.36
SP-5	1.77	0.639	0.118	0.102	0.067	1.02
SP-6	10.16	0.91	0.177	0.65	0.841	5.14
SP-7	1.32	0.569	0.283	0.601	0.317	1.08
TR-1	1.31	0.568	0.353	0.58	0.301	1.1
TR-2	1.21	0.548	0.419	0.31	0.054	0.78
TAP	2.5	0.715	0.267	0.455	0.314	1.11
Possible origin	Ion exchange, except for TR-1, TR-2, SP-7 that indicate to halite dissolution	Ion exchange except for TR-1, TR-2, SP-7 that indicate to halite dissolution	Mainly weathered marl (clay, limestone), except for SP-3 that indicate to deposition of calcite	Removal of calcium through ion exchange or calcium Deposition, except for SP-6, SP-7, TR-1 that calcium originated from carbonates or silicates (a source other than gypsum)	Dissolution of gypsum, SP-6 weathering of silicate or carbonate	Alkaline waters, except for SP-2, SP-4 and TR-2 that are not alkaline

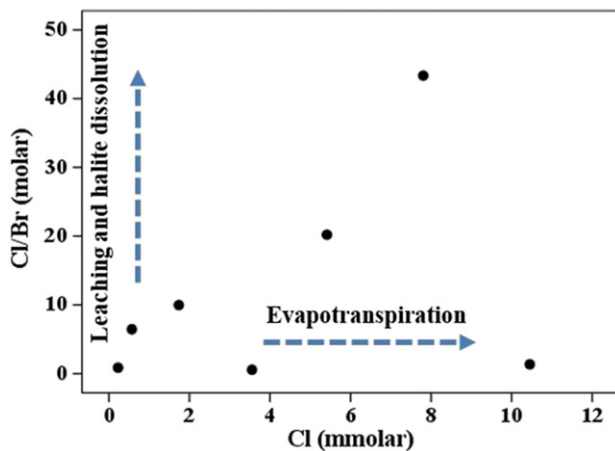


Fig. 6. Relationship between Cl/Br vs. Cl.

important etiology for the increased pH level would be the uptake of protons by mineral-weathering and ion exchange reactions in combination with evaporation (Smedley et al., 2002) in our arid and semi-arid study regions.

Because of two possible sources of SO_4^{2-} in water (sulfide oxidation and gypsum dissolution/precipitation), it is not easy to determine the precise relationship of As and SO_4^{2-} . There is high correlation between As and SO_4^{2-} in studied samples (Fig. 7c). However, due to the presence of such sulfide minerals as realgar, orpiment and arsenopyrite in the argillic alteration zone, the source of As in water can be attributed to oxidation of the As-sulfides.

Boron (B) is found in various environments such as volcanic rock provinces, geothermal systems and highly saline sediments. Because of its high solubility, it tends to accumulate in the evaporites or brines. The process of B sorption and desorption to mineral surfaces is an important control on its concentration in waters associated with sediments.

The $\text{Na}/(\text{Cl} + \text{SO}_4)$ (meq/L) ratios of the studied samples are generally >1 , which indicates they are soda rich waters. The simultaneous enrichment of As and B in soda waters can be related to their elevated alkalinities (Deng et al., 2009). Like As, accordingly (Smedley and Kinniburgh, 2002; Deng et al., 2009), B can also be removed from iron rich soda waters (Fig. 8a and b).

Fig. 8 shows positive correlation of B and pH, B and As, B/Cl ratio vs. Cl and B in studied water samples. The B/Cl vs. Cl and B represents relatively steady trend (Fig. 8c and d), indicating evapotranspiration and B enrichment in the waters (Deng et al., 2009). Therefore, As concentrations increased within As-bearing sulfide-affected waters at high pH (>8) and B levels in semi-arid Chelpu.

5.4. Isotopic composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of water

In a plot of $\delta^{18}\text{O}$ and δD , evaporated waters demonstrate a positive trend (arrow in Fig. 3) that deviates from the LMWL with preferential $\delta^{18}\text{O}$ enrichment (as in Sharp, 2007). In addition, dissolution of evaporative minerals may change the isotopic composition of the water (Horita and Wesolowski, 1994). Dissolution of both anhydrous and hydrated minerals may affect the isotopic ratios of water, however, magnitude of these isotope effects is relatively small (Horita and Wesolowski, 1994). Dissolution of anhydrous minerals change the isotopic ratios of activity (Horita and Wesolowski, 1994); hydrous minerals such as gypsum and clay minerals are enriched in $\delta^{18}\text{O}$, but poor in $\delta^2\text{H}$ compared to water from which they precipitate at isotopic equilibrium (Chacko et al., 2001).

The approach in combining isotopic composition ($\delta^{18}\text{O}$) with Cl^- concentration in water samples lead to a better understanding of the processes that changed the isotopic signatures of the studied water samples (Currell et al., 2010; AL-Charideh and Abou-Zakhem, 2010).

Table 3
Saturation indices of minerals in studied water samples.

Sample ID	$\text{SI}_{(\text{c})}$	$\text{SI}_{(\text{d})}$	$\text{SI}_{(\text{an})}$	$\text{SI}_{(\text{g})}$	$\text{SI}_{(\text{h})}$	$\text{SI}_{(\text{M})}$	$\text{SI}_{(\text{ar})}$
SP-1	0.08	-0.42	-3.38	-3.13	-6.78	-1.05	-0.08
SP-2	-0.09	-0.69	-1.50	-1.26	-6.29	-1.16	-0.24
SP-3	0.36	0.95	-2.56	-2.31	-7.07	0.05	0.21
SP-4	0.34	0.15	-0.31	-0.06	-6.09	-0.75	0.19
SP-5	-0.11	-1.04	-2.04	-1.80	-5.41	-1.49	-0.26
SP-6	-0.02	-0.75	-3.54	-3.29	-7.89	-1.27	0.17
SP-7	-0.01	-0.41	-2.37	-2.12	-6.07	-0.96	-0.16
TR-1	0.83	1.41	-2.26	-2.01	-5.76	0.03	0.68
TR-2	0.43	0.76	-1.27	-1.03	-5.03	-0.23	0.28
TAP	0.38	0.28	-1.66	-1.41	-6.24	-0.64	0.23

Minerals saturation index; $\text{SI}_{(\text{c})}$: calcite, $\text{SI}_{(\text{d})}$: dolomite, $\text{SI}_{(\text{an})}$: anhydrite, $\text{SI}_{(\text{g})}$: gypsum, $\text{SI}_{(\text{h})}$: halite, $\text{SI}_{(\text{M})}$: magnesite, $\text{SI}_{(\text{ar})}$: aragonite.

The processes are categorized in three groups (I, II, III) based on $\delta^{18}\text{O}$ and Cl^- variations (Fig. 9a). The first group is characterized by low Cl^- concentration (mean \pm SD value of 29.9 ± 28.1 mg/L) with enrichment of $\delta^{18}\text{O}$, indicating that the salinity is related to the evaporation effects (Deng et al., 2009; Currell et al., 2010; Xie et al., 2012). The second group is represented by constant $\delta^{18}\text{O}$ values of -8.48% , while the Cl^- concentration increased from 8.0 to 191.9 mg/L, which indicates that the dissolution of evaporites is the origin of salinity in the area (Xie et al., 2012). The third group represents the combination of above two mentioned water groups, where the values of $\delta^{18}\text{O}$ and Cl^- concentration have an intermediate position with mean values of $-7.45 \pm 0.38\%$ and 319.1 ± 251.3 mg/L, respectively; the contribution of salinity and ionic should not be underestimated in etiology of such process as well. Increasing Cl^- reveals similar trend to increased $\delta^{18}\text{O}$ (Fig. 9b), but data plotting above array II confirms further effects of evaporation in studied waters (Currell et al., 2010).

Due to high As concentrations in the water samples and the aim of this study, it should be pointed out that if there is a possibility of seeing a relation between evaporation and As concentrations in the studied waters. In a plot of $\delta^{18}\text{O}$ and As there is no positive trend (Fig. 9c). The relatively negative trend between $\delta^{18}\text{O}$ and As (Fig. 9d), and considering $\delta^{18}\text{O}$ -Cl diagram (Fig. 9a), there would be no likely relation between "evaporation" and "As concentration" in the studied area. On the other hand, high As content waters (Sp-3 and Sp-6) show enrichment of light $\delta^{18}\text{O}$ values (Fig. 9c and d), indicating the contribution of meteoric water to As levels. Meteoric water in contact with arsenic-bearing sulfides of argillic zone boost As dispersion into water.

According to previous observations in the area (Taheri et al., 2016a, b; Mehrzad et al., 2016) and other regions of the world (Zhang et al., 2012; Rodríguez-Lado et al., 2013; Giménez-Forcada and Smedley, 2014) we could confirm that the observed As geo/biodistributions/concentrations pose a health threat, and thus implications of water management policy and health is needed to reduce environmental and public health risk.

6. Conclusion

Geochemical and hydrochemical sources of the ions that affect the saturation indices of the water and water quality itself of Chelpu region were investigated in this study. All samples contained higher dissolved As than WHO standard for drinking water. Because of the presence of As-bearing sulfide minerals hosted within various sedimentary rocks and also because of arid to semi-arid climate of the region, several processes had impacted the water chemistry. Calculated ionic ratios revealed that anions and cations in the waters originated from dissolution of minerals such as gypsum, halite, and also from partial leaching in alteration zones. Source of the ions, and the processes affecting the water chemistry were concluded that the water were influenced by both water-rock interactions (weathering) and evaporation processes. Considering the presence of As-bearing sulfide minerals such as orpiment, realgar and arsenopyrite within argillic-pyrite alteration zones, it

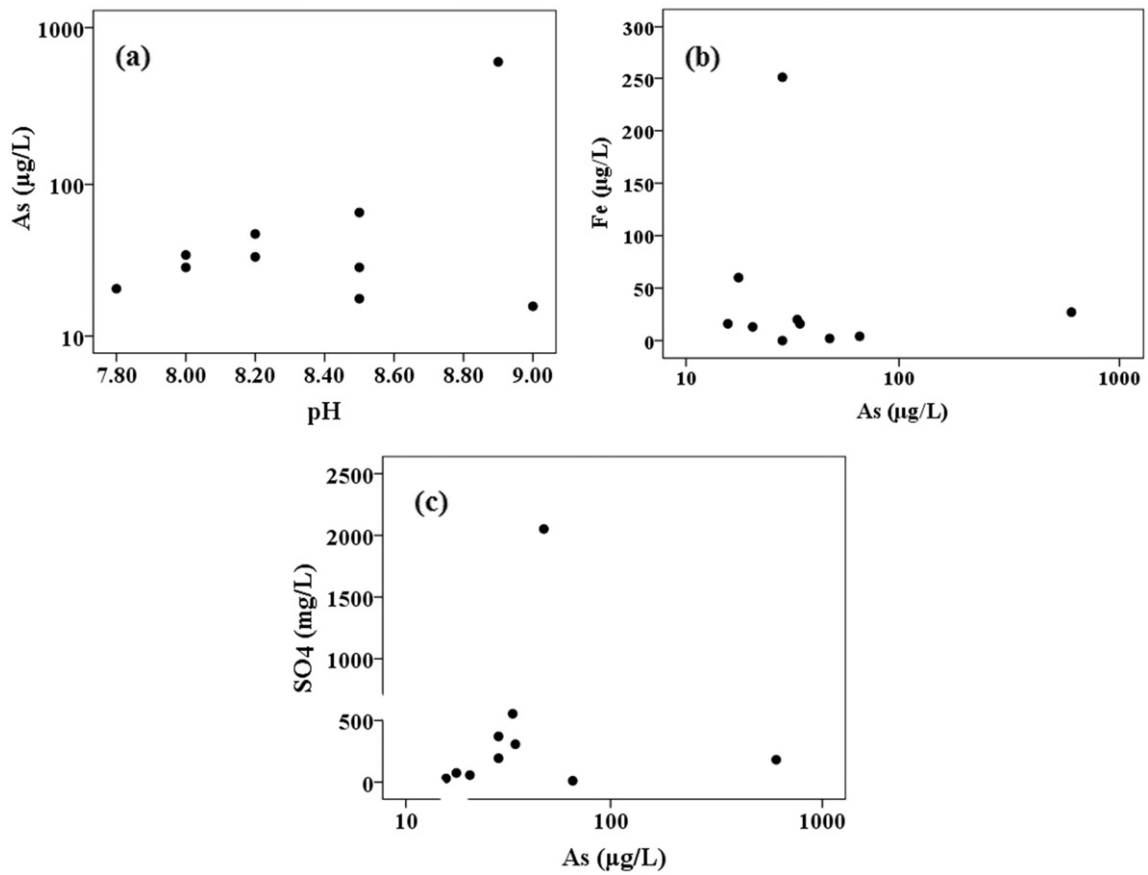


Fig. 7. Relationship between dissolved As concentration with (a) pH; (b) Fe, (c) SO_4 .

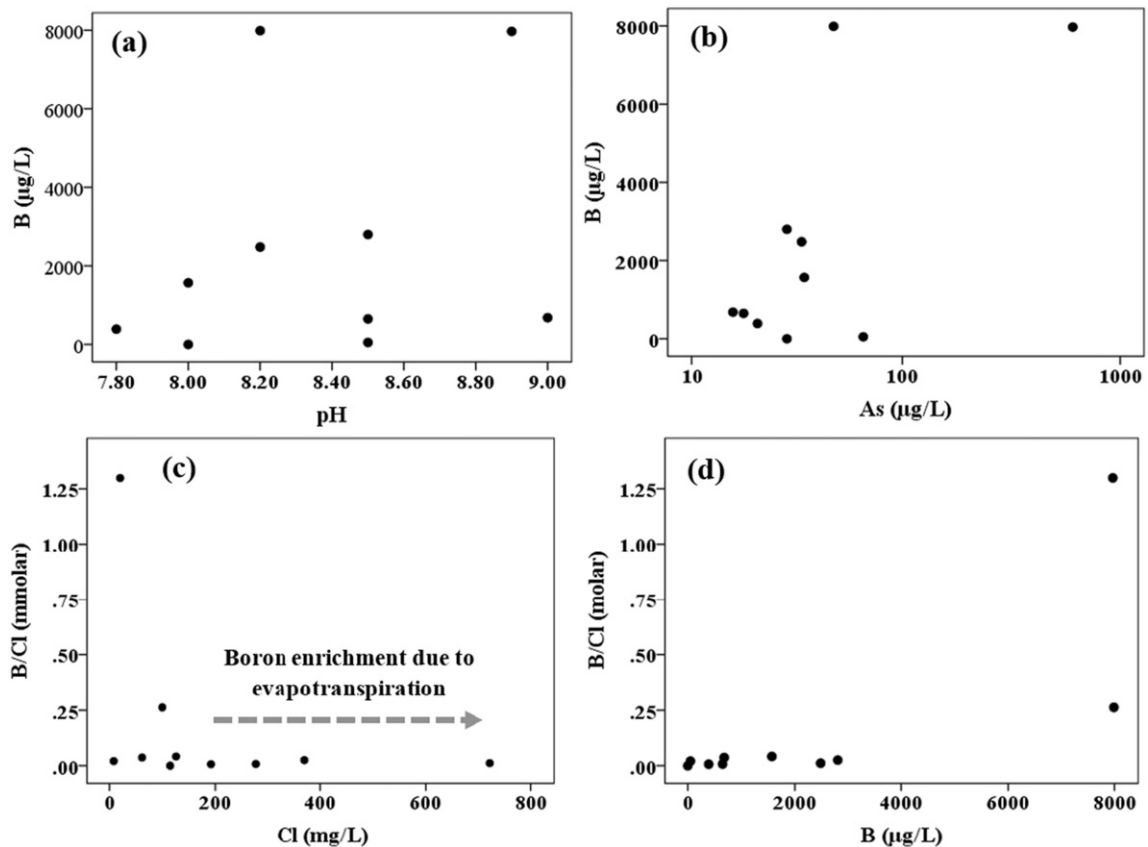


Fig. 8. Correlation plots between (a) dissolved B and pH; (b) dissolved B and As; (c) B/Cl ratio and Cl; (d) B/Cl ratio and B in the water samples.

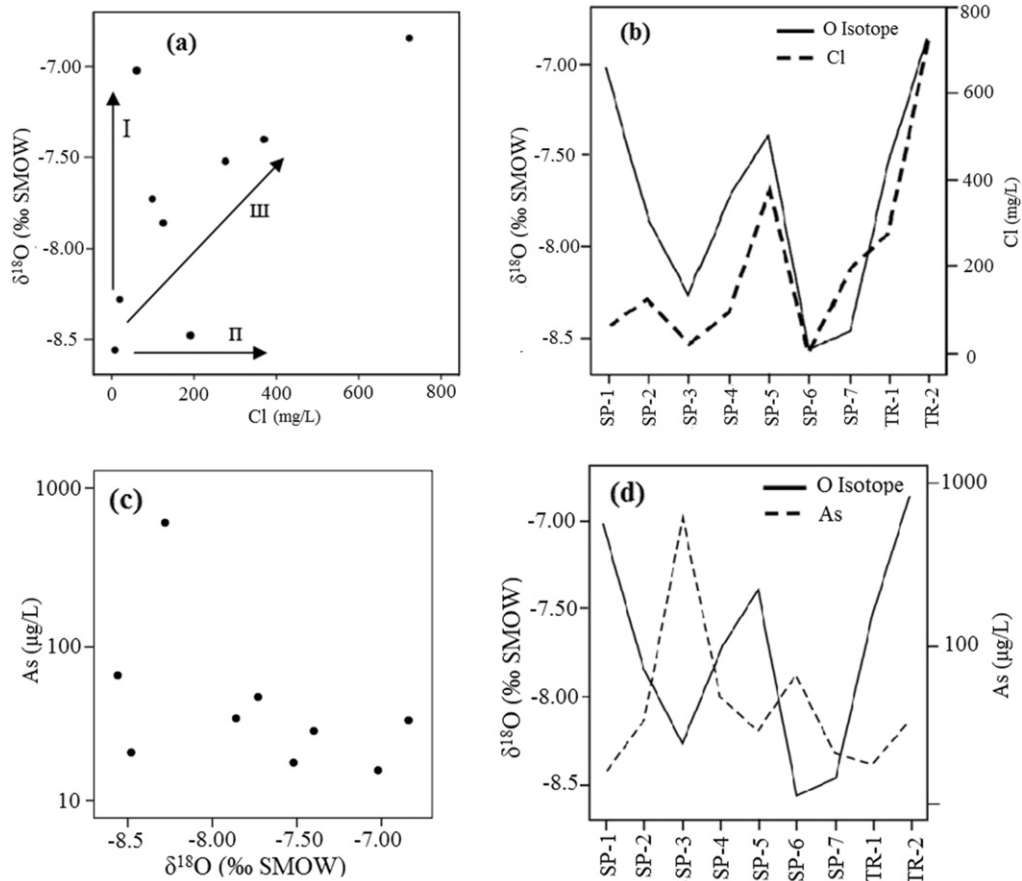


Fig. 9. Relationship between Cl^- and $\delta^{18}\text{O}$ values (a and b); As and $\delta^{18}\text{O}$ values (c and d) of surface and groundwater samples in Chelpu.

is probable that As in the water samples was first released through oxidation under alkaline pH, and in case of previously absorbed onto the surface of free iron oxides; it is also reasonable to suggest that As could be released from the oxide surface through pH increase. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values indicate the source of recharge is precipitation, while evaporation and anion/cation exchanges with evaporites are only partially affecting the water quality in the studied region. High As waters show enrichment of light $\delta^{18}\text{O}$ values, indicating that meteoric water is in contact with Arsenic-bearing sulfidic argillic zone, oxidizes the minerals and releases As into water. Although our current work does not deal with human or ecological health risk assessment, nevertheless, a health risk assessment for the population, in particular infants, is recommended and a small-scale water treatment could also be warranted. Further, since toxic metalloids, especially As, are geogenically and anthropogenically important environmental health issues (Zhang et al., 2012; Rodríguez-Lado et al., 2013; Giménez-Forcada and Smedley, 2014; Taheri et al., 2016a), to broaden this concern in geomedicine, the environmental health impact/concern of As-contaminated area is worth studying.

Conflict of interest

None to be declared.

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References

- Aghanabati, A., 2004. *Geology of Iran*. Ministry of Industry and Mines, Geological Survey of Iran, p. 582.
- Aiuppa, A., Avino, R., Brusca, L., Caliro, V., Chiodini, G., Alessandro, W.D., Favara, R., Federico, C., Ginevra, W., Inguaggiato, S., Longo, M., Pecoraino, G., Valenza, M., 2006. Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: insights from island of Ischia and Phlegrean Fields (Campanian Volcanic Province, Italy). *Chem. Geol.* 229 (4):313–330. <http://dx.doi.org/10.1016/j.chemgeo.2005.11.004>.
- AL-Charideh, A., Abou-Zakhem, B., 2010. Geochemical and isotopic characterization of groundwater from the Paleogene limestone aquifer of the upper Jezireh, Syria. *Environ. Earth Sci.* 59 (5):1065–1078. <http://dx.doi.org/10.1007/s12665-009-0098-1>.
- Argos, M., Kibriya, M.G., Parvez, F., Jasmine, F., Rakibuz-Zaman, M., Ahsan, H., 2006. Gene expression profiles in peripheral lymphocytes by arsenic exposure and skin lesion status in a Bangladeshi population. *Cancer Epidemiol. Biomark. Prev.* 15 (7):1367–1375. <http://dx.doi.org/10.1158/1055-9965.EPI-06-0106>.
- Banerjee, N., Banerjee, S., Sen, R., Bandyopadhyay, A., Sarma, N., Majumder, P., Das, J.K., Chatterjee, M., Kabir, S.N., Giri, A.K., 2009. Chronic arsenic exposure impairs macrophage functions in the exposed individuals. *J. Clin. Immunol.* 29 (5):582–594. <http://dx.doi.org/10.1007/s10875-009-9304-x>.
- Chacko, T., Cole, D.R., Horita, J., 2001. Equilibrium oxygen, hydrogen and carbon isotope fractionation factors applicable to geologic systems. In: Valley, J.W., Cole, D.R. (Eds.), *Stable Isotope Geochemistry* Vol. 43. Mineralogical Society of America, Washington, DC, 1–81. <http://dx.doi.org/10.2138/gsrmg.43.1.1>.
- Clark, I., 2015. *Groundwater Geochemistry and Isotopes*. Taylor & Francis Group, International Standard Book Number-13 (ISBN: 978-1-4665-9174-5).
- Currell, M., Cartwright, I., Bradley, C., Han, D., 2010. Recharge history and controls on groundwater quality in the Yuncheng Basin, North China. *J. Hydrol.* 385 (1–4):216–229. <http://dx.doi.org/10.1016/j.jhydrol.2010.02.022>.
- Davis, S.N., Whittemore, D.O., Martine, J.F., 1998. Uses of chloride/bromide ratios in studies of potable water. *Ground Water* 36 (2):338–350. <http://dx.doi.org/10.1111/j.1745-6584.1998.tb01099.x>.
- Deng, Y., Wang, Y., Ma, T., 2009. Isotope and minor element geochemistry of high arsenic groundwater from Hangjinhouqi, the Heto Plain, Inner Mongolia. *Appl. Geochem.* 24 (4):587–599. <http://dx.doi.org/10.1016/j.apgeochem.2008.12.018>.
- Deutsch, W.J., 1997. *Groundwater Geochemistry: Fundamentals and Applications to Contamination*. Lewis Publishers, New York.
- Fillol, C., Dor, F., Labat, L., Boltz, L., Bouard, J.L., Mantey, K., Mannschott, C., Puskarszyk, E., Viller, F., Momas, I., Seta, N., 2010. Urinary arsenic concentration and speciation in

- residents living in an area with naturally contaminated soils. *Sci. Total Environ.* 408 (5):1190–1194. <http://dx.doi.org/10.1016/j.scitotenv.2009.11.046>.
- Gibbs, R.J., 1970. Mechanisms controlling world water chemistry. *Science* 170 (3962), 795–840.
- Giménez-Forcada, E., Smedley, P.L., 2014. Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain. *Environ. Geochem. Health* 36 (6):1029–1047. <http://dx.doi.org/10.1007/s10653-014-9599-2>.
- Gómez, P., Turrero, M.J., Garralón, A., Peña, J., Buil, B., de Cruz, B., Sánchez, M., Sánchez, D.M., Quejido, A., Bajos, C., Sánchez, L., 2006. Hydrogeochemical characteristics of deep groundwaters of the Hesperian Massif (Spain). *J. Iber. Geol.* 32 (1), 113–131.
- Hall, M., Chen, Y., Ahsan, H., Slavkovich, V., Geen, A.V., Parvez, F., Graziano, J., 2006. Blood arsenic as a biomarker of arsenic exposure: result from a prospective study. *Toxicology* 225 (2–3):225–233. <http://dx.doi.org/10.1016/j.tox.2006.06.010>.
- Henke, K., 2009. Arsenic Environmental Chemistry, Health Threats and Waste Treatment. p. 588 (ISBN: 978-0-470-02758-5).
- Hogan, F.J., Mills, S.K., Hendrick, J.M.H., Ruiz, J., Chesley, J.T., Asmerom, Y., 2007. Geologic origins of salinization in a semi-arid river: the role of sedimentary basin brines. *Geology* 35 (12):1063–1066. <http://dx.doi.org/10.1130/G23976A.1>.
- Hogue, C.A., 2001a. A sip of arsenic? Debate over allowable level in drinking water focuses on health effects, removal cost. *Chem. Eng. News* 79 (21):50–55. <http://dx.doi.org/10.1021/cen-v079n021.p051>.
- Hogue, C., 2001b. Cancer risk from arsenic confirmed. New study strengthens evidence for lower drinking water standard. *Chem. Eng. News* 79 (38):12. <http://dx.doi.org/10.1021/cen-v079n038.p012>.
- Horita, J., Wesolowski, D.J., 1994. Liquid-vapor fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature. *Geochim. Cosmochim. Acta* 58 (16):3425–3437. [http://dx.doi.org/10.1016/0016-7037\(94\)90096-5](http://dx.doi.org/10.1016/0016-7037(94)90096-5).
- Hounslow, A.W., 1995. *Water Quality Data: Analysis and Interpretation*. CRC Press LLC, Florida, pp. 47–126 (ISBN 9780873716765 - CAT# L676).
- IARC, 2004. Monographs on the Evaluation of Carcinogenic Risks to Humans. Some Drinking-water Disinfectants and Contaminants, Including Arsenic. p. 84.
- Karakaya, N., Karakaya, M.C., Nalbantçilar, M.T., Yavuz, F., 2007. Relation between spring-water chemistry and hydrothermal alteration in the Saplica volcanic rocks, Sebinkarahisar (Turkey). *J. Geochem. Explor.* 93 (1):35–46. <http://dx.doi.org/10.1016/j.jgexplo.2006.08.012>.
- Kozul, C., Hampton, T., Davey, J., Gosse, J., Nomikos, A., Eisenhauer, P., Weiss, D., Thorpe, J., Ihnat, M., Hamilton, J., 2009. Chronic exposure to arsenic in the drinking water alters the expression of immune response genes in mouse lung. *Environ. Health Perspect.* 117 (7):1108–1115. <http://dx.doi.org/10.1289/ehp.0800199>.
- Lengke, M.F., Tempel, R.N., 2001. Kinetic rates of amorphous As₂S₃ oxidation at 25 to 40 °C and initial pH of 7.3 to 9.4. *Geochim. Cosmochim. Acta* 65 (14):2241–2255. [http://dx.doi.org/10.1016/S0016-7037\(01\)00592-0](http://dx.doi.org/10.1016/S0016-7037(01)00592-0).
- Lengke, M.F., Tempel, R.N., 2003. Natural realgar and amorphous AsS oxidation kinetics. *Geochim. Cosmochim. Acta* 67:859–871. [http://dx.doi.org/10.1016/S0016-7037\(02\)01227-9](http://dx.doi.org/10.1016/S0016-7037(02)01227-9).
- Lengke, M.F., Tempel, R.N., 2005. Geochemical modeling of arsenic sulfide oxidation kinetics in a mining environment. *Geochim. Cosmochim. Acta* 69 (2):341–356. <http://dx.doi.org/10.1016/j.gca.2004.06.032>.
- Lengke, M.F., Sanpawanitchakit, S., Tempel, R.N., 2009. The oxidation and dissolution of arsenic bearing sulfides. *Can. Mineral.* 47 (3):593–613. <http://dx.doi.org/10.3749/canmin.47.3.593>.
- Mazloumi Bajestani, A., 1992. *Geology and Geochemical Study of Gold-bearing Aliabad and Altered Koohsorkh Areas in North of Kashmar, NE Iran*. (M.Sc. Dissertation). Shahid Beheshti University, p. 254.
- Mehrzad, J., Mahmudy Gharai, M.H., Taheri, M., 2016. Effects of arsenic on porcine dendritic cells in vitro. *J. Immunotoxicol.* In press. [10.1080/1547691X.2016.1249985](http://dx.doi.org/10.1080/1547691X.2016.1249985).
- Mohammadzadeh, H., 2010. *The Meteoric Relationship for ¹⁸O and ²H in Precipitations and Isotopic Compositions of Water Resources in Mashhad Area (NE Iran)*. The 1st International Applied Geological Congress. Department of Geology, Islamic Azad University - Mashhad Branch, Iran, pp. 26–28.
- Naderi Mighan, N., 1999a. Geological Map of Shamkan, 1: 100000. Geological Survey of Iran. No. 7661.
- Naderi Mighan, N., 1999b. Geological map of Kadkan, scale 1:100000. Geological Survey of Iran. No.7761.
- Nath, B., Jean, J., Lee, M.K., Yang, H.J., Liu, C.C., 2008. Geochemistry of high arsenic groundwater in Chia-Nan Plain, southwestern Taiwan: possible sources and reactive transport of arsenic. *J. Contam. Hydrol.* 99:85–96. <http://dx.doi.org/10.1016/j.jconhyd.2008.04.005>.
- Nriagu, J.O., 1989. A global assessment of natural sources of atmospheric trace metals. *Nature* 338:47–49. <http://dx.doi.org/10.1038/338047a0>.
- Piper, A.M., 1994. A geographic procedure in the geochemical interpretation of water analysis. *Trans. Am. Geophys. Union* 25, 914–928 (Washington, D.C.).
- Ravenscroft, P., Brammer, H., Richards, K., 2009. *Arsenic Pollution: A Global Synthesis*. John Wiley & Sons, West Sussex, UK (ISBN: 978-1-405-18602-5).
- Robertson, F.N., 1989. Arsenic in groundwater under oxidizing conditions, south-west United States. *Environ. Geochem. Health* 11 (3):171–185. <http://dx.doi.org/10.1007/BF01758668>.
- Rodríguez-Lado, L., Sun, G., Berg, M., Zhang, Q., Xue, H., Zheng, Q., Johnson, C.A., 2013. Groundwater arsenic contamination throughout China. *Science* 341 (6148):866–868. <http://dx.doi.org/10.1126/science.1237484>.
- Sarkar, D., Datta, R., Hannigan, R., 2007. *Concepts and Applications in environmental Geochemistry*. first ed. 5. Elsevier, Amsterdam [etc.], pp. 229–243 (eBook ISBN: 9780080549736).
- Sharp, Z., 2007. *Principles of Stable Isotope Geochemistry*. Pearson Education, Inc., p. 344 (ISBN-13: 978-0130091390).
- Smedley, P.L., Kinniburgh, D.G., 2002a. A review of the source, behavior and distribution of arsenic in natural water. *Appl. Geochem.* 17 (5), 517–568.
- Smedley, P.L., Kinniburgh, D.G., 2002a. A review of the source, behavior and distribution of arsenic in natural water. *Appl. Geochem.* 17 (5):517–568. [http://dx.doi.org/10.1016/S0883-2927\(02\)00018-5](http://dx.doi.org/10.1016/S0883-2927(02)00018-5).
- Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J., Tullio, J.O., 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. *Appl. Geochem.* 17 (3):259–284. [http://dx.doi.org/10.1016/S0883-2927\(01\)00082-8](http://dx.doi.org/10.1016/S0883-2927(01)00082-8).
- Taheri, M., Mehrzad, J., Mahmudy Gharai, M.H., Afshari, R., Radsetan, A., Hami, S., 2016a. High soil and groundwater arsenic levels induce high body arsenic loads, health risk and potential anemia for inhabitants of northeastern Iran. *Environ. Geochem. Health* 38 (2):469–482. <http://dx.doi.org/10.1007/s10653-015-9733-9>.
- Taheri, M., Mehrzad, J., Afshari, R., Saleh-Moghaddam, M., Mahmudy Gharai, M.H., 2016b. Inorganic arsenic can be potent granulotoxin in mammalian neutrophils in vitro. *J. Immunotoxicol.* 13 (5):686–693. <http://dx.doi.org/10.3109/1547691X.2016.1159625>.
- Tamasi, G., Cini, R., 2004. Heavy metals in drinking waters from Mount Amiata (Tuscany, Italy). Possible risks from arsenic for public health in the province of Siena. *Sci. Total Environ.* 327 (1–3):41–51. <http://dx.doi.org/10.1016/j.scitotenv.2003.10.011>.
- Todd, D.K., Mays, L.W., 2005. *Groundwater Hydrology*, third ed. John Wiley and Sons, Inc., NY, p. 636.
- Warren, J.K., 2006. *Evaporites: Sediments, Resources and Hydrocarbons*. pp. 91–93 ISBN 978-3-540-32344-0. (Chapter 2).
- World Health Organization, 2011. *Guidelines for Drinking-Water Quality*.
- Xie, X., Wang, Y., Su, C., Huaqing, L., Duan, M., Xie, Z., 2008. Arsenic mobilization in shallow aquifers of Datong basin: hydrochemical and mineralogical evidences. *J. Geochem. Explor.* 98 (3):107–115. <http://dx.doi.org/10.1016/j.jgexplo.2008.01.002>.
- Xie, X., Wang, Y., Chunli, S., Li, J., Li, M., 2012. Influence of irrigation practices on arsenic mobilization: Evidence from isotope composition and Cl/Br ratios in groundwater from Datong basin, northern China. *J. Hydrol.* 424–425:37–47. <http://dx.doi.org/10.1016/j.jhydrol.2011.12.017>.
- Yin, L., Hou, G., Dou, Y., Tao, Z., Li, Y., 2011. Hydrogeochemical and isotopic study of groundwater in the Habor Lake Basin of the Ordos Plateau, NW China. *Environ. Earth Sci.* 64 (6):1575–1584. <http://dx.doi.org/10.1007/s12665-009-0383-z>.
- Zhang, Q., Rodríguez-Lado, L., Johnson, C.A., Xue, H., Shi, J., Zheng, Q., Sun, G., 2012. Predicting the risk of arsenic contaminated groundwater in Shanxi Province, Northern China. *Environ. Pollut.* 165:118–123. <http://dx.doi.org/10.1016/j.envpol.2012.02.020>.