

Environmental geochemistry and sources of natural arsenic in the Kharraqan hot springs, Qazvin, Iran

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Received: 9 June 2014 / Accepted: 11 October 2014 / Published online: 29 October 2014
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Abstract The Kharraqan hot springs are located in the historic city of Abe-Garm, famous for its hot springs, in Qazvin province, in northwestern Iran. Thermal waters with temperatures ranging from 28.7 to 52 °C vary in chemical composition and TDS contents. Those waters generally are enriched in Na–Cl–HCO₃ and suggest deep water circulation. Chemistry of all of the water samples are graphed in the Cl–SO₄–HCO₃ ternary diagram. There is a trend of mixing along a line of constituent proportions between recently recharged water and older water. The trend toward the chloride corner is mainly the result of contact in the subsurface with evaporite-bearing formations and/or mixing with brines. Relatively high concentrations of Na, Ca, K, Cl, and SO₄ resulted from rock/water interactions. These hot spring waters show high concentrations of arsenic (0.14–0.95 mg L⁻¹). The diffusion of As-bearing spring waters into shallow aquifers could contaminate the groundwater which is used for drinking purposes. Also discharges of this As-enriched water into streams and rivers could affect irrigated crops in downstream fields. In both cases, the health of local residents could be at risk.

Keywords Environmental impact · Hot spring · NW of Iran

Introduction

The Abe-Garm area is located in the northwestern part of Iran which is related to the volcanic belt of the Orumieh-Dokhtar zone (Bolourchi et al. 1979; Aghanabati 2004) (Fig. 1). It is a well-known geothermal area in Iran (Yousefi et al. 2010). These hot springs are used for swimming, bathing, and medical purposes. Visitors and local people use these resources and there is substantial room for expansion of use of this water as international and domestic tourism becomes established in Iran (Erfurt-Cooper and Cooper 2009; Navi et al. 2012). The natural contamination of local rivers and groundwater resources as a result of hot spring discharges is a global occurrence, yet the characteristics of toxic elements in hot spring waters have rarely been addressed. The purpose of this study was to establish the geochemical characteristics and possible adverse environmental impacts of the hot spring waters in the Abe-Garm geothermal field and surrounding areas.

The host rocks of the area are Cambrian to Recent age, but are interrupted by several unconformities and gaps. Lithologic aspects of different rock units reveal the presence of several sedimentary environments. The oldest exposed rocks are Carboniferous sediments (Sink Formation) consisting of sandstone and dolomite. The early Permian sandstone, conglomerates and shales of Dorud Formation are underlain by the older Paleozoic sediments and overlain by the Ruteh Formation and Nesen Formation. Triassic sediments (Elika Formation), consisting of limestone and dolomite, also rest on an erosional surface of Permian sediments. Plant-bearing sandstone and shales of Rhaeto-Liassic Shemshak Formation transgressively overlie the Triassic dolomite. The Shemshak Formation is overlain by ammonite-rich marly limestone of Middle Jurassic Dalichay Formation which transitions into the Late Jurassic Lar

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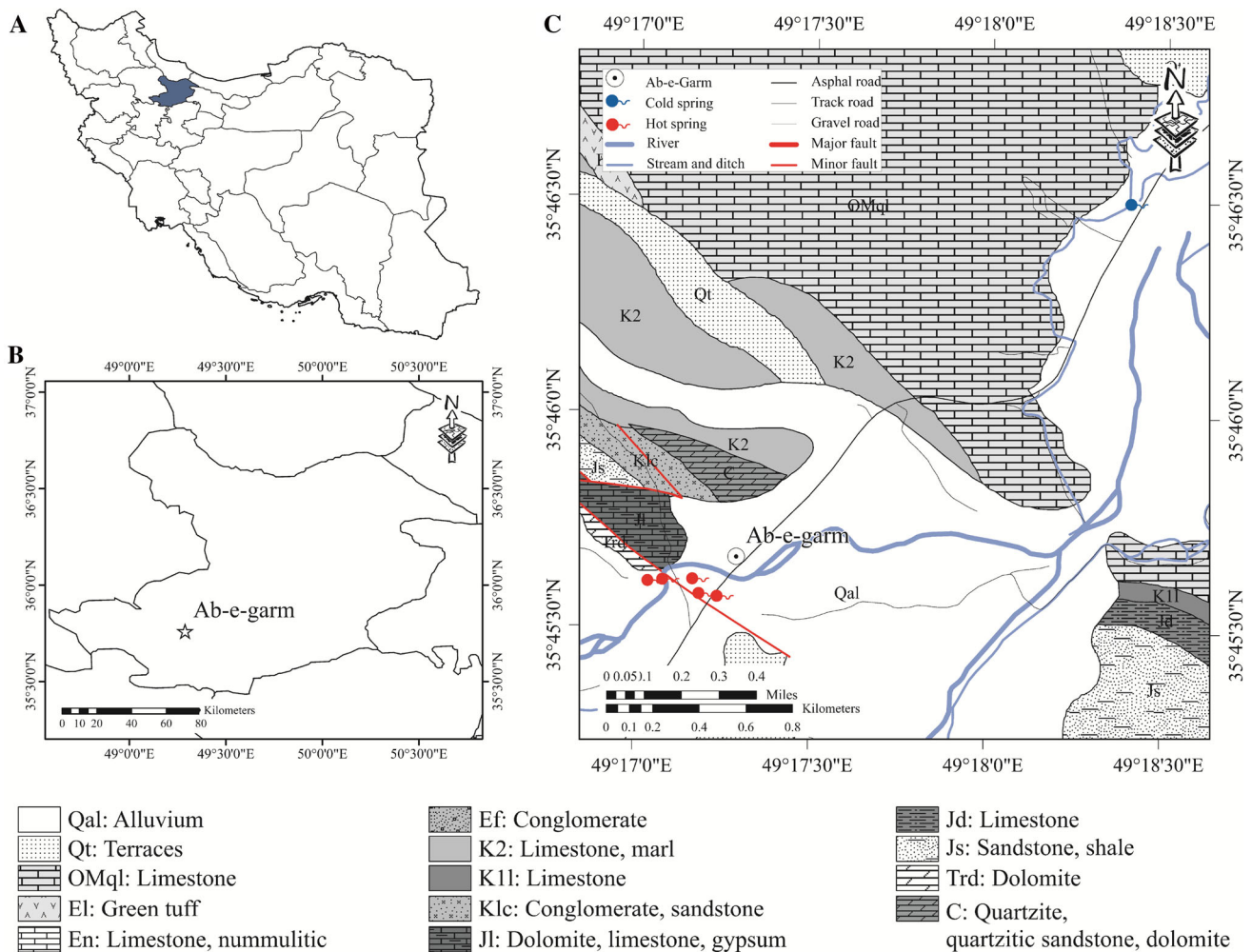


Fig. 1 Location map of the Abe-Garm area (a, b). Geological map of Abe-Garm area (c) (Bolourchi et al. 1979)

Formation, consisting of dolomite, limestone, marl, gypsum and volcanic rocks. Lower Cretaceous rocks unconformably overlie the Jurassic sediments consisting of conglomerate, sandstone, Orbitolina limestone and volcanic rocks. A clear disconformity is seen between the Upper Cretaceous marly limestones and limestones, and the Lower Cretaceous rocks. The Eocene is represented mainly by thick volcanic rocks and tuffaceous sediments of the “Karaj Formation”, locally having a basal limestone (Ziarat Formation) and conglomerate (Fajan Formation) and resting with distinct angular unconformity on various older formations. The Oligocene clastic deposit (Lower red formation) and Oligo-Miocene marine deposit (Qom Formation) unconformably overlie the older formations. The Qom Formation is overlain by the Miocene upper red formation consisting of sandstone, marl and conglomerate, locally with salt dome and gypsum. The young deposits are Quaternary terraces, travertine and alluvium, which unconformably overlie the older rocks (Bolourchi et al. 1979).

The Abe-Garm range is the southeastern continuation of the Soltanieh Mountains. It has a NW–SE strike and is separated into two longitudinal ranges by Hassanabad fault (Bolourchi et al. 1979). The continuation of the Hassanabad fault extends to the Ipak active fault (Berberian 1971). In addition to the longitudinal faults and thrusts, the range displays a great number of transverse faults in various directions that disrupt the pre-Tertiary formations into a complicated mosaic-like fault block pattern (Bolourchi et al. 1979; Taheri et al. 2012b; Yazdi et al. 2013).

Sampling and analytical methods

A total of five thermal and one cold water samples were collected from the Abe-Garm area. To investigate the seasonal changes of field and chemical parameters and to trace element concentrations in dry and wet seasons, springs were sampled twice in May and November. The locations of the

Table 1 Basic features and major compositions of spring waters from the Abe-Garm area. (Dry season)

Parameter	HS-1	HS-2	HS-3	HS-4	HS-5	CS-6	WHO
Temp. (°C)	52	28.7	28.7	51	44.3	17	
pH	6.46	6.58	6.3	6.36	6.6	7.35	6.5–8.5
EC (µs/cm)	12,660	12,520	8,348	12,380	12,360	3,532	2,000
TDS (mg L ⁻¹)	7,760	7,750	5,060	7,650	7,660	2,000	1,000
Ca (mg L ⁻¹)	409	406	242	381	431	112	50
K (mg L ⁻¹)	115	122	51	116	126	8	10
Mg (mg L ⁻¹)	66	70	52	70	73	37	30
Na (mg L ⁻¹)	2,190	2,284	1,018	2,213	2,299	280	200
Cl ⁻ (mg L ⁻¹)	3,403	3,474	1,631	3,403	3,474	425	250
SO ₄ ²⁻ (mg L ⁻¹)	760	812	438	780	758	288	250
HCO ₃ ⁻ (mg L ⁻¹)	1,244	1,263	854	1,171	1,215	256	

HS Hot spring, CS Cold spring

water samples are shown in Fig. 1. Temperature, pH and electrical conductivity (EC) of the water samples were measured on-site. Water samples were collected into 250-ml polyethylene containers. All water samples were collected as two filtered batches. 2.5-ml ultrapure Merck HNO₃ was added into one of the batches for cation analyses. The other batch taken for anion analyses was untreated. Water analyses were performed using standard methods in the “Geological Survey of Iran” Laboratories. Bicarbonate and chloride analyses were measured by titration methods, sulfate concentration by spectrophotometry and cations by flame photometry. Acidified samples were analyzed for major and trace elements with an ICP-OES method.

Results and discussion

Main chemical characteristics

The main physical and chemical characteristics of the hot springs and cold spring waters are shown in Table 1. The arbitrary temperature for considering a spring as a thermal spring is 36.7 °C according to Pentecost et al. (2003). Temperatures of the thermal springs range from 28.7 °C (sample HS-3) to 52 °C (sample HS-1). pH values in the samples were between 6.30 and 7.35 (Table 1).

Total dissolved solids (TDS) is the term used to describe the inorganic salts and small amounts of organic matter present in solution in water. The principal constituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, bicarbonate, chloride, sulfate, and nitrate anions (WHO 2003). Excluding the sample CS-6 (drinking water), TDS contents of the thermal waters range from 5,060 to 7,760 mg L⁻¹. Reliable data on possible health effects associated with the ingestion of TDS in drinking water are not available. Water containing TDS concentrations below 1,000 mg/liter is usually acceptable to consumers, although acceptability may vary according to circumstances.

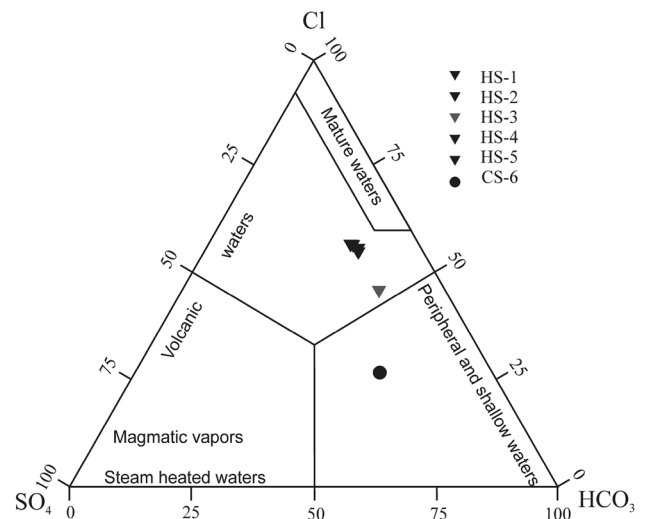


Fig. 2 Relative Cl, SO₄ and HCO₃ contents of the Abe-Garm spring waters (Giggenbach 1988) (Wet season)

However, the presence of high levels of TDS in water may be objectionable to consumers owing to the resulting taste and to excessive scaling in water pipes, heaters, boilers, and household appliances (WHO 2003). The spring waters have apparently high EC values and high Ca, K, Mg, Na, Cl, HCO₃, and SO₄ concentrations. Cations show the following order of abundance: Na > Ca > K > Mg and anions follow the order of Cl > HCO₃ > SO₄.

The values in the WHO guidelines for drinking water quality can be used to screen for potential risks arising from swimming pools and similar environments, while making appropriate allowance for the much lower quantities of water ingested, shorter exposure periods and non-ingestion exposure (WHO 2006).

Since thermal springs emanate from a hydrothermal reservoir beneath their surface manifestation, geochemical investigation of water samples can reveal the processes occurring or occurred recently in the hydrothermal reservoir and give indications on the source of elements

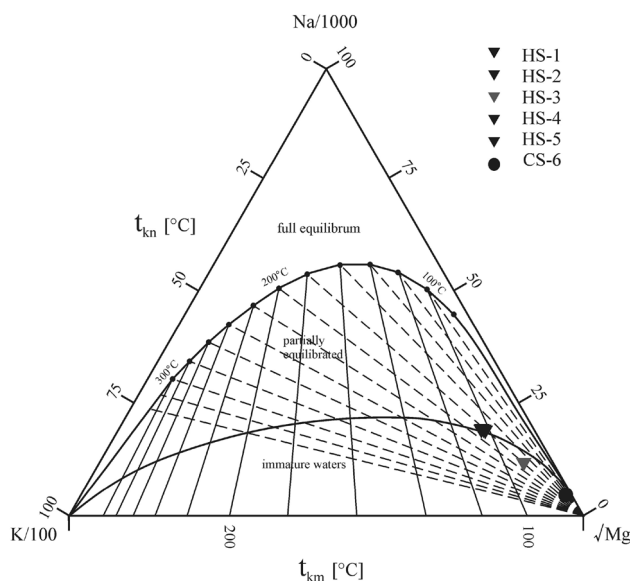


Fig. 3 Graphical evaluation of the water–rock equilibration temperatures (Giggenbach 1988) using relative Na, K and Mg concentrations of the Kharraqan thermal waters (Dry season)

(Modabberi and Jahromi Yekta 2014). Information on the geochemistry of thermal waters is scarce or limited to major ions (Chudaev et al. 2006). The Cl–SO₄–HCO₃ triangular plot is used for an initial classification of geothermal water samples (Giggenbach 1988; Marini 2000). All of the samples listed in Table 1 are plotted in the Cl–SO₄–HCO₃ ternary diagram (Fig. 2). The waters of Abe-Garm plot between HCO₃ and Cl fields yielding a mixing along the line between peripheral and mature water fields, but they never attain maturity. The trend toward the chloride corner is mainly the result of contact in the subsurface with evaporite-bearing formations and/or mixing with brines (Karimi and Moore 2008).

Figure 3 shows that none of the Kharraqan waters attains a water–rock chemical equilibrium. The model is based on the following geothermometers assuming that activities of minerals are close to unity.

The plot of 10 Mg/(10 Mg + Ca) versus 10 K/(10 K + Na) (Giggenbach 1988) for waters of the Abe-Garm area is presented in Fig. 4. Like the model given in Fig. 3, the positions of the samples do not indicate equilibration between the rock and waters. Another result deduced from Fig. 4 is that the waters of the Abe-Garm area have not been produced through the dissolution of average crustal rock or they have gained their salinity by simple rock leaching or mixing.

Assuming equilibrium with calcite, CO₂ partial pressures (P_{CO_2}) of the Kharraqan thermal waters can be evaluated in the K–Mg–Ca geoinicator diagram (Fig. 5). In the diagram, all of the values for the hot waters are below the full equilibrium line.

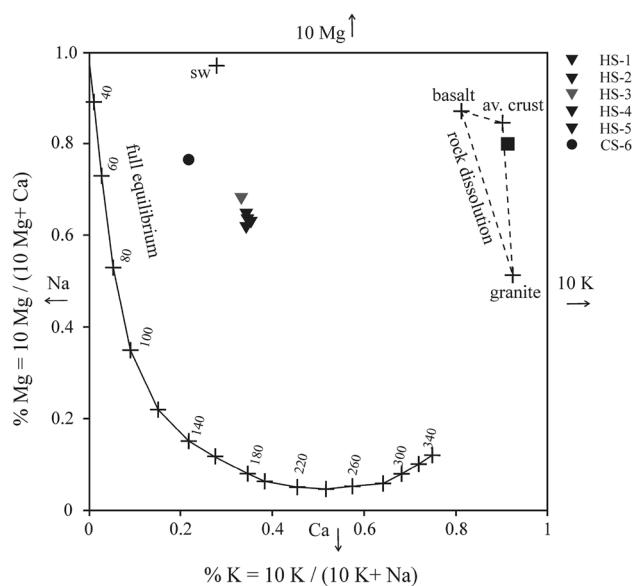


Fig. 4 Plot of 10 K/(10 K + Na) vs. 10 Mg/(10 Mg + Ca) (Giggenbach 1988) of the Kharraqan thermal waters (Dry season)

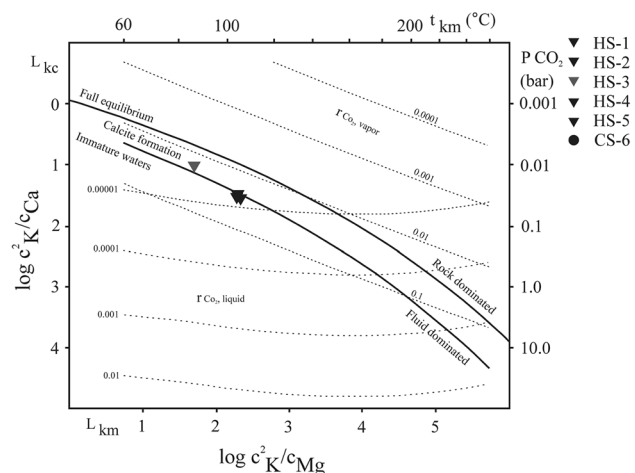


Fig. 5 K–Mg–Ca geoinicator diagram (Giggenbach 1988) for the Kharraqan thermal waters (Dry season)

The presence of many active fault systems, the widespread occurrence of highly fractured carbonate rocks, and large hydraulic head differences allow a deep, large-scale (regional) circulation of waters before their emergence at the surface as springs (Minissale 1991). Based on chemical analyses of the thermal waters, data interpretations, and lithologic aspects in the study area, earlier investigators concluded that the waters discharged from the hot springs are of meteoric origin (Ghafouri 2003). The waters are heated as they circulate in the system through joints, fractures and the Hassanabad fault. During their circulation, the waters come into contact with evaporite-bearing formations and brines, resulting in an increase in dissolved ion concentrations. High surface heat flow is perhaps due to

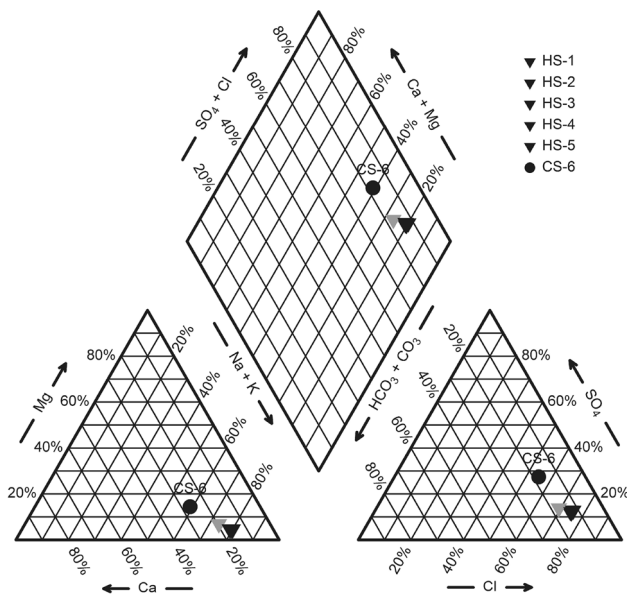


Fig. 6 Piper trilinear diagram for spring water classification in the area (dry season)

the Orumieh-Dokhtar volcanic belt, with an attendant high-temperature gradient with depth (Taheri et al. 2012b).

The diagnostic chemical character of water solutions in hydrologic systems has been determined with the application of the concept of hydrochemical facies (Back 1966), which enables a convenient subdivision of water compositions by identifiable categories and reflects the effect of chemical processes occurring between the minerals within the subsurface rock units and the groundwater. Statistical distribution diagrams such as Piper trilinear (Piper 1944) are used to gain better insight into the hydrochemical processes operating in the groundwater system. The Piper trilinear diagram was used for the purpose of characterizing the water type present in the area. It permits the cation and anion compositions of many samples to be represented on a single graph in which major groupings or trends in the data can be discerned visually (Freeze and Cherry 1979). Water types are often used in the characterization of waters as a diagnostic tool (Leybourne et al. 1998; Pitkanen et al. 2002). The Piper trilinear diagram (Fig. 6) for the study area shows that hot spring waters are of the Na–Cl type.

Travertine currently precipitates all around the Abe-Garm area. A sudden drop in the pressure and the decreasing temperature are accompanied by CO₂ loss cause calcite to precipitate mostly at shallow depths (Mutlu 1998).

Trace elements in spring waters

As the usable water availability is rapidly decreasing globally, the quality of the drinkable water is also

becoming a major concern. Specifically, the presence of geogenic, non-point source, natural contaminants like arsenic (As) and other oxyanion-forming metals and metalloids (e.g., Mo, V, W, Se, Sb), can limit the availability of suitable potable water sources in some of the most densely populated parts of the world (Welch et al. 2000; Charlet and Polya 2006; Nicolli et al. 2012; Mukherjee et al. 2008, 2011; Kim et al. 2011; Thakur et al. 2011; Raychowdhury et al. 2013). Trace element concentrations in the hot and cold spring waters are given in Table 2. The hot spring waters show high concentrations of arsenic and other trace elements (Taheri et al. 2012a). In natural environments, As is present in four oxidation states: –III, 0, +III, +V. Of these, in hydrologic systems, it exists most commonly as arsenite [As(III), e.g., H₃AsO₃ and H₂AsO₃[–]] and arsenate [As(V), e.g., H₂AsO₄[–] and HAsO₄^{2–}] (Smedley and Kinniburgh 2002; Choong et al. 2007; Raychowdhury et al. 2013). In neutral oxygenated waters, As(V) is the thermodynamically favored form, whereas As(III) is stable under reducing conditions (Caporale et al. 2013). The presence of these inorganic, oxyanions of As in groundwater is dependent on climatic conditions, geomorphology/geology, tectonic setting, hydrogeochemical characteristics like pH, redox potential, ionic strength, ionic concentrations, organic matter content and microbial activities, among others (Scanlon et al. 2009). The level of arsenic in natural waters, including open ocean seawater, generally ranges between 1 and 2 µg L^{–1} (Hindmarsh and McCurdy 1986; USNRC 1999). Concentrations may be elevated, however, in areas with volcanic rock and sulfide mineral deposits (Hindmarsh and McCurdy 1986); in areas containing natural sources, where levels as high as 12 mg L^{–1} have been reported (WHO 2011); near anthropogenic sources, such as mining and agrochemical manufacture; and in geothermal waters (mean 500 µg L^{–1}, maximum 25 mg L^{–1}). Mean arsenic concentrations in sediment range from 5 to 3,000 mg kg^{–1}; the higher levels occur in areas of contamination (USNRC 1999) but are generally unrelated to arsenic concentrations in water.

In the Abe-Garm geothermal field all of the spring water samples contained arsenic concentrations that were significantly higher than the 10 µg L^{–1} guideline set by the World Health Organization. The actual source of groundwater arsenic contamination, in the Abe-Garm area, is yet to be established. The sources of arsenic are geothermal or may be derived from sedimentation and mining. There is no proof regarding the volcanic emission of As in the Abe-Garm area so far. However, the release of As, by the natural processes in groundwater has been recognized, from the Miocene sediments comprising sandstone, marl and conglomerate, locally with salt dome and gypsum (Upper red formation) and plant-bearing sandstones and shales of the Rhaeto-Liassic Shemshak Formation.

Table 2 Trace element concentrations of spring waters from the Abe-Garm geothermal areas. (Wet season)

Parameter	HS-1	HS-2	HS-3	HS-4	HS-5	CS-6	WHO
Ag	0.02	0.02	0.02	0.02	0.02	0.01	0.1
Al	<0.01	0.01	0.02	0.12	0.03	0.02	
As	0.95	0.95	0.14	0.84	0.79	0.06	0.01
B	16.15	16.41	7.48	16.08	16.28	0.82	0.5
Ba	0.08	0.09	0.05	0.09	0.09	0.03	0.7
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Cd	<0.01	<0.01	0.01	0.01	0.01	<0.01	0.003
Co	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Cr	0.02	0.02	<0.01	<0.01	0.03	<0.01	0.05
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Dy	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	
Er	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Eu	0.02	0.03	0.01	0.02	0.02	0.01	
Fe	0.02	0.01	<0.01	0.01	0.02	<0.01	
Gd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Ge	<0.01	0.08	0.07	0.02	0.17	0.04	
Hf	0.28	0.41	0.02	0.22	0.14	0.02	
Hg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.001
Ho	0.01	0.02	0.01	0.01	0.01	<0.01	
Ir	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	
La	0.03	0.03	0.01	0.03	0.03	<0.01	
Li	2.71	2.87	1.19	2.74	2.82	0.09	
Lu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Mn	0.13	0.12	0.1	0.11	0.11	0.03	0.4
Mo	0.11	0.12	0.12	0.08	0.07	<0.01	0.07
Nb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Nd	0.13	0.06	0.09	0.09	0.1	0.05	
Ni	0.08	0.03	0.06	<0.01	<0.01	<0.01	0.07
Os	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	
P	0.14	0.28	0.14	0.45	0.37	0.21	
Pb	0.21	0.17	<0.01	<0.01	0.1	0.31	0.01
Pd	0.04	0.05	0.04	0.01	0.01	<0.01	
Pr	0.1	0.1	0.09	0.14	0.1	<0.01	
Rb	1.22	1.29	0.71	0.33	0.48	0.42	
Re	0.04	0.04	<0.01	0.1	<0.01	0.04	
Rh	0.01	0.03	0.04	0.03	0.01	0.04	
Ru	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	
Sc	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Se	0.48	0.32	<0.01	0.59	0.29	0.01	0.01
Si	8.79	8.88	5.74	8.83	8.91	3.5	0.01
Sm	0.03	0.01	<0.01	0.03	0.02	<0.01	
Sn	0.16	<0.01	<0.01	0.25	0.3	0.1	
Sr	7.52	7.53	4.3	7.4	7.47	3.26	
Ta	<0.01	<0.01	0.03	<0.01	<0.01	0.01	
Tb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Te	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Th	0.16	<0.01	0.24	0.23	0.11	0.07	

Table 2 continued

Parameter	HS-1	HS-2	HS-3	HS-4	HS-5	CS-6	WHO
Ti	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Tl	<0.01	0.25	<0.01	0.41	0.62	1.02	
Tm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
V	0.04	0.02	0.02	0.02	0.01	0.02	
W	0.03	<0.01	0.23	0.21	0.09	<0.01	
Y	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Zn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	3
Zr	0.01	0.01	<0.01	0.02	0.01	0.01	

All values in mg L⁻¹

HS hot spring, CS cold spring

Arsenic adsorbs to and reacts with hydrous iron and aluminum oxides, and is, therefore, preferentially adsorbed in soils with high clay content (Woolson 1983). Arsenic can leach out if reactive concentrations of iron, aluminum, and exchangeable calcium are low (WHO 2011). The clay fraction can apparently behave either as a source or as a sink of arsenic (Carmen Blanco et al. 2012).

Smedley and Kinniburgh (2002) identified two distinct ‘triggers’ that can lead to the release of As on a large scale. The first is the development of high pH (>8.5) conditions in semiarid or arid environments usually as a result of the combined effects of mineral weathering and high evaporation rates. This pH change leads either to the desorption of adsorbed As [especially As(V) species] and a range of other anion-forming elements (V, B, F, Mo, Se and U) from mineral oxides, especially Fe oxides, or it prevents them from being adsorbed (see also Nicolli et al. 1989; Percy et al. 2011). Because arid regions are typically characterized by low biomass compared to more humid regions, dissolved organic C concentrations in groundwaters and aquifer sediments in these settings tend to be low, and groundwaters are commonly oxidic (Percy et al. 2011).

The second trigger for large-scale arsenic release is the development of strongly reducing conditions at near-neutral pH values, leading to the desorption of As from mineral oxides and to the reductive dissolution of Fe and Mn oxides, also leading to As release. Iron(II) and As(III) are relatively abundant in these groundwaters and SO₄ concentrations are small (typically 1 mg L⁻¹ or less). Large concentrations of phosphate, bicarbonate, silicate and possibly organic matter can enhance the desorption of As because of competition for adsorption sites (Smedley and Kinniburgh 2002; Ravenscroft et al. 2009). The second environment where naturally occurring, high-As groundwaters appear common are geologically young (Holocene) fluvial sedimentary deposits associated with modern deltas that have strongly reducing conditions owing to abundant sedimentary organic matter (i.e., peat) (McArthur et al. 2004; Polya et al. 2005).

Table 3 Trace element concentrations of rock samples as determined by ICP-OES

Parameter	Crust ^b	Limestone ^a	R3 ^c	R5 ^d	R7 ^e	R12 ^f
Ag	0.07	0.1	0.9	0.2	0.3	0.3
As	1.5	1	990.9	91.2	15.9	101.3
B	10	20	74	11.4	24.8	237.3
Ba	500	90	5,244.4	1,877.5	5,423.9	2,769.6
Be	3	<1	3.7	0.5	0.1	1
Bi	–	–	15.1	6.9	9.4	3.7
Cd	0.15	0.03	1.2	0.9	1.6	0.8
Ce	70	20	15.2	23	113.3	8.9
Co	22	0.1	4.4	3.6	4.1	1.9
Cr	100	11	40.7	25.3	32	112
Cs	3	0.5	16.2	4.6	8.4	9.2
Cu	50	5.5	28.4	19.1	15.8	14.2
Dy	6	2	6.2	5	5.3	4.8
Er	–	–	1	0.1	0.2	0.1
Eu	–	–	1.4	2.5	1.6	1.8
Ga	18	2.5	6.3	1.5	5.4	6.9
Gd	–	–	0.8	0.3	0.3	0.3
Ge	–	–	0.6	1	0.2	0.8
Hf	5	0.3	2.1	3	5	5
Hg	0.05	0.2	<0.05	<0.05	<0.05	<0.05
Ho	–	–	1.3	1.1	1.8	0.4
La	35	10	13.2	4.3	4.9	13.5
Li	20	7.5	15.9	0.7	0.7	19.2
Lu	–	–	0.1	<0.1	<0.1	<0.1
Mn	1,000	620	460	366.3	204.7	426.6
Mo	1.5	0.2	0.6	1.6	1	0.8
Nb	20	0.3	4.2	<1	<1	4.9
Nd	30	9	8.5	18.9	24.4	14.5
Ni	75	7	13.3	4.3	3.2	6.4
P	1,100	700	317.1	99.3	252.9	201.1
Pb	14	6	23.4	9.9	11.7	28.3
Pr	9	3	0.9	0.5	0.3	0.2
Rb	90	50	65.5	51.5	48.7	57.4
S	300	1,100	1,184	382.7	632.9	464.2
Sb	–	–	4.7	1.4	1.9	4.3
Sc	20	1	2.9	1.3	0.8	2.9
Se	0.05	0.03	5	3.4	5.2	4.5
Sm	7	2	2.2	0.1	0.1	0.8
Sn	2.5	0.5	1.9	1	1.5	0.7
Sr	375	610	649	120	903.5	156.1
Ta	2	0.05	0.8	0.4	0.3	0.7
Tb	–	–	0.3	0.1	0.2	0.3
Te	–	–	0.1	0.04	0.04	0.1
Th	12	2	2.3	9.4	6	<0.5
Ti	5,600	300	1,356.3	53	116.6	1,520.9
Tl	–	–	2.6	3.7	4.2	3
Tm	–	–	2.2	2.5	2	2.5
U	3	2	1.2	1	0.9	1.2
V	150	45	26.8	3.3	2.9	27.4

Table 3 continued

Parameter	Crust ^b	Limestone ^a	R3 ^c	R5 ^d	R7 ^e	R12 ^f
W	–	–	11.8	12.2	5.5	2.1
Y	35	23	30.6	7.7	4.8	12.6
Yb	–	–	1.6	0.7	0.3	0.8
Zn	75	20	24	8	42.6	17.5
Zr	190	20	140.7	105.5	122.9	166.8

All values in ppm

^a Source for limestone: Bowen (1979)

^b Main sources for crust: Wedepohl (1969–1974); Taylor (1964)

^{c, d} Collected samples from vicinity of the HS-2 hot spring

^e HS-3

^f HS-4

Trace elements in geothermal rock samples

The concentrations of As in sinter deposits and rock samples around the Kharaqan hot springs are much higher than the average earth crust and limestone values (Table 3; Krauskopf and logue 2002). The sinter precipitated around the hot springs is able to entrap As from the discharged waters and act as a sink for this toxic element. However, As minerals such as orpiment, realgar, and stibnite were not identified in these deposits.

Potential environmental impact of hot spring effluents

Hot spring waters tend to have high contents of total dissolved solids (TDS) and may contain toxic elements such as arsenic, uranium and other trace elements (Smedley and Kinniburgh 2002; Vaughan 2006; Zhang et al. 2008; Yoshizuka et al. 2010; Bundschuh et al. 2013). The release of these waters into the surrounding environment may not only raise concern about the aquatic ecology (Mroczek 2005), but could also pose a health risk to local residents (Webster 1999; Pehlivan 2002; Robinson et al. 2003).

Hot springs water from the Abe-Garm geothermal field flow into the Khareh-roud River between the Kharaqan hot springs (upstream) and Chehel-Cheshme cold spring (downstream) sampling sites (Fig. 1). The influence of the thermal springs on the chemistry of the cold spring water is obvious. Downstream from the springs the water in the cold spring contained considerably higher concentrations of Ca, K, Na, SO₄, Cl, As, B, Mo, Pb, Se and other trace elements (see Tables 1, 2). Downstream from the point where the hot spring water flows into a small stream, the water is used to irrigate crops. The potential health threat posed by the hot spring water would be related to (1) the drinking of ground and surface waters that may have mixed with the hot spring discharge and/or (2) field irrigation with As-contaminated water, leading to an accumulation of As

in the crops. Consumption of the crops by humans, cattle and poultry could lead to serious health problems that deserve further investigation. Heavy metal toxicity which is frequently the result of long-term, low-level exposure to pollutants has often been investigated in air, water, food and numerous consumer products (Eleni et al. 2006).

The presence of arsenic in groundwater in concentrations sufficient to affect human health constitutes a worldwide high-priority groundwater quality problem (Duker et al. 2005). Long-time exposure to arsenic may cause various diseases including skin disorders (Tondel et al. 1999; Ahmad et al. 1997; Rahman et al. 2001), circulatory system problems (Chen et al. 1996; KarimiNezhad et al. 2010), cardiovascular disease (Wang et al. 2007), neurological complications (Mukherjee et al. 2003), reproductive disorders (Ahmad et al. 2001), respiratory effects (Milton et al. 2001; Guha Mazumder et al. 2000), diabetes mellitus (Rahman et al. 1998) and an increased cancer risk, especially of the skin, bladder, lungs and kidney (KarimiNezhad et al. 2010; Chen et al. 1992; Smith et al. 1998; Bates et al. 1992; Chiou et al. 1995; Rahman et al. 2009). Increased risks of lung and bladder cancer and of arsenic-associated skin lesions have been reported to be associated with ingestion of drinking water at concentrations below 50 µg of arsenic per liter (WHO 2011). An interim water quality guideline for total arsenic of 100 µg L⁻¹ in irrigation water is recommended for the protection of agricultural crop species (CCME 1999). Data on the toxicity of arsenic were available for 25 crop species. Beans, peas, and spinach seem to be the most sensitive, while cabbage was found to be the least sensitive. The recommended water quality guideline for total arsenic for the protection of livestock is 25 µg L⁻¹ (CCME 1999).

Conclusions

Relatively high concentrations of Na, Ca, K, Cl, and SO₄ resulting from rock/water interactions have been observed in the hot springs water of the Abe-Garm area. The presence of As and related trace elements in these hot spring waters is of considerable concern, especially the high level of total As. The problem becomes even greater if we consider the high fraction of As(III) in some of these thermal water samples. As is trapped in the sinter precipitating at the spring outlets, but most As enters the surrounding environment and contaminates soils, as well as surface and ground water sources. In the Abe-Garm area the diffusion of As spring waters into shallow aquifers could contaminate the groundwater used for drinking purposes. Also, the thermal spring discharges into the streams and rivers could affect irrigated crops in downstream fields. In both cases, the health of local residents could be at risk.

Acknowledgments The authors would like to express their thanks to the Geological Survey of Iran and Shahid Beheshti University for providing the funds for this project.

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