DOI 10.1007/s12665-013-2660-0

ORIGINAL ARTICLE

Environmental geochemistry and sources of potentially toxic elements in thermal springs in the Sabalan volcanic field, NW Iran

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Received: 10 November 2012 / Accepted: 4 July 2013

Abstract Thermal springs are attractive geological features interesting for tourists because of their balneological and therapeutic applications. In Iran, the thermal springs surrounding Mount Sabalan are famous and unique in this regard. Two clusters of thermal springs consisting of 16 springs and mostly used as spas occur in Neer and Meshkinshahr areas. In order 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. Field data including *T*, EC, pH and *Q* were measured on-site and major cations and anions were analysed in the laboratory along with 72 trace elements. Cations show the following order of abundance: Na Ca C K [Mg and anions follow the order of Cl [HCO_3 [SO_4. Trace element concentrations indicate that most of the elements show concentrations well beyond the standard guideline values for drinking water. pH, *T*, spring discharge and elevation are not correlated with each other and with other parameters, indicating that they have had no role on concentrating or depleting trace elements in spring waters. While the two sets of samples were taken within a 6 month interval, the elements and parameters show slight or no variation from the first period to the second and in some cases, they show less than 5 % decrease or increase in the second sampling period. Correlation coefficient and principal component analysis of analytical data indicate that EC, K, Cl, HCO_3, As, B, Ba, Br, Li, Na, Rb, Sr and V show very strong mutual correlation coefficients implying their relationship and common source and fate in the hydrothermal fluid that carries them out of the geothermal system. Moreover, they all fall in the component 1 of PCA. This group of elements is supposed to be derived from the magmatic-hydrothermal system through the interaction of hydrothermal fluids with the rocks they have passed through. The mean As value is 160-fold higher than the guideline values (10 lg/l) and Mn and Sb shows an exceedance of 12- and 11.5-fold, respectively. Arsenic shows a variation of 5–5,834 lg/l. Hence, it is supposed that potentially toxic elements may have adverse effects on tourists using the springs as a treatment or recreation. Indeed, the discharge of springs with high values of As and other elements represents a threat for downstream water uses. The higher concentrations of most elements including As, Pb, S, Cl and Sb and the higher pH values found in Neer area springs seem to be more related to an older hydrothermal system present in this area than the Meshkinshahr system that is still active today.

Keywords Potentially toxic elements · Thermal springs · Environmental geochemistry · Hydrothermal system · Arsenic · Sabalan volcano · Iran

Introduction

Thermal springs are frequently found in active or recently active volcanic areas around the world and are considered as the surface expression of underlying hydrothermal systems. In most places, they are used for balneological and bathing purposes, e.g. in Turkey, Italy, Iceland, New Zealand, Portugal, etc. Turkey has about 1,200 thermo-mineral springs due to its favourable geological situation resulted from young volcanic activities (Tarcan et al. 2005). The Turkish thermal springs have been well-studied

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Published online: 27 July 2013

by many authors including Davraz (2008), Elhatip et al. (2004), Gemici et al. (2004), Gemici and Filiz (2001), Gemici and Tarcan (2004), Gultekin et al. (2011), Yalcin (2007). In fact, the Turkish baths owe their fame to the geological features producing them. In the neighbourhood, Iranian thermal springs exhibit similarities and also differences. However, they are less studied and few information is available on their geochemistry.

The arbitrary temperature for considering a spring as a thermal spring is 36.7 °C according to Pentecost et al. (2003).

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. Information on the geochemistry of thermal waters is scarce or limited to major ions (Chudaev et al. 2006).

In addition to the role of trace elements in deciphering the source and also processes occurring in the hydrothermal reservoir, they are frequently used in monitoring of hydrothermal, geothermal, and volcanic activities and also environmental and geomedical impacts (Guo and Wang 2009; Bargagli et al. 1997; Elhatip et al. 2004; Loppi 2001; Cruz and França 2006; Federico et al. 2004; Brombach et al. 2000; Valentino et al. 1999; Valentino and Stanzione 2003, 2004; Tassi et al. 2003; Vengosh et al. 2002; Bagnato et al. 2009).

Since thermal springs originate from an underlying hydrothermal system capable of producing hydrothermal mineral deposits in different levels of the earth's crust, they are apparently enriched in several potentially toxic elements inherited from a common hydrothermal reservoir. Hence, in many parts of the world, volcanic activities and their associated thermal springs indicate enrichment of some elements that may be regarded as a natural source of contamination conferring potential adverse health effects. Arsenic, mercury, boron and antimony are among the most important and frequently mentioned elements reported by authors in Turkey, Italy, Japan and New Zealand (Aiuppa et al. 2003, 2006a, b; Yoshizuka et al. 2010; Bagnato et al. 2009; Pehlivan 2003; Lima et al. 2003).

Thermal springs in Iran are mostly concentrated around Quaternary volcanic centres or along major faults. A large number of thermal springs are located in NW Iran in Ardabil province due to the geological situation mainly related to Sabalan volcano last activities.

The Renewable Energy Organization of Iran has recently started a project to study the geothermal potential of the Sabalan area and a geothermal power plant has been established in Meshkinshahr with the purpose of utilizing energy from deep wells. The wells were planned to be drilled to a depth of about 3,200 m to reach the expected reservoir and four wells were successfully penetrated into the reservoir at depths of 3,197 m (NWS1); 3,177 m (NWS3); 2,265 m (NWS4) and 2,174 m (NWS6).

Significant and large amount of information was produced on the geothermal power potential, physicochemical properties of deep geothermal waters and borehole geology of wells. However, less attention has been focused on their trace element geochemistry and particularly on surface manifestation of a deep reservoir. Hence, this study attempts to investigate the concentration of trace elements in spring waters, to characterize their geochemical specifications in addition to the source region processes. In this paper, we suggest that trace elements can be used to identify the processes and stages of alteration and evolution of the studied geothermal system.

Furthermore, the possible impact of thermal springs on the environment and public health needs to be investigated since annually hundreds of thousands of tourists use thermal springs for bathing, exposing themselves to potentially toxic elements. Moreover, the water discharging from the springs and flowing into Khiav Chay constitutes the habitat of brown trout species (*Salmo trutta*) and is used as the main water supply of Meshkinshahr city.

Study area

Mount Sabalan, a Quaternary volcano and one of the youngest volcanic domes in Urmia-Dokhtar volcanic belt, is located in NW Iran (Fig. 1). The area has a temperate weather in summers and a cold one in winters with a mean annual temperature of 8 °C. The Sabalan peak is covered with snow and ice in all seasons. The mean annual precipitation is 350 mm in the region which falls mainly as snow and runs numerous springs and streams in spring and summer.

The study area is located between the latitudes 37°55′ and 38°20′E and longitudes 47°35′ and 48°05′N at a distance of about 600 km from Tehran, the capital city of Iran. Thermal and mineral springs are distributed in three main clusters around Mount Sabalan: Sar Eyn in east, Neer in southeast and Meshkinshahr in NW of Sabalan peak. Springs in Sar Eyn area are uniform in temperature and physicochemical characteristics with no temporal and spatial variation in parameters whereas in the two other areas, large variations in hydrochemical and physicochemical properties are observable. We thus focused on Neer and Meshkinshahr springs in this study.

Neer and Meshkinshahr clusters include six and ten thermal springs, respectively. Their general information is reported in Table 1.

Khiav Chay river originates from northern flank of Sabalan and flows in Mooeel valley. The river collects the

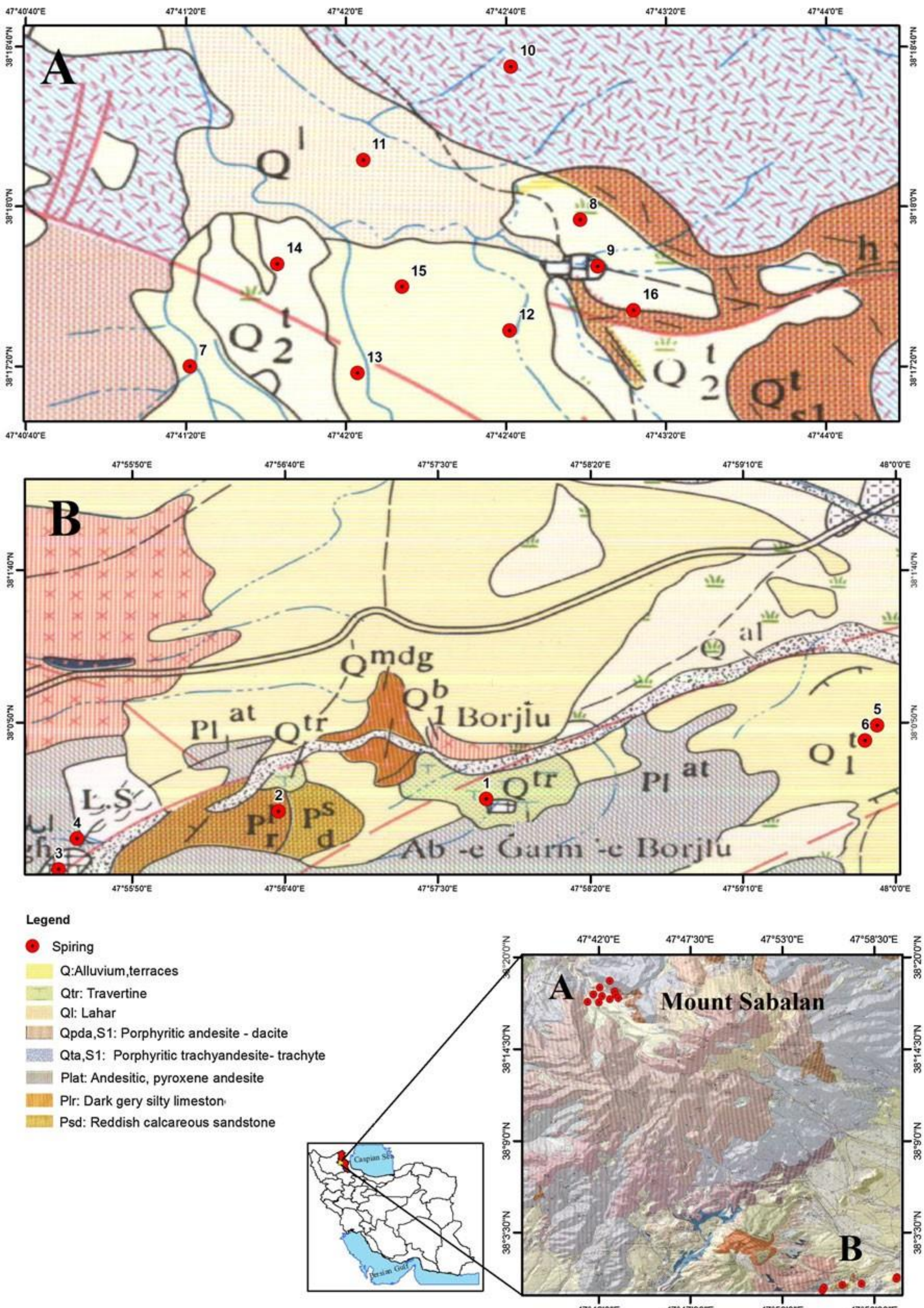

Fig. 1 Location of thermal springs on geological map of Mount Sabalan clustered in Meshkinshahr (*A*) and Neer (*B*) areas

Table 1 Geographic situation and some physicochemical parameters of the thermal springs

Cluster	Spring name	Spring code	Elevation (m)	Latitude	Longitude	Q (l/s)	T (°C)	EC (1s/cm)	TDS (mg/l)	pH
Neer	Borjloo	N1	1,648	38°00′25″	47°57′46″	1	46.6	10,730	6,420	7.3
	Qeynarjeh	N2	1,704	38°00′21″	47°56′38″	0.9	67.1	10,800	5,900	7.0
	Ilanjiq 1	N3	1,707	38°00′02″	47°55′26″	1.5	34.4	1,010	467	7.4
	Ilanjiq 2	N4	1,709	38°00′12″	47°55′32″	0.5	41.2	10,800	6,429	6.8
	Saqezchi 1	N5	1,657	38°01′02″	48°01′38″	1.8	35.5	10,300	5,840	6.5
	Saqezchi 2	N6	1,665	38°00′57″	48°01′34″	1.5	40.3	11,400	6,823	6.4
Meshkin Shahr	Qeynarjeh	M1	2,139	38°17′11″	47°41′26″	10	80.1	6,010	2,950	6.4
	Mooeel 1	M2	2,229	38°17′45″	47°43′03″	2	45.2	1,070	540	5.2
	Mooeel 2	M3	2,229	38°17′45″	47°43′03″	1	46.3	1,123	570	5.4
	Ilando 1	M4	2,011	38°17′55″	47°42′05″	2.3	33.2	2,150	1,080	5.9
	Ilando 2	M5	2,027	38°17′54″	47°42′05″	14	36.1	2,190	1,090	6.1
	Ilando 3	M6	2,015	38°17′54″	47°42′05″	1	36.1	2,210	1,110	5.9
	Dodo 1	M7	2,030	38°17′33″	47°41′58″	0.8	45.0	1,005	560	6.3
	Dodo 2	M8	2,032	38°17′33″	47°41′58″	1.2	46.0	1,010	540	6.4
	Dodo 3	M9	20,205	38°17′37″	47°41′58″	1.4	44.0	1,330	800	6.7
	Maleksooei	M10	2,289	38°17′34″	47°43′12″	1.5	42.0	1,320	780	6.3
Max						14	80.1	11,400	6,823	7.4
Min						0.5	33.2	1,010	467	5.2
Ave						2.9	44.8	5,166	2,912	6.4
SD						3.96	13.22	4,539.52	2,683.8	0.58

Cluster	Spring name	Spring code	Ca	Mg	Na	K	HCO_3	SO_4	Cl
Neer	Borjloo	N1	72.14	41.80	2078.28	215.42	1350.28	380.40	2784.48
	Qeynarjeh	N2	72.14	34.03	2009.31	255.70	1144.05	383.28	2820.29
	Ilanjiq 1	N3	48.10	5.83	36.09	7.04	148.27	30.26	32.97
	Ilanjiq 2	N4	91.38	10.69	2069.08	265.48	1250.22	325.16	2857.16
	Saqezchi 1	N5	232.46	53.47	2149.55	205.66	1700.52	570.60	2404.78
	Saqezchi 2	N6	232.46	46.18	2000.11	208.39	1840.24	600.38	2424.63
Meshkin Shahr	Qeynarjeh	M1	113.83	15.56	1149.49	112.21	228.20	337.17	1519.16
	Mooeel 1	M2	94.59	27.22	71.96	33.23	7.93	494.23	6.03
	Mooeel 2	M3	96.99	50.1	73.73	18.04	8.01	320.84	6.21
	Ilando 1	M4	88.18	24.30	289.67	47.31	156.20	330.45	425.44
	Ilando 2	M5	88.18	24.31	298.86	43.01	148.27	315.08	461.24
	Ilando 3	M6	83.37	21.39	289.67	126.29	151.93	330.45	437.49
	Dodo 1	M7	51.10	20.04	119.24	11.02	40.48	46.49	91.38
	Dodo 2	M8	52.91	12.64	140.01	23.07	131.79	120.08	167.69
	Dodo 3	M9	64.19	12.64	175.87	32.06	144.00	164.26	243.56
	Maleksooei	M10	36.87	15.56	200.01	35.97	140.34	99.90	287.52
Max			232.46	53.47	2149.55	265.48	1840.24	600.38	2857.16
Min			36.87	5.83	36.09	7.04	7.93	30.26	6.03
Ave			94.93	25.98	821.93	102.49	536.92	303.06	1060.63
SD			57.54	14.91	899.80	95.57	661.51	172.59	1172.07

Cations and anions in mg/l

runoff produced from snow melting in all seasons and also from spring waters. This river is the main water supply of the Meshkinshahr city and local people. The area irrigated by this river is an important agricultural region in northwest of Iran. Khiav Chay is an important habitat of rare species of brown trout (*S. trutta*) in Iran with a fragile environment that needs protection against any degradation.

Geologically, Quaternary volcanic rocks indicate the last magmatic activities in Iran resulted in formation of large stratovolcanoes including Damavand (5,671 m) in north-central, Sabalan (4,820 m), Sahand (3,695 m) in northwestern, Taftan (3,940 m) and Bazman (3,490 m) in the southeastern part of Iran.

Sabalan volcano, which is responsible for the existence of thermal springs in the studied area, is located in the northwest of Iran (Fig. 1) and is a part of the volcanic belt which starts from Turkey and runs through Iran toward the south-central Iran. It is called Urmia-Dokhtar volcanic belt by various authors in structural subdivisions of Iran (Stocklin 1968). Lava flows of the Sabalan volcano spread in an area of 1,200 km^2 and the youngest activity dates back to about 20,000–70,000 years ago (Aghanabati 2006). Currently, the activity of this volcano is limited to numerous emanations of hot springs and some fumarolic activities in its flanks and caldera.

Springs in the Meshkinshahr area are located in the northwestern and southern flanks of Sabalan (Fig. 1). This area is mostly covered by Quaternary volcanic—sedimentary rock units.

As it has been mentioned previously, the Sabalan geothermal project has provided vital information on subsurface geology of the studied area. According to Porkhial et al. (2010), at the beginning, the wells encountered Quaternary terrace deposits (Dizu formation) and Pliocene andesite-trachyandesitic volcanics (Valhazir formation) that have been exposed in most parts of the area (Fig. 2). Down the hole, a unit composed of Pliocene to Neogene volcanics has been penetrated by wells in some parts. Subsequently, a sequence of Eocene volcanics has been drilled, which unconformably overlies the Paleozoic metasedimentary rocks. The Paleozoic rock units make up the basement of the area. These rocks were intruded during Miocene by a regional monzonite batholith.

All the springs in Meshkinshahr area emerge in the old alluvial terrace unit that covers the volcanic rocks and especially dacites, andesites, trachytes and trachyandesites. On the other hand, in the Neer area, Paleozoic rock units have been cropped out composed of limestones, calcareous sandstones and also of the youngest alluvial deposits. However, the volcanic rocks are not as widespread as in Meshkinshahr area and are limited to andesitic lava flows and lahars. The springs emerge within the older rock units especially of Neogene porphyritic trachytes. This area is much farther from the volcanic vent of Sabalan and has not been covered by younger rocks (Amini 1994).

The rocks have been affected by a series of faults which control the location of many springs especially in Meshkinshahr area.

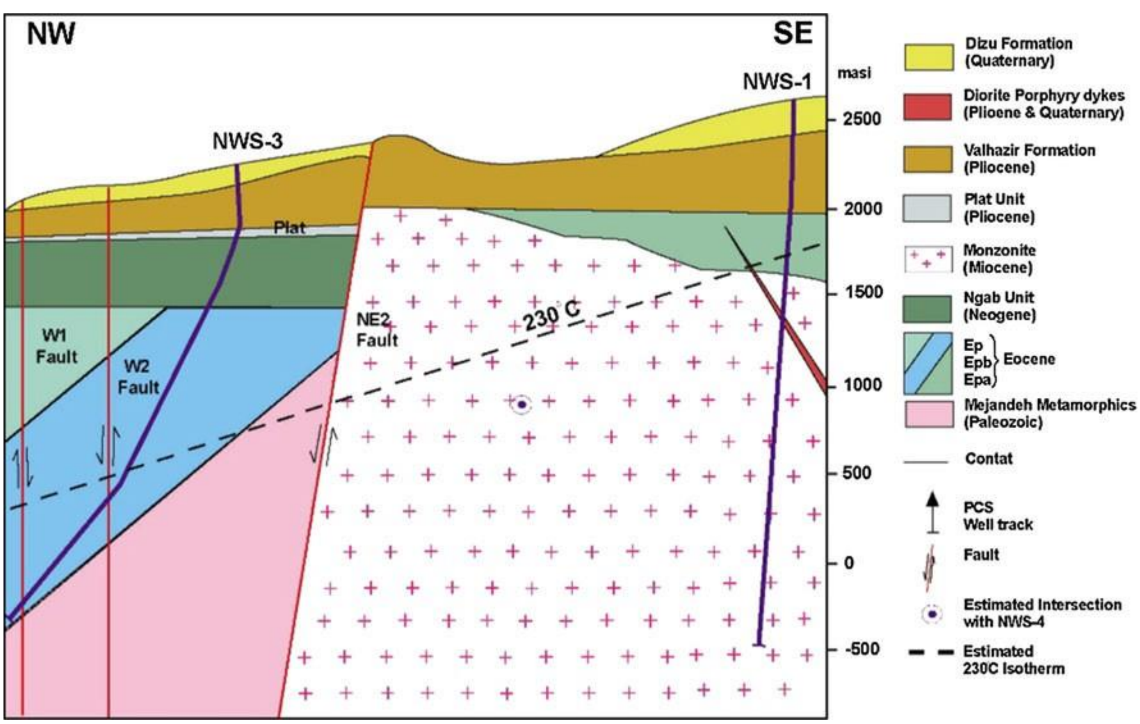

Fig. 2 Geologic cross-section of northwest Sabalan derived from well data produced in the Sabalan geothermal project (after Porkhial et al. 2010)

Methods and materials

Mount Sabalan is covered with snow in all seasons and therefore it might be expected that there would be numerous perennial springs in the area. However, field study and review of previous works indicate that most of the springs are seasonal with very low discharges. Hence, they were ignored in this study and just 16 perennial springs were selected (Fig. 1; Table 1) including 10 thermal springs in Meshkinshahr and 6 springs in Neer area. As indicated in Table 1, all the springs show temperatures higher than 32 °C and most of them can be regarded as thermal springs. In fact, no perennial cold spring was found in the area with a significant discharge. The spring waters were sampled twice in wet (May) and dry (November) seasons to investigate the trace elements' chemistry and also physicochemical characteristics of thermal springs. Some springs are very closely spaced with a distance of less than 10 m of each other (for example Ilando 1, 2 and 3 or Dodo 2 and 3). However, they were selected and sampled due to the apparent variability between them.

Field parameters including spring discharge, temperature, pH and electrical conductivity (EC) of the water samples were measured on-site. Parameters were measured by the HACH multiparameter instrument which has been calibrated for all parameters shortly before measurements. Before reading the values of field parameters, the instrument was thermally equilibrated with the sample water to consider the difference between air and water temperature. Where possible, parameters were measured by immersing probes directly into the source, as close to the sampling point as possible. Otherwise, probes were immersed into an unfiltered sample collected in the container.

Water samples were collected in unused 250 ml polyethylene bottles that had been acid washed previously and rinsed with spring water three times before sampling.

At each sampling station, three bottles were filled, one for major cations, one for anions and the last one for trace element analyses. 2.5 ml ultrapure Merck HNO_3 was added to the third sample to pH 2 immediately after sampling, to prevent the formation of heavy metal complexes. After sampling, the third bottle was tightly closed and shaken to properly mix the acid with the water.

Cations and anions were measured at the central laboratory of the Department of the Environment of Iran. Bicarbonate and chloride analyses were measured by titration methods, sulphate concentration by spectrophotometry and cations by flame photometry. Acidified samples were analysed for major and trace elements (72 elements) with an ICP-MS at ACME Labs, in Canada.

Results

Water chemistry

The field parameters of the thermal springs studied in this work are presented in Table 1. As indicated in the Table, discharge of springs has a variation between 0.5 and 14 l/s, corresponding to Ilanjiq 2 (N4) and Ilando 2 (M5), respectively. Most of the springs have a discharge between 1 and 2 l/s. As mentioned previously, they are perennial and their discharges do not vary significantly during different seasons. Therefore, the rate of precipitation is not considerably effective in the spring discharges.

Other parameters also show remarkable heterogeneity in different springs. Water temperature at the surface ranges from 33.2 to 80.1 °C, mainly between 34 and 45 °C. Hence, they are mostly considered as thermal water, according to Pentecost et al. (2003). Water temperature of Qeynarjeh spring (M1) in Meshkinshahr is exceptionally high (80.1 °C) and intolerable for tourists. The spring waters are slightly acidic to circum-neutral in Meshkinshahr springs with pH values ranging from 5.2 to 6.7 and the springs in Neer area show values between 6.4 and 7.4. The lowest pH value (5.2) was observed in Mooeel spring (M2) and the highest value (7.4) was found in Ilanjiq spring.

EC and TDS of water samples range between 1,010–11,400 ls/cm and 407–6,823 mg/l, respectively.

Springs in Meshkinshahr area have a uniform composition regarding major cations of Ca, Mg, Na and K whereas Neer springs are more variable in composition. In Saqezchi 1 spring (N5), most of cations indicate the highest values and Ilanjiq 1 spring shows the lowest values among the springs studied. Comparatively, Meshkinshahr springs also show the highest anion values in the study area.

Among the cations, Na followed by K show the highest values in almost all of the springs with lower concentrations of Ca and Mg, while the most abundant anion is Cl followed by HCO_3.

Trace element geochemistry of thermal springs

Trace element analysis results of thermal springs in two periods of sampling are presented in Table 2. The chemical analysis of water samples were performed in ACME labs of Canada for 72 elements. However, in this paper we focus on more frequent elements. By contrast, other elements with values lower than detection limits have been disregarded.

Comparison of trace elements in two series of analysis indicate that water samples of the first series (sampled in

Table 2 Trace element analysis results of thermal spring samples in two seasons (1 May; and 2 November)

Code	Al		As		B		Ba		Br		Cl (mg/l)		Cu		Fe		Li	
Period	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
N1	19	59	5,834	4980.7	23,366	22,914	140	138.9	8,144	6,623	2,820	2,219	4.5	4	160	147	9787.4	9417.7
N2	<10	10	4,956	4037.6	24,370	20,395	164.55	154.53	8,086	6,410	2,853	2,244	3.3	2	<100	<100	10397.5	8378.1
N3	11	5	23.5	10	952	898	73.2	78.22	445	414	120	126	1.2	0.7	26	45	303.1	289.9
N4	580	115	4,633	3961.7	24,894	23,849	165.56	163.04	8,293	6,726	2,886	2,361	5	3.4	459	108	10,688	9296.1
N5	216	95	4,101	3450.5	24,178	20,258	64.22	67.26	8,060	6,825	2,512	2,190	2.8	2.3	3,343	3,209	8606.3	7140.2
N6	234	169	3168.5	2472.7	22,280	18,246	63.98	66.02	7,552	6,321	2,467	1,950	3.3	2.9	2,370	1,626	7887.7	6239.8
M1	26	20	2486.3	2493.7	12,112	11,299	121.8	119.6	3,415	2,798	1,525	1,337	2.8	1.9	1,739	1,627	4585.4	4121.3
M2	877	647	30.1	21.3	74	69	23.48	21.75	47	48	13	11	2.5	1.3	13,478	12,867	27.9	21.8
M3	894	660	32.9	22.9	74	76	22.69	22	50	30	7	7	2.1	1.3	13,447	13,457	26.9	22.6
M4	48	39	585	324.4	3,497	2,754	3.09	2.6	898	652	405	332	1.6	1	<10	<10	1294.3	973
M5	27	32	455	333.8	3,293	2,888	3.08	2.3	899	694	416	350	1.3	1.3	<10	<10	1239.2	986
M6	35	24	540.8	347.2	3,409	2,919	2.71	2.1	921	699	421	353	1.7	1.4	<10	<10	1294.4	1081.1
M7	19	45	28.2	35.8	221	240	13.97	16.21	112	79	27	34	1.2	2.4	80	217	75.3	66.8
M8	10	12	299.3	225.7	1,764	1,378	27.9	30.35	478	350	200	163	0.9	1.1	1,375	1,703	589.8	413.4
M9	12	8	158.5	135.4	1,866	1,703	30.14	30.34	561	443	236	210	1	1.1	479	482	645.3	537
M10	40	6	272	211.3	2,169	1,917	26.65	22.85	557	478	262	245	4.1	3.1	47	<10	297.7	248.8
G	200		10		2,400		700		–		0.5		2,000		300		–	
Min	10	5	23.5	10	74	69	2.71	2.1	47	30	7	7	0.9	0.7	26	45	26.9	21.8
Max	894	660	5,834	4980.7	24,894	23,849	165.56	163.04	8,293	6,825	2,886	2,361	5	4	13,478	13,457	10,688	9417.7
Ave	109.8	121.6	1725.2	1441.5	9282.4	8237.7	59.2	58.6	3032.4	2474.4	1073.1	883.2	2.4	1.95	2316.8	3226.2	3609.1	3077.1
SD	308.9	212.6	2105.7	1793.5	10505.8	9,412	57.8	56.4	3564.1	2929.4	1194.7	964.1	1.3	0.98	4463.1	5009.6	4265.1	3691.5

Code	Mn		Pb		Rb		S (mg/l)		Sb		Si		Sr		V		Zn	
Period	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
N1	76.27	68.15	<1	1.5	1635.68	1672.3	117	112	153.47	89.46	34,459	30,815	6167.56	5867.44	51.6	12.8	<5	<5
N2	61.15	45.81	<1	<1	1619.68	1606.05	109	97	206.9	125.72	39,858	33,274	5881.42	5450.14	57.4	34	5	<5
N3	0.9	0.53	0.6	0.6	25.62	21	11	13	77.6	0.64	30,611	28,154	555.14	598.61	7	4.9	2.8	0.9
N4	37.51	21.03	6.7	2.6	1612.75	1670.37	102	100	192.7	125.94	43,827	38,332	5965.54	5877.82	62.2	36.1	11.6	<5
N5	214.03	198.27	1.4	<1	1190.19	1290.01	191	194	67.17	0.64	32,523	29,134	7889.63	8201.08	42.1	27.7	9.1	6.8
N6	264.5	228.78	1.9	<1	1097.85	1154.98	193	187	70.66	0.52	37,515	33,018	7487.15	7556.65	40	27.5	21.3	19
M1	612.68	584.47	1	<1	837.2	895.35	110	115	253.88	206.25	73,323	68,758	3165.03	3252.18	29.8	20	<5	<5
M2	545.99	579.64	0.4	0.2	64.65	63.76	183	191	14.4	0.48	14,919	13,178	177.2	172.12	0.9	0.5	53.6	40.2
M3	541.13	575.93	0.3	0.5	62.47	61.98	175	188	23.36	0.52	14,237	12,667	175.54	167.95	0.6	0.3	49.6	39.5
M4	4.71	6.72	0.9	0.4	181.07	173.92	98	106	45.61	2.99	73,481	62,312	1533.74	1335.05	14.7	11.7	25.2	21.3

Table 2 continued

Code	Mn		Pb		Rb		S (mg/l)		Sb		Si		Sr		V		Zn	
Period	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
M5	4.21	3.64	0.4	0.5	178.3	179.48	99	105	41.21	2.82	71,193	64,664	1,497	1378.1	15.3	12.1	23.3	17.1
M6	3.33	2.43	0.7	0.2	183.63	184.13	98	103	39.32	2.63	73,027	64,752	1550.41	1409.41	15.3	11.8	24.9	17.4
M7	17.3	47.57	0.3	0.9	24.41	27.75	8	9	49.24	0.82	44,552	43,032	254.91	269.68	16.7	15.2	1.3	2.3
M8	419.01	348.55	0.1	0.5	152.7	143.68	55	53	38.67	0.93	46,255	41,700	578.63	524.49	3.9	5.4	4.3	4.7
M9	282.76	277.63	0.3	0.3	162.94	176.61	61	66	43.35	1.97	47,603	44,303	615.52	623.76	7.5	6.8	4.1	3.2
M10	315.14	277.41	2	0.4	102.23	108.94	30	37	35.17	0.54	86,305	82,264	237.18	241.87	25.3	20.6	12.1	6.1
G	50		10		–		–		20		–		–		–		5,000	
Min	0.9	0.53	0.1	0.2	24.41	21	8	9	14.4	0.48	14,237	12,667	175.54	167.95	0.6	0.3	1.3	0.9
Max	612.68	584.47	6.7	2.6	1635.68	1672.3	193	194	253.88	206.25	86,305	82,264	7889.63	8201.08	62.2	36.1	53.6	40.2
Ave	212.5	204.16	1.2	0.7	570.7	589.4	102.5	104.7	84.5	35.2	47730.5	43147.3	2733.2	2682.9	24.4	15.4	15.7	14.9
SD	219.9	218.9	1.7	0.69	641.8	662.2	60.4	60.9	74.0	64.5	21739.7	20182.9	2889.2	2890.6	20.5	11.2	16.5	13.7

All values in lg/l, otherwise mentioned in parenthesis. Rows specified by *G*, shows the guideline values for different elements defined by WHO (2011) in bold and USEPA (2009) in regular letters

May) are generally more enriched in trace elements, i.e. the higher the discharge of the spring, the higher the concentration of trace elements.

According to the Table 2 and Fig. 3, thermal springs of Neer area are more enriched in most of trace elements including As, B, Ba, Br, Cl, Cu, Li, Rb, S, Sr and V in comparison with the springs of Meshkinshahr area. Instead, springs in the latter area are more enriched in Al, Fe, Mn, Si and Zn. Pb indicates the lowest variation, however, slightly enriched in Neer springs. Most of these elements show concentrations much higher than the guideline values (Table 2).

The lowest concentration of arsenic was measured in dry season in N3 spring. However, all other samples in the Neer area show the higher amounts of As up to 5,835 lg/l with average values of 4,538 and 3,781 lg/l in wet and dry seasons, respectively. Meshkinshahr springs indicate lower As concentrations while M1 has a concentration of about 2,500 lg/l. It is important to note that all the samples showed higher concentrations than the guideline values (10 lg/l) defined by regulatory organizations (WHO, EPA and EU) (Tables 2, 4).

Boron is ubiquitous in thermal springs of Tethyan region including Turkish springs. Boron concentration is higher in Neer springs than Meshkinshahr springs with a maximum content of 24,894 lg/l in N4. Once again, N3 shows the lowest values of B concentration in Neer area. M1 and M2 springs in Meshkinshahr area have the highest and lowest values in that region, respectively. Other springs show values lower than 3,500 lg/l.

Discussion

The analytical data for two periods of sampling indicate no significant difference between trace element concentrations in these two periods (Fig. 3). In fact, the concentrations of elements are very close to each other or show the same values in all sampling stations in wet and dry seasons, probably indicating that infiltration of meteoric/ground water and its mixing with the uprising hydrothermal waters had no significant effect on the chemistry of thermal springs.

pH shows no relation and correlation with any element. On the other hand, correlation coefficient between temperature and EC values shows a value of about 0.2, indicating that the temperature has also had no effect in concentrating and transporting elements into the hydrothermal fluid. Several samples with the lowest temperatures show the highest EC values (N1, N4, N5 and N6) and some of them indicate the lowest values (N3, M7 and M8) while M1 spring with the highest temperature corresponds to an intermediate EC value.

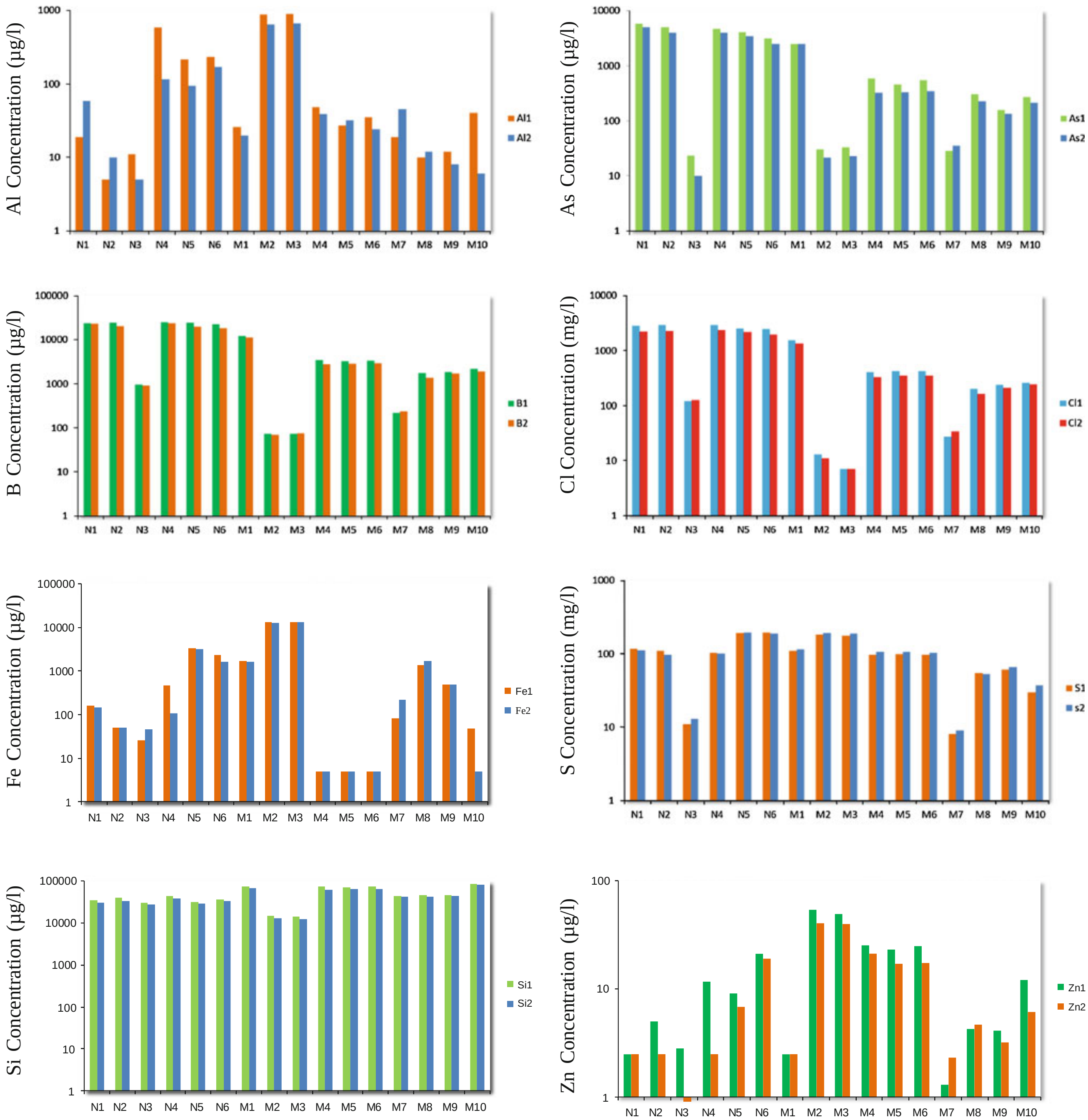

Fig. 3 *Bar diagrams* illustrating the absolute values of trace element concentrations in thermal springs and their variation in different sampling periods. According to the diagrams, there is no significant variation in the different periods. *1* and *2* next to the *element symbols* indicate the concentration in the first and second period of sampling, respectively

In almost all samples, the content of Cl is much higher than the concentration of sulphate ions, and in some cases, it may be 15-fold higher.

The concentration of bicarbonate ions is twofold lower than the content of the sulphate ions in Meshkinshahr area. However, its concentration is much higher than that of sulphate in Neer area.

It is obvious that trace element concentrations are closely related to the amount of TDS and EC. EC/TDS shows a correlation coefficient of higher than 0.9 with K, HCO_3, Cl, As, B, Br, Li, B, Sr and V and correlations between 0.6 and 0.8 with Na, Ba, Cu, Mn, SO_4 and Sb. This relationship in addition to the lack of correlation with Al, Fe, Mn and Si indicate that alkali and alkali

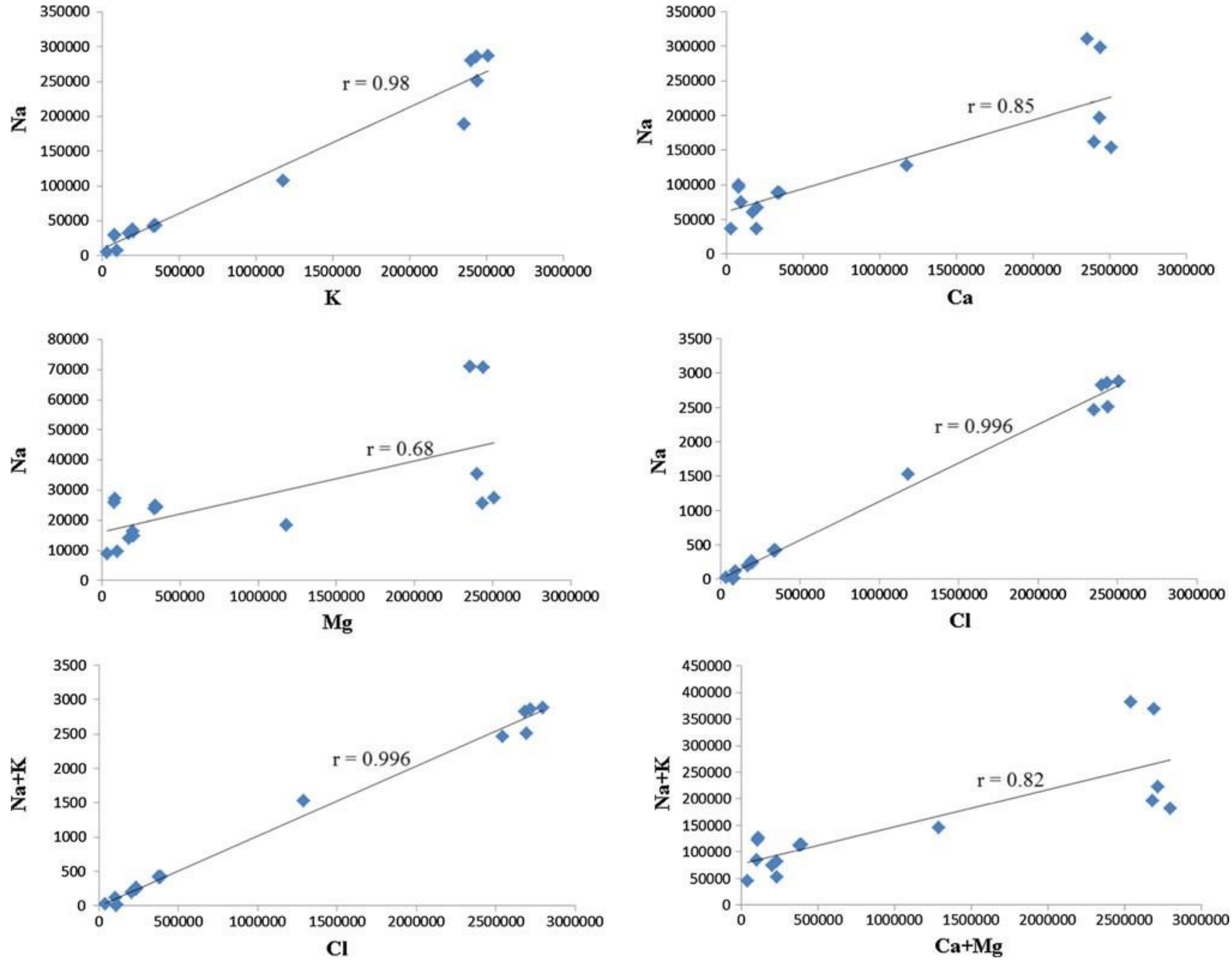

Fig. 4 Correlation between major cations and anions and their ratios in spring waters. Concentrations are in μg/l

earth metals have a significant role in the salinity of thermal springs and are mostly combined to chloride species.

The ratios used by Gemici et al. (2004) and Sanliyuksel and Baba (2011) show a wide range in this area including Na/K = 1–13, Na/Ca = 1–16, Na/Mg = 3–95, Na/Cl = 0.8–11, Na?K/Cl = 1–8 and Na?K/Ca?Mg = 1–13. The relationship between major cations and Cl is represented in Fig. 4. As it is apparent in this figure, Na is very strongly correlated with K and Cl and shows a strong correlation with Ca and Mg. These high values and their correlation are evidence of prolonged water–rock interaction in time.

Na is a cation with the highest concentration in the area. It is a major constituent of most hydrothermal fluids and it is supposed that it has been derived from decomposition of Na plagioclase found in abundance in volcanic rocks, according to following equations (Pirajno 2009):

$$1.5NaAlSi_3O_{8(albite)} + H^+ \rightarrow 0.5NaAl_3Si_3O_{10}(OH)_{2(paragonite)} + Na^+ + 3SiO_2$$

$$0.5NaAl_3Si_3O_{10}(OH)_{2(paragonite)} + 3SiO_2 + H^+ \rightarrow 1.5Al_2Si_4O_{10}(OH)_{2(pyrophylite)} + Na^+$$

$$1.5NaAlSi_3O_{8(albite)} + H^+ \rightarrow 0.5Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_{2(Na\text{—}montmorillonite)} + 1.67SiO_2 + Na^+$$

$$3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + H^+ + 3.5H_2O \rightarrow 3.5Al_2Si_2O_5(OH)_4 + 4SiO_2 + Na^+:$$

The K/Rb ratio ranges between 128 and 494, indicating strong predominance of potassium over rubidium. Like Na, the high content of potassium in water samples is probably mainly controlled by hydrogen ion metasomatism or cation-exchange processes. Hydrothermal alteration of volcanic rocks, in which hydrolysis of different minerals, especially of K-feldspars by acidic fluids, results in a bilateral cation exchange according to the following reaction:

$$1.5KAlSi_3O_8 + H^+ \rightarrow 0.5KAl_3Si_3O_{10}(OH)_2 + K^+ + 3SiO_2.$$

In this process, H^+ is introduced into the rock minerals and converts the anhydrous minerals into the hydrous minerals (K-micas) while releasing K^+ into the fluid.

The Sabalan volcanics, comprising mainly of trachy-andesite, tuff and monzonite, and pyroclastic rocks, have been profoundly altered by hydrothermal solutions and four alteration assemblages including phyllic, argillic, propylitic and carbonate zones have been recognized, based on deep well drilling in the geothermal field (Jamadi 2010). During alteration phases, major and trace elements are enriched or leached from the host rocks depending on the type of alteration. In general, Al ? K and Mg ? Ca ? Fe were enriched in the argillic ? sericitic and propylitic alteration types, respectively. On the other hand, the effects of the leaching of Ca, Mg and Fe have been observed in the argillic alteration zone, and the concentration of Fe therein has led to hematite formation. Strong leaching of Na has been observed in all alteration types. Silica generally decreases in the argillic (kaolinitic and alunitic) alteration zones. According to Karakaya et al. (2007), most of the potentially toxic elements, such as Mo, Cr, Co, Ni and Zn, show high mobility in acidic aqueous systems. Therefore, they will be depleted in the argillic alteration zone which is produced by a fluid with very low ratio of K^+/H^+. In the argillic and kaolinitic zones, Rb and Sr contents are high. Chemical analyses show that Pb and Cu contents are elevated in the propylitic zone (Karakaya and Karakaya 2001a, b, Karakaya et al. 2007).

Considering the predominance of K to Rb in all samples, Rb concentration remains high with maximum value of more than 1,600 μg/l. This is related to preferential dissolution of illite and K-bearing micas, as the second source to the more limited ability of Rb to enter crystal lattices of newly formed minerals or the reactions of ion exchange on clay minerals (Kralj 2004).

Cl is by far the most abundant anion in the region in most of the springs. The high value of Cl is related to its derivation from magmatic-hydrothermal system (Pirajno 2009). In addition, there is no known source for chlorine in the area such as evaporite deposits.

Bicarbonate is the second abundant anion in samples and could be related to CO_2 released from magmatic processes.

A significant concentration of sulphate ion in some samples is also ascribed to the oxidation of sulphides precipitated previously in hydrothermal veins and also to H_2S gases.

The meteoric recharge of the hydrothermal reservoir is supposed to be responsible for the supply of Mg, Ca and SO_4, since, based on the analytical and statistical data, these elements may have a different source than other elements especially of K, Cl, As, B, Ba, Br, Li, Sr, Rb and V. The latter group of elements are ascribed to the magmatic source of the hydrothermal fluid and also to the interaction of the fluid with country rocks passing through it, while rising toward the surface and before mixing with meteoric-ground water.

Most of the thermal waters in the Neer area contain more than 18,000 μg/l of boron. High boron content is attributed to deep water circulation of hydrothermal fluid through the volcanic rocks. Vengosh et al. (2002) used the B/Cl ratio to assess the maturity of the thermal system. They suggested that fluids from older systems are expected to be depleted in B relative to young systems. They consequently deduced that the overall B budget of a geothermal system can also be controlled by the original B concentrations in the rock or original parent magma fluids, as well as the degree of maturation, in which water–rock interactions can contribute B to the thermal system.

Si concentration varies between 14,237 and 86,306 μg/l and its obvious source is alteration of silicate minerals especially of K-feldspar, as mentioned above.

Al and Fe values are interestingly low compared to other elements. Their maximum concentrations are 894 and 13,478 μg/l, respectively. However, in most of the samples, they show very low contents.

As is highly enriched in all samples which is in accordance with the idea that young volcanism in NW Iran is accompanied by arsenic enrichment, mentioned previously by Modabberi and Moore (2004). The As enrichment in water samples is referred to water–rock interactions and also to the rising of hot fluids. It is also suggested that progressive increase of As in waters with increasing time of residence is generally associated by Hg depletion due to the introduction of mercury into newly formed alteration minerals. This suggestion has been also pointed out by Valentino and Stanzione (2003). In the study area and in most of the samples, Hg has a concentration below the detection limit of the analysis (0.1 μg/l).

Pb, Zn and Cu concentrations are also very low in thermal water samples and by no means, reach the guideline values for environmental protection and drinking water.

Surprisingly, all of the elements show very close correlations in two series of analysis. Correlation coefficient calculated for each element and its comparison for two sampling period presented values higher than 0.9 for most of elements (Pb = 0.906, Al = 0.934, Sb = 0.970, Zn = 0.985, Mn = 0.992, B, Si and S = 0.995, Li = 0.996, As = 0.997, Cl, Fe, and Sr = 0.998, and Ba,

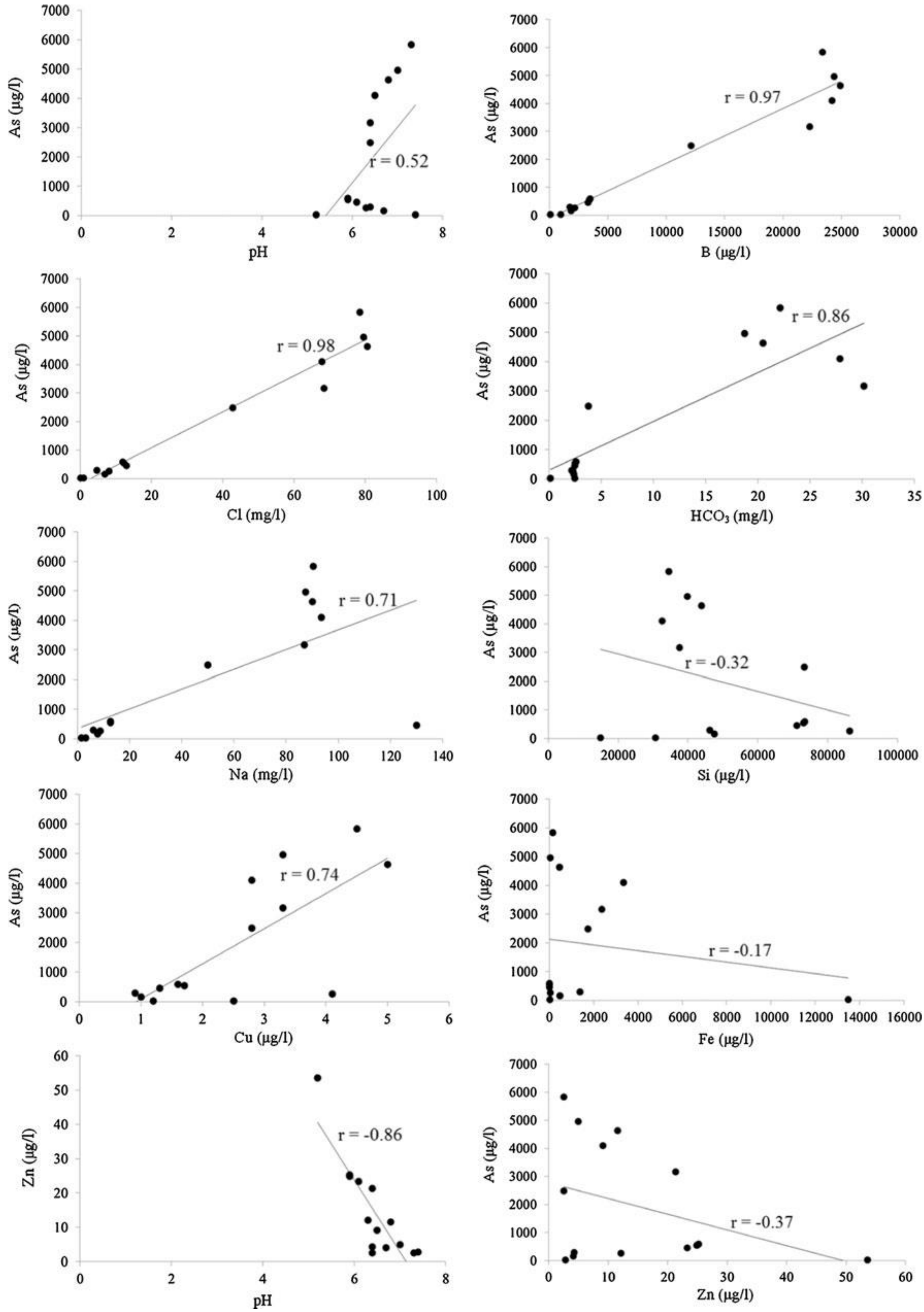

Fig. 5 Correlation coefficient between trace elements and parameters measured in spring waters

Table 3 Principal component analysis results calculated by SPSS 19 software indicating the relationship between elements and other parameters

	Component				
	1	2	3	4	5
T (°C)	0.271	−0.242	0.688	0.561	−0.174
EC (1s/cm)	0.996	0.019	−0.033	0.020	−0.031
pH	0.445	−0.743	−0.096	−0.182	−0.331
Ca	0.543	0.576	−0.306	0.209	−0.123
Mg	0.628	0.513	−0.397	0.203	−0.225
Na	0.747	0.030	−0.267	0.336	0.240
K	0.964	−0.005	−0.013	−0.065	0.078
HCO_3	0.929	0.136	−0.239	−0.110	−0.131
SO_4	0.624	0.722	−0.102	0.216	0.005
Cl	0.996	−0.065	0.012	0.023	0.004
Al	0.137	0.709	0.461	−0.410	0.206
As	0.974	−0.112	0.045	0.008	−0.045
B	0.997	−0.023	−0.028	−0.003	−0.028
Ba	0.797	−0.373	0.424	−0.066	−0.056
Br	0.996	−0.016	−0.043	−0.042	−0.049
Cu	0.743	−0.024	0.301	−0.220	0.333
Fe	−0.118	0.839	0.459	−0.090	−0.154
Li	0.993	−0.072	0.019	−0.033	−0.005
Mn	−0.178	0.342	0.663	0.322	−0.291
Pb	0.469	−0.082	0.202	−0.458	0.570
Rb	0.981	−0.116	0.094	−0.006	−0.020
Sb	0.660	−0.437	0.481	0.271	0.069
Si	−0.336	−0.382	−0.170	0.417	0.562
Sr	0.968	0.102	−0.179	0.042	−0.070
V	0.949	−0.200	0.034	−0.045	0.182
Zn	−0.291	0.838	0.059	−0.102	0.324

Br, and Rb = 0.999). However, Cu shows a lower value (0.861) (Fig. 3).

On the other hand, correlation coefficient calculated for pairs of trace elements indicate interesting facts: EC, K, Cl, HCO_3, As, B, Br, Li, Rb, Sr and V show very strong mutual correlation coefficients, higher than 0.8, indicating their relationship in the hydrothermal fluid which carries them out of the geothermal system. Ba, Cu and Na have a coefficient between 0.6 and 0.8 with these parameters. It is interesting to note that Ca, Mg and SO_4 correlate with each other with values between 0.8 and 0.9 but they show medium to weak relationship with other parameters. Some important correlations have been illustrated in Fig. 5.

pH has a negative strong correlation with Zn (Fig. 5); however, shows a medium coefficient with other parameter. Al only shows a strong correlation with Fe. Si has a medium but negative correlation with Al and Fe.

Principal component analysis calculation using SPSS 19 software produced data presented in Table 3. The derived factors indicate that the same elements with strong correlation coefficients show a close relationship. Here again, in the first component, parameters of EC, K, Cl, HCO_3, As, B, Ba, Br, Li, Na, Rb, Sr and V show values higher than 0.750 and have probably the same source and mode of transport for which the most plausible source is suggested to be the magmatic-hydrothermal source, according to the discussion presented above.

In the second component, SO_4, Al and Fe have been located and the third one only consists of Mn. Ca is also more related to second component than others. These elements may have been leached by the circulating fluid from the rocks in their passage. The other two components defined by the software do not show a significant relation between parameters.

The hot springs flows into Khiav Chay and other streams on which two dams are under construction are supposed to supply the water for drinking and agricultural—industrial demands. Hence, the impact of thermal springs on the deterioration of water quality in main rivers is of vital importance and should be modelled, based on discharge and concentration of trace elements.

By comparison of guideline values proposed by the WHO (2011) and the USEPA (2009) for drinking water, it is suggested that almost all of the thermal waters in the region are enriched in trace elements with values much higher than the guidelines. The range of concentration of some elements and their guidelines have been presented in Table 4.

As Table 4 indicates, the absolute values are tremendous in some cases. In addition, the factor of exceedance i.e. the measure of exceedance of the trace element average concentration compared to the guideline values is very large for As, Cl, Mn and Sb. It actually appears that As is

Table 4 The range, average and guideline values for some elements that may be suggested as potentially toxic element

Element	Range	Average	Guideline	Factor of exceedance
As	5–5,834	1,600	10	160
B	69–24,894	9,000	2,400	3.75
Cl	7,000–2,886,000	2,500,000	500	5,000
Fe	↘10–13,478	1,350	300	4.5
Mn	↘1–613	600	50	12
Sb	0.5–254	230	20	11.5

Data in lg/l

Table 5 Comparative physicochemical properties of thermal springs in Neer and Meshkinshahr areas

Parameter	Neer area	Meshkinshahr area	Parameter	Neer area	Meshkinshahr area
Elevation (m asl)	1,650–1,700	Higher than 2,000	Cl	>2,400	<500
Q (l/s)	<2	Up to 14	Al, Fe, Mn and Zn	Lower	Higher
T (°C)	34–67	33–80	As	3,000–6,000	<350
EC (1s/cm)	>10,000	1,000–6,000	B	18,000–25,000	<3,500
pH	6.4–7.4	5.2–6.7	Li	>6,000	<1,300
Ca, Mg	Higher	Lower	Pb, Cu and V	Higher	Lower
Na	>2,000	<300	Rb	>1,200	<900
K	>200	<50	Sb	>70	<50
HCO_3	>1,000	<200	Si	3,000–4,000	13,000–86,000
SO_4	300–600	100–340	Sr	>5,500	<1,500

the most important environmental and health concern in the area.

Different characteristics of thermal springs in the Neer and Meshkinshahr areas are summarized in Table 5.

Conclusion

Thermal springs have clustered around the Mount Sabalan in three areas. The thermal springs in two areas were studied in this research including Neer (situated in the southern part, far from the young caldera of the volcano and discharged from the older volcanic flows) and Meshkinshahr (located in northwestern part, near to the caldera and on the youngest volcanic lava flows).

The distance from the main vent resulted in major differences in two areas, so that, as indicated in Table 5, the springs in the former area present very high values of EC and concentrations of Na, K, Ca, Mg, Rb, Sr, but also HCO_3, Cl, SO_4, As, B, Pb, Cu, Sb and V. The latter springs are more enriched in Al, Fe, Mn, Zn and Si. Considering the fact that pH values at the surface are very different from the values in the subsurface reservoir, the pH values in the Neer springs are, however, neutral to slightly alkaline. Whereas in Meshkinshahr area, pH is mostly acidic to neutral. The major differences, including distance from the main volcanic vent, pH values and chemical composition led the authors to conclude that due to the proximity of the Meshkinshahr springs to the vent and also due to the age of the hydrothermal system, they should be emanations of younger hydrothermal systems that are still at work at depths. The lower acidity corresponds to the earlier stages of hydrothermal alteration and has not yet produced profound and pervasive alteration of volcanics. This is in accordance with the geochemistry of trace elements in these springs. Conversely, the springs in the Neer area are related to an older and more evolved hydrothermal system in which pervasive hydrothermal alteration acted previously on the volcanic rocks and released substantial amounts of Na, K and other elements that are now found in the springs. The enrichment of trace elements in water samples shows the maturity of this hydrothermal system that has not been yet developed in the first area to release huge amounts of As and associated elements. The springs acquired their high content of trace elements from the hydrothermal water released from magmatic system and also through interaction of the hydrothermal fluids with the surrounding volcanic rocks. Na and K concentrations in thermal waters are mainly controlled by metasomatic hydrolytic ion exchange and by converting the alkali feldspars into micas and clay minerals.

The lower discharge of springs in the Neer area is attributed to the low permeability of the rocks in the reservoir due to the closure of the fractures and open spaces resulting from a mineralization carried out by the hydrothermal fluids during their ascent.

Finally, these springs with very high concentrations of potentially toxic elements, especially of arsenic, are used for balneological purposes. Moreover, the runoff of the springs finds its way to Khiav Chay River that is used for drinking and agricultural water and constitutes the habitat of a rare species of brown trout. Therefore, they may have adverse environmental and health impacts on the local communities and also on the hundreds of thousands of tourists using the springs annually, which requires further research.

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