

## Environmental Geochemistry of Potentially Toxic elements in thermal springs in the Sabalan Volcanic Field, NW Iran

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**Abstract.** Thermal springs are widely used by tourists for treatment of dermal diseases and other therapeutic applications. In Iran, thermal springs occur in Northwestern part mainly surrounding the Mount Sabalan which attract hundreds of thousands of tourists annually. Two clusters of springs in Neer and Meshkinshahr areas including 16 thermomineralic springs have been studied in this research and they were sampled twice in May and November in order to investigate the seasonal changes of trace elements in dry and wet seasons. The samples were analyzed in Acme Lab, Canada for 72 elements. Trace element concentrations indicate that most of the elements show concentration well beyond the guideline values for drinking water. While the two sets of samples were taken within a 6 months interval, the elements show slight or no variation from first period to the second and in some cases. Arsenic shows a variation of 5-5834 $\mu\text{g/l}$  and the mean As value is 160 times the guideline values (10  $\mu\text{g/l}$ ). Other toxic elements with high concentration are B, Fe, Mn, Sb, and Si. Mn and Sb shows exceedance of 12 and 11.5 times respectively. Correlation coefficient and principal component analysis of analytical data indicate that Cl, As, B, Ba, Br, and V show very strong mutual correlation coefficients implying their relationship and common source and fate in the hydrothermal fluid carrying them. These elements fall in the component 1 of PCA. This group of elements is supposed to be derived and sourced from the magmatic-hydrothermal system and through the interaction of hydrothermal fluids with rocks they passed through. Because of discharge of the thermal springs into the nearby streams intended to be used for drinking water and also vast application of spring waters in balneological uses, they may have adverse environmental and health impacts on tourists that expose themselves to this contaminants through balneological applications.

**Keywords:** Environmental Geochemistry, Sabalan, Thermal Springs, Trace elements, Arsenic contamination, Iran

### Introduction

Thermal springs are frequently found in active or recently active volcanic areas around the world. In most places they are used for balneological and bathing purposes, e.g. in Turkey, Italy, Iceland, New Zealand, Portugal and so on. They have been well-studied in Turkey which have numerous spring by Davraz (2008), Elhatip et al., (2004), Gemici et al., (2004), Gemici and Filiz (2001), Gemici and Tarcan (2004), Gultekin et al., (2011), Yalcin (2007) and many others. In fact the Turkish baths owe their fame to the geological features producing them. In the neighborhood, Iranian thermal springs exhibit similarities and also differences however they are least studied and few information are available especially on their geochemistry of trace elements.

In addition to the role of trace elements in

deciphering the source and processes occurring in the hydrothermal reservoir, they are frequently used in monitoring environmental and geomedical impacts (Guo and Wang 2009, Bargagli et al. 1997, Elhatip et al. 2004, Loppi 2001, Cruz and Franza 2006, Federico et al. 2004, Valentino and Stanzione 2004, Vengosh et al. 2002).

Thermal springs are usually enriched in some potentially toxic elements inherited from the same hydrothermal reservoir. According to Smedley and Kinniburgh (2002), and Yoshizuka et al. (2010), arsenic is a ubiquitous and persistent element found in volcanic gases and emanations. It is estimated that about 1.9 Gg arsenic are annually released to the atmosphere by volcanoes (Nriagu 1989).

As is regarded as the first hazardous contaminant

found frequently in groundwater and drinking water resources all around the world and the list of arsenic affected areas is monthly updated and new areas are added to it. Gemici and his colleagues found also high concentrations of potentially toxic elements in Turkish hot spring including As, B, Hg, Pb, Zn, Mn, Li. Pehlivan (2003) reported Kirkgecit and Ozancik hot springs in Turkey rich in Hg, Ni, Cr, Cu and Fe. Natural contribution of harmful elements (As, Be, Mn, Sb, Se, Hg, W, U, Mo, V, Cr, ) has been mentioned by Lima et al. (2003) in thermal groundwaters of Ischia Island, southern Italy.

Thermal springs in Iran are mostly concentrated around Quaternary volcanic centers 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 last activities of Sabalan Volcano. Annually hundreds of thousands of tourists use them for bathing and balneological purposes. However, the thermal springs of this area have not been studied in detail especially their trace element geochemistry. This paper attempts to investigate the concentration of trace elements in spring waters, to characterize the source processes and geochemistry of waters, to genetic deduction and to study their possible impacts on tourists exposing themselves to potentially toxic elements.

## Methods and Materials

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 600km from Tehran, the capital city of Iran. In this study, 16 thermal springs have been studied in two areas of Neer and Meshkinshahr.

The spring waters were sampled twice in wet (May) and dry (November) seasons. Water samples were collected in 250 ml polyethylene bottles which had been acid washed previously and rinsed with spring water three times before sampling. 2.5 ml ultrapure Merck HNO<sub>3</sub> was added to the sample to pH 2 immediately after sampling, in order to prevent the formation of heavy metal complexes. Acidified samples were analyzed for major and trace elements (72 elements) with an ICP-MS at ACME Labs, Canada.

## Results

Water temperature at the surface ranges from 33.2 to 80.1°C, mainly between 34-45°C. 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 are showing values between 6.4-7.4.

Trace element analysis results for thermal springs in two periods of sampling are presented in Table 1. Comparison of trace elements in two series of analysis indicate that water samples of the first series (sampled in 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 1, thermal springs of Neer area are more enriched in most of trace elements

Tab.1 The summarized results of trace element analysis in thermal springs of Neer (n=6) and Meshkinshahr (n=10). Concentration of elements in µg/l except for Cl which is in mg/l. Guideline values are presented in parentheses

Parameter	Neer springs			Meshkinshahr springs		
	Min	Max	Ave.	Min	Max	Average
<b>Elevation</b>	1648	1709	1682	2011	2289	2102
<b>Q (l/s)</b>	0.5	1.8	1.2	0.8	14	3.52
<b>T (°C)</b>	34.4	67.1	44.2	33.2	80.1	45.4
<b>EC (µS/cm)</b>	1010	11400	9173	1005	6010	1942
<b>pH</b>	6.4	7.4	6.9	5.2	6.7	6.1
<b>Al (200)</b>	5	580	126	6	894	172
<b>As (10)</b>	10	5834	3470	21.3	2493	452
<b>B (2400)</b>	952	24894	18883	69	11299	2847.9
<b>Cl (mg/l) (0.5)</b>	120	2886	2062	7	1525	327
<b>Cu (2000)</b>	1.2	5	2.95	0.9	4.1	1.76
<b>Fe (300)</b>	26	3343	966	5	13478	3052
<b>Mn (50)</b>	0.53	264.5	102	2.43	612.68	273
<b>Pb (10)</b>	0.5	6.7	1.5	0.1	2	0.54
<b>Sb (20)</b>	0.52	206.9	93	0.48	254	40
<b>Si</b>	28154	43827	34294	12667	86305	52126
<b>Zn (5000)</b>	0.9	21.3	7.2	1.3	53.6	17.8

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 are more enriched in Al, Fe, Mn, Si, and Zn however slightly enriched in Neer springs. Most of these elements show concentrations much higher than guideline values.

The lowest concentration of arsenic was measured in dry season in N3 spring however all other samples in the Neer area show the highest amount of As up to 5835µg/l with average values of 4538 and 3781 µg/l in wet and dry seasons respectively. Meshkinshahr springs indicate lower As concentrations while M1 has a concentration of about 2500µg/l. It is significant to note that all of the samples fall above the guideline values (10µg/l) defined by regulatory organizations (WHO, EPA and EU) (Tables 2 and 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 24894µg/l.

## Discussion

The analytical data for two periods of sampling indicate no significant difference for trace elements concentrations in these two periods.

The meteoric recharge of the hydrothermal reservoir is supposed to be responsible for the supply of Mg, Ca

and SO<sub>4</sub>, 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 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 18000 µg/l of boron. High boron content is attributed to deep water circulation of hydrothermal fluid through the volcanic rocks.

Si concentration varies between 14237 to 86306 µg/l and its obvious source is alteration of silicate minerals especially of K-feldspar.

Al and Fe values are interestingly low compared to other elements. Their maximum concentrations are 894 and 13478 µg/l respectively however in most of the samples they show very low contents.

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

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

EC, Cl, As, B, Cu, and V show very strong mutual correlation coefficients higher than 0.8 indicating their relationship in the hydrothermal fluid carrying them out of the geothermal system.

pH has a negative strong correlation with Zn, however shows a medium coefficient with other parameters. Al only shows a strong correlation with Fe. Si has a medium but negative correlation with Al and Fe. Principal component analysis calculation indicates that the same show a close relationship. In the first component, parameters of EC, As, B, Na, and V show values higher than 0.75 and probably have the same source and fate of transport for which the most plausible source is suggested to be magmatic –hydrothermal source. In second component, Al and Fe have been located and the third one only consists of Mn.

The hot springs flows into Khiav Chay and other streams on which two dams are under construction and they are supposed to supply the water for drinking and agricultural –industrial needs. Hence, the impact of thermal springs with the high concentrations of potentially toxic elements on the deterioration of water quality in main rivers is of vital importance and it should

be modeled based on discharge and concentration of trace elements.

By comparison of guideline values proposed by WHO (2011) and USEPA (2009) for drinking water (mentioned in the first column Table 1), it is suggested that most of the thermal waters in the region are enriched in trace elements with values much higher than the guidelines. The absolute values are tremendous in some cases, and in addition, the factor of exceedance that indicates the measure of exceedance of the trace element average concentration compared to the guideline values is very large for As, Cl, Mn and Sb. In fact it appears that As is the most important environmental and health concern in the area.

## Conclusion

The thermal springs in two areas studied in this research include Neer (situated in the southern part and far from the young vent of volcano and issued from the older volcanic flows) and Meshkinshahr (located in northwestern part near to the volcanic vent and on the youngest volcanic lava flows). The distance from the main vent resulted in major differences in two areas so that, the springs in the former area show very high values of EC and Cl, As, B, Pb, Cu, Sb and V. The latter springs are enriched in Al, Fe, Mn, Zn, and Si. The pH values in the Neer springs are neutral to slightly alkaline while in the Meshkinshahr area, pH are mostly acidic to neutral.

The springs acquired their high content of their trace elements from the hydrothermal water released from magmatic system and also through interaction of the hydrothermal fluids with the surrounding volcanic rocks.

Finally, these springs with very high concentrations of potentially toxic elements such as arsenic are used for balneological purposes and also the runoff of the springs find their way to the streams in the area which are intended to be used for drinking water. Therefore, they would have adverse environmental and health impacts on the local communities and also on the hundreds of thousands of tourists using the springs annually.

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