Hydrogeochemistry of hydrothermal waters from Salams magma chamber: Case study of Isti Su hot spring, NW of Iran

Mohammad Yazdi[1, *], Gohar Farajpour[1], Pedram Navi[2]

1- Department of Geology, Shahid Beheshti University, Iran.
2- Geological Survey and Mineral Exploration of Iran.

* Corresponding Author: m-yazdi@sbu.ac.ir

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Abstract

The Isti Su hot spring is located in southeast of Salmas, in Western Azerbaijan, Iran. The area is a small part of Sanandaj-Sirjan geological zone which hosts many hot springs. The magma chamber of Salmas region is the main heat source of the hot springs in Isti Su area. Abundant rainfall and relatively long duration of snowfall as well as several deep faults in the area create the best conditions to have several hot springs in the area. The host rocks of the area are sedimentary and metamorphic rocks of Cambrian to Recent sediments which are intruded by several granite and ophiolite bodies. Several hot springs have been formed in the vicinity of these plutonic to sub-volcanic bodies. The Isti Su hot spring is one of the most typical hot springs of the Salmas region. Eight samples were collected from the study area. In order to investigate the seasonal changes in the field and chemical parameters and to measure trace element concentrations in dry and wet seasons, springs were sampled twice in May and November. Temperature, pH and electrical conductivity (EC) of the water samples were measured on-site. Temperatures of the selected samples range from 26.3 °C to 38.5 °C. The pH values of the samples vary between 6.4 and 7.5. TDS contents range from 9200 to 1790 mgL^{-1}. The results of geochemical analysis show that the As, Li, Fe, Hg, Na, and Cr are not more than WHO's standard level. As and B are two times more than WHO's standard level. The As and B concentrations in the hydrothermal and geothermal solutions rise higher than its standard level. WHO's recommended As level for drinking water is 0.01 mg/l^{-}. The Na-SO_4-HCO_3 triangular diagram shows that the samples are of HCO_3 and Na types. Open skin scars, gangrene, malignant cancers and environmental problems are among the consequences of high concentrations of As and B. The high content of As and B in water of this hot spring can be harmful to the environment and people of the area.

Keywords: Hydrogeochemistry, toxic elements, hot spring, Salam, Iran.

1- Introduction

Hydrothermal activity generates chemical interactions between hot water (hydrothermal fluid) and the host rocks, so that the composition of the fluid changes, becoming enriched in many trace elements (e.g. V, Co, Ni, Cu, Zn, As, Se, Al, Ag, Cd, Sb, Cs, Ba, W, Au, Tl, Pb and REE (German and Von Damm, 2003). Type and origin of these springs have a major role in determination of their physical and chemical properties for different sources at the same event that have completely different properties; some are pathogenic and sometimes healing to many factors such as the source of spring water, the composition of ground water that has passed, pressure, temperature, speed and time depends on the flow of water in the ground (Ghafouri, 2003).

Arsenic concentrations in geothermal fluid are usually two or three times more than those in uncontaminated surface and groundwater (Webster and Nordstrom, 2003). Geothermal fluids and springs are found around the world. Arsenic (As) is a well-known toxic and carcinogenic metalloid that is found in a wide variety of chemical species throughout the environment and can be readily transformed and mobilized by microbes, changes in geochemical conditions, and other environmental processes. The release of As from rocks into geothermal fluids occurs predominantly along active tectonic plate boundaries (Chandrasekharam and Bundschuhj, 2008). One of the worlds's As anomaly sources are hot springs and geothermal waters. Natural B is derived from geothermal discharges, leaching from a large variety of rocks, or the mixing of groundwater with connate or fossil brines. High As and B concentrations of thermal waters cause environmental problems in groundwater and surface waters (Gemici and Tarcan, 2002; Vengosh et al., 2002, Craw et al., 1999). In addition, B is derived from geothermal sources, and is leached from many varieties of rocks. 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 mg of arsenic per liter (WHO, 2011). Some of the hot springs in Azarbjan zone , because of having some chemical materials, hold a particular color, odor or taste and they are used enormously in the fields of health and tourism (Taheri et al., 2012; Esmaeili et al., 2015; Modabberi, 2013). The main aim of the following paper is to investigate geological features, geochemical composition and environmental impacts (especially As and B) of the Isti Su hot spring.

2- Geological Setting

The Isti Su hot spring is located in SE of Salmas, Western Azerbaijan, Iran. The Isti Su hot spring is one of the most typical hot springs of the Salams region. The area is a part of Sanandaj- Sirjan geological zone, which is host of many hot spring of Iran (Yazdi et al., 2015). The host rocks of the area are sedimentary and metamorphic rocks of Cambrian to recent age, which are interrupted by several granitic and basaltic bodies. Several hot springs have been formed near these plutonic to sub volcanic bodies. Plutonic rocks are granite, meta-granite and meta-diorite. The basic rocks belong to ophiolitic sequence which consists of meta-basalt and ultramafic such as dunite. Sedimentary rocks are limestones, dolomite, gypsum and marl of Permian (Ruteh Formation) to Miocene (Qom Formation), Quaternary travertine and alluvium sediments (Stocklin, 1968). Metamorphic rocks are different type of Cambrian schists (Figs. 1 and 2).

3- Materials and methods

A total of 8 thermal water samples were collected from the different manifestations of the hot spring in Isti Su area. In order to investigate the seasonal changes of field and chemical parameters and trace element concentrations in dry (summer) and wet (spring) seasons. Hot spring waters were collected during May and August 2015. Water samples were collected into 250-ml polyethylene bottles. 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 by ICP-OES in the "Geological Survey of Iran" Laboratory. Temperature, pH and electrical conductivity (EC) of the water samples were measured on-site, bicarbonate and chloride analyses were measured by titration methods, sulfate concentration by spectrophotometry and cations by flame photometry in the "Geological Survey of Iran" Laboratory.

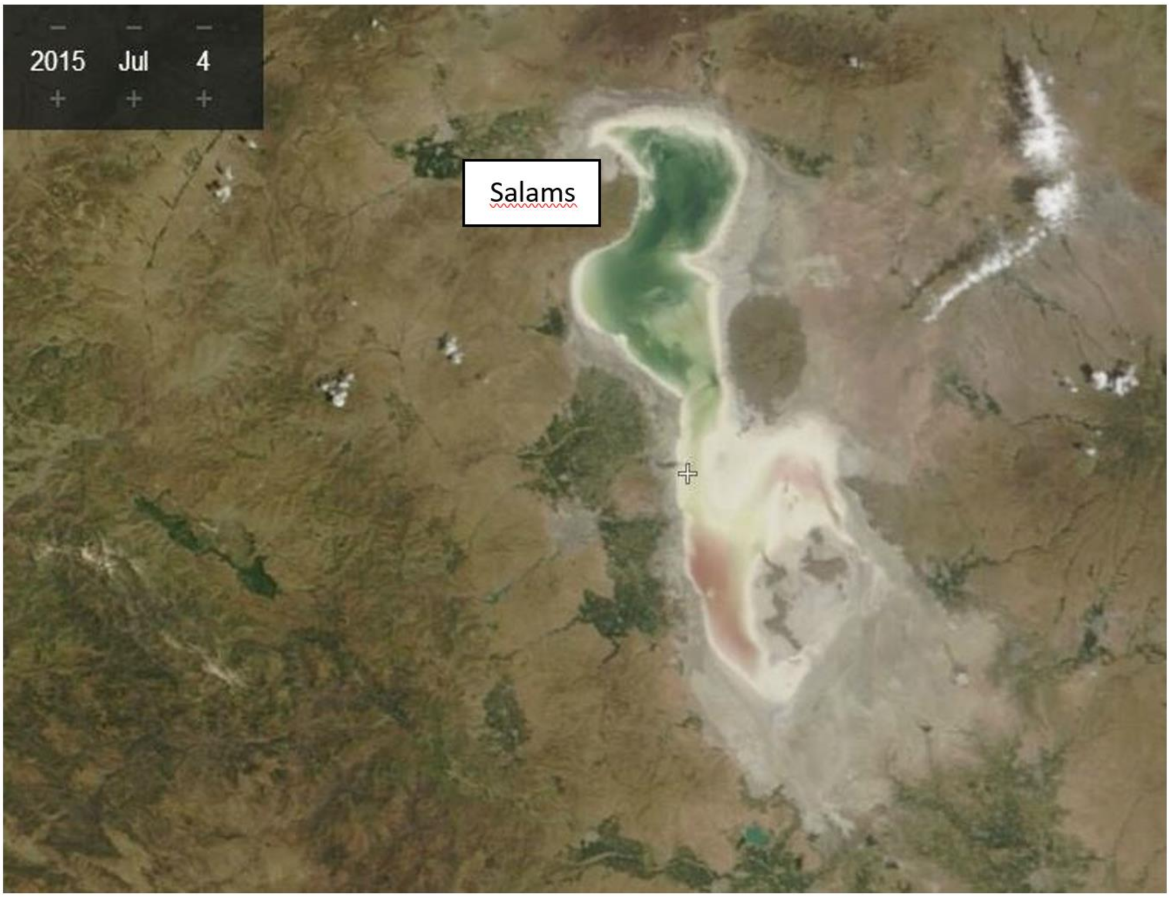

Figure 1) The location of Isti Su hot springs in the NW of Iran.

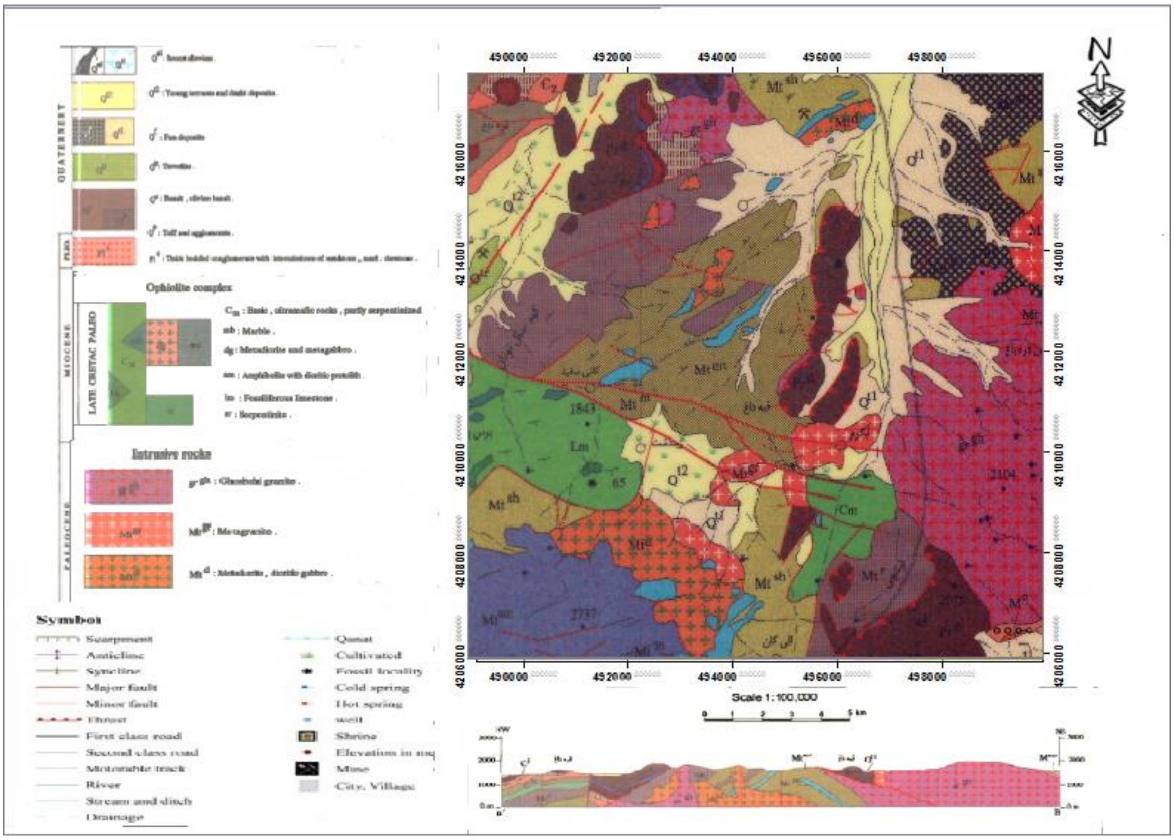

Figure 2) Geological map of Salams region (Alavi et al., 1994; Khodabande et al., 2002)

4- Results and discussion

One of the worlds's As and B anomaly sources are hot springs and geothermal waters. Normally, As and B concentrations in the hydrothermal and geothermal solutions for water rise higher than its standard level for drinking water. WHO's recommended As level in drinking water is 0.01 mg/l (WHO, 2011). The results for field parameters are given in Table 1.

Table 1) Field parameters concentrations of the Isti Su hot springs (mg/l). Summer (dry) season.

Parameter	Isti Su -1	Isti Su -2	WHO
Temp. (ºC)	37.6	26	-
pH	7.5	6.4	6.5-8.5
TDS	9200	1790	1,000
EC (ms/cm)	14750	3146	2,000
Ca (mg l^{-1})	11	311	1,000
K (mg l^{-1})	193	11.5	50
Mg (mg l^{-1})	16.6	116	10
Na (mg l^{-1})	3788	97.7	30
Cl^- (mg l^{-1})	1064	2.5>	200
SO_4^{2}- (mg l^{-1})	3284	213	250
CO_3^{-2} (mg l^{-1})	420	0.3>	-
HCO_3^{-} (mg l^{-1})	7800	1464	250

Temperatures of the thermal springs range from 26 to 37.6 ºC. According to the temperature classification by Kovačić and Perica (1998) (Kovačić and Perica, 1998), the spring water in the spring water in Isti Su is thermal type. The pH values in these samples were between 6.40 and 7. 5 (Table 1). The pH is controlled by dissolution of gases (such as CO_2, H_2S, NH_3, CH_4) which are entering the aquifer system and geochemical processes such as the synthesis and mineralization of biomass, redox processes etc. in the aquifer (Judit et al., 2015). The higher the amount of dissolved gases in the aquifer system, the lower the pH value will be. The highest EC value is observed at the Isti Su hot springs, with a value of 14750 to 3146 ms/cm. The EC value is influenced by the amount of dissolved solids in the water. If the water contains a high amount of dissolved solids, the EC values will be higher, and vice versa. Total dissolved solids (TDS) is the term used to describe the inorganic salts and small amounts of organic matter present in solution in drinking water (Kresic, 2010). TDS contents of the thermal waters ranges from 9200 to 1790 (mg/l). The principal constituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, bicarbonate, chloride, sulfate, and nitrate anions (WHO, 2003). Waters containing TDS values below 1,000 mg/l are usually acceptable to consumers, although acceptability may vary according to circumstances 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).

Major ion concentrations are also in Table 1 and spring waters are plotted in the Piper diagram in Fig. 2. The Piper plot shows that cations in the springs generally plot in the sodium plus field. Most anions in the Piper plot show that these springs generally HCO_3^- rich type. In the Isti Su hot spring, the water is of Na- SO_4^{2-}- HCO_3^- type. These values (Table 1) were also plotted in the Schoeller diagram (Schoeller, 1962). The diagram (Fig.3) depicts the following arrangement of anions and cations: $(Na^{+}+k^{+})>Ca^{2+}>Mg^{2+}$, $HNO_3^{-}> SO_4^{2-}>Cl^{-}$. The results derived from the Piper diagram are compatible with those obtained from the Schoeller diagram.

Table 2) Chemical analysis results of Isti Su hot springs (mg l-1) in (Wet season).

Parameter	Isti Su -1	Isti Su -2	WHO
Ag(mgl^{-1})	<0.01	<0.01	0.1
Al(mg l^{-1})	0.148	0.07	0.02
As(mg l^{-1})	>100	>.01	0.01
B(mg l^{-1})	>100	4.617	0.5
Ba(mg l^{-1})	0.735	0.167	0.3
Be(mg l^{-1})	<0.01	<0.01	-
Co(mg l^{-1})	<0.01	<0.01	5
Cd(mg l^{-1})	<0.01	<0.01	0.003
Cr(mg l^{-1})	0.496	0.299	0.05
Cu(mg l^{-1})	0.054	0.011	2
Eu(mg l^{-1})	<0.01	<0.01	-
Fe(mg l^{1})	<0.01	<0.01	0.3
Gd(mg l^{-1})	0.631	0.011	-
Ge(mg l^{-1})	1.101	0.0180	-
Hf(mg l^{-1})	<0.01	<0.01	-
Hg(mg l^{-1})	0.218	<0.01	0.001
Ir (mg l^{-1})	<0.01	<0.01	**
La (mg l^{-1})	<0.01	<0.01	**
Li (mgl^{-1})	22.147	0.0200	**
Lu (mg l^{-1})	<0.01	<0.01	**
Mo(mg l^{-1})	0.0024	0.0031	0.07
Mn(mg l^{-1})	0.0245	0.188	0.5
Nb(mg l^{-1})	0.0053	0.0015	**
Nd(mg l^{-1})	<0.01	<0.01	**
Ni(mg l^{-1})	0.0061	0.183	0.07
Os(mg l^{-1})	<0.01	<0.01	**
p(mg l^{-1})	0.218	0.0328	20
Pb(mg l^{-1})	<0.01	<0.01	0.01
pr(mg l^{-1})	<0.01	<0.01	**
Rb(mg l^{-1})	0.306	0.046	**
Re(mg l^{-1})	<0.01	<0.01	**
Sb(mg l^{-1})	0.066	0.035	0.01
Se(mg l^{-1})	0.028	<0.01	0.01
Si(mg l^{-1})	>0.2	>0.2	**
Sm(mg l^{-1})	0.0157	<0.01	**
Sn(mg l^{-1})	<0.01	<0.01	**
Sr(mg l^{-1})	3.417	1.581	7
Ta(mg l^{-1})	<0.01	<0.01	**
Tb(mg l^{-1})	<0.01	<0.01	**
Te(mg l^{-1})	<0.01	<0.01	**
Th(mg l^{-1})	<0.01	<0.01	**
Ti(mg l^{-1})	0.119	0.0169	**
Tl(mg l^{-1})	<0.01	<0.01	0.0001
Tm(mg l^{-1})	<0.01	<0.01	**
V(mg l^{-1})	0.033	0.0094	**
W(mg l^{-1})	6.435	0.0084	**
Y(mg l^{-1})	<0.01	<0.01	**
Zn(mg l^{-1})	0.0642	0.0860	3
Zr(mg l^{-1})	0.030	0.01	**

Therefore the high mineral hot springs were not suitable for drinking. Wilcox graph was plotted for hot spring. Wilcox graph based on two criteria in irrigation water SAR (sodium levels) and specific electrical conductivity (salinity hazard) divided into 16 categories. C1S1 water level is the best and C4S4 is the worst water for use in agriculture (Kresic, 2010). Wilcox plot for Isti Su hot spring is shown in Figure 5. The studied spring water is not in the category of agriculture water.

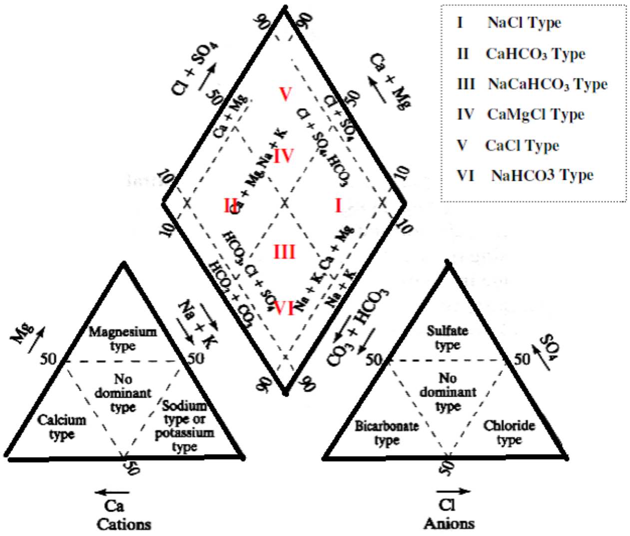

Figure 3) Piper triangle diagram showing the composition of geothermal waters in Isti Su hot spring (dry season).

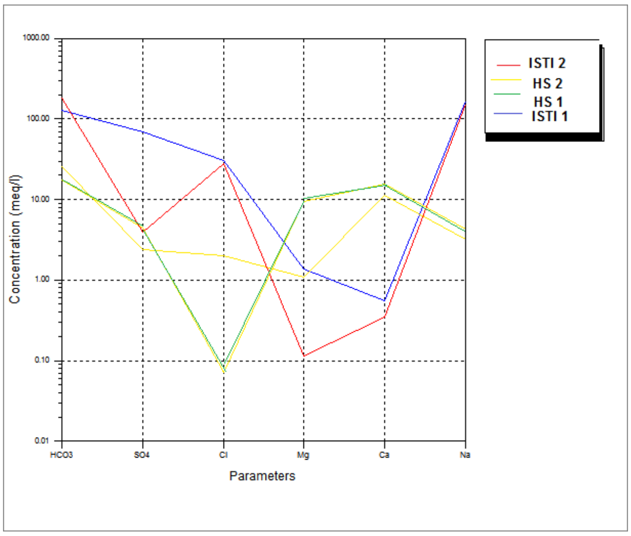

Figure 4) Schoeller plot showing the major cations and anions of ISti Su hot springs (dry season).

Trace element analysis shows the distribution of pollutants in the water samples. These analysis show that some elements such as SO_4^{2-}, and those of As and B are enriched. Enrichment of B, As and some major and trace elements in hot spring is directly related to the leaching of the limestone rocks. The hot water emerges as springs along fracture zones and contacts with limestones. Hot springs are formed when water percolates through permeable rock or fractures, is heated by the earth's crust at depth, and is then driven to the earth's surface by a combination of artesian flow and thermal convection (Woodsworth, 1997). Hot water is able to dissolve minerals over time, so that elevated levels of metals and metalloids are often associated with hot springs. Of the various sources of As in the environment, drinking water probably poses the greatest threat to human health (Smedley and Kinniburg, 2002). In our study area we observed high concentrations of As, Sb and B in the hot spring fluids which have a direct impact on human health through mixing with freshwater resources used for drinking and irrigation. For example, high As and B concentrations has carcinogenic effects to human health and potentially accumulate in agricultural produce. High B concentrations can cause human health effects. Additionally high B concentrations can have a dirty mental effect to crops (Gunduz et al, 2010).

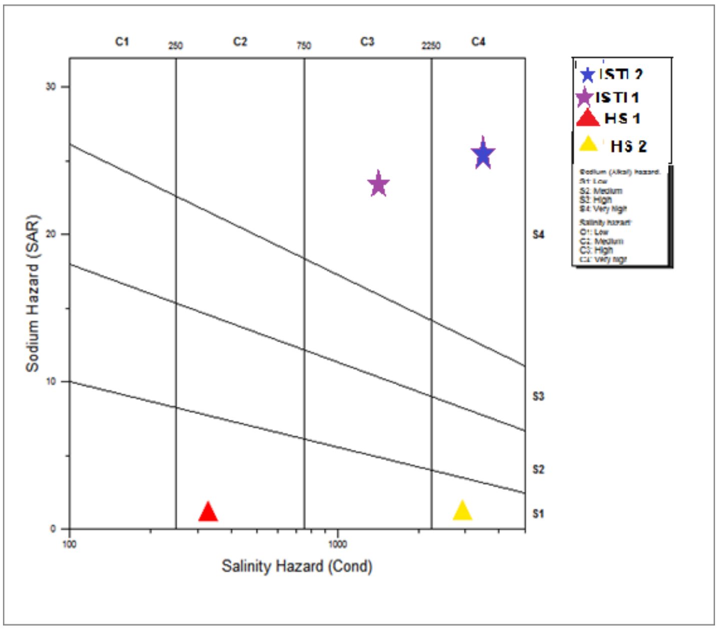

Figure 5) Showing Wilcox diagram for Isti Su hot spring.

The studied geothermal waters contain higher concentrations of As, B, and other trace elements relative to WHO drinking water guidelines. The contamination of surface and subsurface waters with As from hydrothermal waters can constitute a severe environmental impact (Gemici et al, 2004; Baba et al., 2006). Hydrothermal waters change their physical and chemical nature during their rise from the deep geothermal reservoir to or near to the earth's surface due to physical, chemical and biological processes (Chandrasekharam and Bundschuhj, 2008).

5- Conclusions

The thermal springs in Salmas region include Isti Su and Dorik areas. The study area is situated in the Southeastern part of volcanic area of Salmas region. This part is the main heat source of hot springs. The results of the research show that Isti Su hot springs have very high values of EC and As, B, Cl, Ag, Pb, Cu, Sb, Li, Ge and V. Chemically, they are NaCl and Na-SO_4^{2-}-HCO_3^- hot spring types which confirm that the influence of the geological Formations dominated by carbonate and evaporitic rocks. Trace elements from the hydrothermal water released into the springs, caused them to acquire the high content of impurities. The magmatic system and interaction of the hydrothermal fluids with the surrounding volcanic rocks are the main factor for high content of impurities. The studied hot spring contains higher concentrations of As, B and other trace elements relative to WHO drinking water standard. As can cause toxic effects on plants or may accumulate in plants and thus enter the food chain of animals and humans. Inorganic As is the most toxic form, too. This pollutant must be recognized as such its harmful effects on aquatic and terrestrial organisms and human health is ultimately imposed. In addition, these thermal spring discharges into the streams and rivers could affect irrigated crops in downstream fields. Therefore, they would have adverse environmental and health impacts on the local communities and on the hundreds of thousands of tourists using the springs annually.

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References

Alavi, M. 1994. Tectonics of Zagros orogenic belt of Iran, new data and interpretation, Tectonophysics: 229, 211–238.

Aghanabati, A. 1990. Explanatory Text of the Bakhtaran Quadrangle Map 1:250.000, Geological Survey of Iran.

Baba, A., Ármannsson, H. 2006 Environmental impact of the utilization of a geothermal area in Turkey. Energy Source: 1, 267–278.

Chandrasekharam, D., Bundschuh, J. 2008. Low-enthalpy geothermal resources for power generation. 1st ed. The Netherlands: CRC Press/Balkema; Francis and Taylor.

Esmaeili, V.M., Rasa, I., Yazdi, M., Amiri, V., Pazand, K. 2015. Evaluation of groundwater quality and assessment of scaling potential and corrosiveness of water samples in Kadkan aquifer, Khorasan-e-Razavi Province, Iran. Environmental Monitoring Assessment. 187:53, 1-18.

Esmaeili V. M., Rasa I., Yazdi M. and Pazand K. (2015) The hydrochemical assessment of groundwater resources in the Kadkan basin, Northeast of Iran, Carbonates Evaporates, 05/2015; pp.1–15.

German, C. R., Von Damm, K. L., 2003. Hydrothermal processes. In: Holland, H. D., Turekian, K. K. (Eds.): Treatise on Geochemistry. Elsevier, pp. 181 –221.

Ghafouri, M. R. 2003. Mineral water and mineral springs of Iran, University of Tehran, book publication, 388p.

Gunduz, O., Simesk, C., Hasozbek, A. 2010. Arsenic pollution in the groundwater of Simav Plain, Turkey: its impact on water quality and human health. Water Air and Soil Pollution: 205, 43–62.

Déri-Takács, J., Erőss, A., Kovács, J. 2015. The chemical characterization of the thermal waters in Budapest, Hungary by using multivariate exploratory techniques. Environmental Earth sciences: 74, 7475–7486.

Kresic, N. 2010. Types and classifications of springs. Groundwater Hydrology of Springs, pp 31–85.

Khodabandeh, A. A., Soltani, G., Sartipi, A. 2002. 1:100,000 Geological Map of Salmas. Geological Survey of Iran, Tehran.

Modabberi, S. 2013. Environmental Geochemistry of Potentially Toxic elements in thermal springs in the Sabalan Volcanic Field, NW Iran. E3S Web of Conferences, DOI: 10.1051/C /20130132003.

Piper, A. M. 1994. A graphic procedure in the geochemical interpretation of water-analyses, Eos Transactions American Geophysical Union: 25, 914–928.

Schoeller, H. 1962. Les eaux souterraines. Masson and Cie, Paris, 642pp.

Smedly, P. L., Kinniburg, D. G. A. 2002. Review of the source, behavior and distribution of arsenic in natural waters. Applied Geochemistry: 17, 517–568.

Stocklin, J. 1968. Structural history and tectonics of Iran: a review. The American Association of Petroleum Geologists Bulletin: 52, 1258–1229.

Taheri, M., Yazdi, M., Navi, P. 2012. Health hazards and arsenic pollutants in Kharaqan Hot springs, Qazvin. In: proceedings of4th Symposium of Iranian Society of Economic Geology, August 30–31, Birjand university.

Tarcan, G., Gemici, U. 2005. Effects of the contaminants from Turgutlu–Urganlı thermo- mineral waters on cold ground and surface waters. Bulletin of Environmental Contamination and Toxicology: 74, 485–492.

Vengosh, A., Helvaci, C., Karamanderesi, H. 2002. Geochemical constraints for the origin of thermal waters from western Turkey. Applied Geochemistry: 17, 163–183.

Webster, J. G., Nordstrom, D. G. 2003. Geothermal arsenic. Welch, A. H., Stollenwerk, K. G. (Eds.): Arsenic in Ground Water: Geochemistry and Occurrence, Springer, New York, USA, pp. 101–125.

W.H.O. 2011. Guidelines for drinking-water quality, World Health Organization. 4th edition. On line: http://www.who.int/publications/2011/9789241548151_eng.pdf.

W.H.O. 2003. Arsenic in drinking water. Background document for preparation of WHO Guidelines for drinking water quality. Geneva, Switzerland: World Health Organization, WHO/SDE/WSH/03.04/75.

Wilcox, L. V. 1948. The Quality of Water for Irrigation Use, U.S. Dept. of Agriculture, Bull. 962., Washington, 19p.

Yazdi, M., Taheri, M., Navi, P. 2015. Environmental geochemistry and sources of natural Arsenic in the Kharaqan hot springs, Qazvin, Iran. Environmental Earth sciences: 73, 5395–5404.