

Geogenic Arsenic Contamination in Northwest of Iran; Role of Water Basin Hydrochemistry

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ABSTRACT

Introduction: Arsenic contamination of surface and groundwater has been categorized among high profile environmental problems around the world. The matter is of most concern where unsafe water is used for drinking. Sahand region reservoir in northwest of Iran supplies water for drinking, industrial and agricultural purposes through irrigation of 11000 hectares of lands.

Materials and Methods: The hydrochemistry status of Sahand dam basin and arsenic plume distribution in water resource was evaluated by analyzing 308 water samples from surface and ground water according to the standard methods. In addition, geological features information of basin were obtained based on recent site studies and field investigations.

Results: Elevated concentrations of arsenic (range = 0-1440 ppb, mean = 171.68 ppb) were detected in water basin and dam. According to the delineating evidences, regional geological background and volcanic activities can be considered as the main sources of the natural genesis of arsenic in the study area.

Conclusion: Notable amounts of arsenic sulfide were recorded in seams, gaps, fractures of limestone, marl, sandstone and an overlying ferruginous conglomerate. Concentrations of arsenic varied seasonally highlighting the maximum concentration observed in autumn and early winter (December). Seasonal fluctuations can be probably attributed to changes in geochemical conditions in sediments at the bottom of reservoir.

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Introduction

Natural contamination of water resources (both surface and groundwater) by arsenic is an important concern in many countries¹. In spite of low average abundance of arsenic in the upper

earth's crust (1.5-2 µg/g), it can accumulate in rocks to concentrations of much higher magnitude than this value^{2,3}. Accumulation of As and metals in soils can affect the quality of water which can potentially affect terrestrial and aquatic

communities, it consequently can affect the quality and quantity of drinking water directly and indirectly^{4, 5}. Over 200 different mineral arsenic forms can be present in natural soils⁶. However, orpiment (As_2S_3), realgar⁷, and arsenopyrite (FeAsS) are the most common solid phases of As in the subsurface environment^{8, 9}. One of the main processes that control distribution of arsenic in water is its reaction at water-mineral interfaces^{10, 11}. Likewise arsenic amount in the geological source material, the environmental conditions control chemical and biological transformation of materials¹² and therefore arsenic mobilization mechanisms vary with location, depending on hydrogeological and redox conditions¹³.

Regarding the environmental problems caused by the presence of arsenic in water resources, the geochemistry of groundwater and arsenic contamination mechanisms have been widely investigated^{14, 15}. As reported by Tisserand et al. groundwater arsenic of geogenic origin in the western Alps is generally associated with arsenic-bearing sulfide minerals, such as pyrite, arsenian pyrite, and arsenopyrite in the crystalline rocks¹⁶.

Arsenic contamination of water resources in Iran was first recognized in Kurdistan province, in the West of Iran, where a high concentration of arsenic less than 1 mg/L in some villages was reported⁷. Since then a number of studies were undertaken to investigate the occurrence of arsenic and its possible health effects in this area. For example, Mosaferi et al.¹⁷, in their study in Kurdistan province, reported hyperkeratosis and hyperpigmentation as a result of chronic exposure with arsenic.

The spatial coincidence between the arsenic anomaly in groundwater and the distribution of travertine springs was found by Keshavarzi et al. in water resources of Kurdistan and West Azerbaijan provinces¹⁸.

Sahand dam with capacity of $135 \times 106 \text{ m}^3$ is located in East Azerbaijan province and is an important reservoir in the region. The reservoir is located in the south western part of Hashtrud County (Figure 1) and in addition to supplying

water for drinking and industrial purposes, provides water for irrigation of about 11000 hectares of agricultural lands. According to preliminary limited unpublished studies conducted in the area by the local Water Organization (Bandab), contamination to arsenic and heavy metals has been reported in reservoir water. Due to the importance of this issue for water supplies of the region, the present study was conducted to determine the extent and severity of arsenic contamination problem, as well as the hydrogeochemical properties of water in Sahand reservoir and related surface and groundwater resources. The study also aimed to identify the sources of arsenic pollution to assist management of the problem.

Materials and Methods

The study area description and geology

The study area is located in the north west of Iran in the south-eastern part of East Azerbaijan province and is 26 km from Hashtrud County (UTM: X= 644000 to X= 677000 East longitude and Y= 4134000 to 4155000 North latitude) (Figure 1). The area is a part of Hashtrud County close to Sahand volcanic mountains and has been severely affected by volcanic activity. The study district is also located in the basin of Caspian Sea and in the sub-basin of the Sefidrud River.

The largest river in the basin is Qarranqu River and as mentioned earlier, the main purpose of constructing the Sahand dam was to provide a reservoir on this river with sufficient capacity for the development of irrigated agriculture in the south western part of Hashtrud County in addition to provision of water for industrial and potable use. The Qarranqu River basin has an area of 820 km^2 , initiates from Sahand Mountain (height: 3542 m) and after 51 km reaches to dam site (height: 1560 m). Sahand dam was constructed with soil and an impervious central core. The length, width, and height of the dam are 405 m, 10 m, and 35 m, respectively. Six village and 320 hectares of agricultural land were submerged by dam.

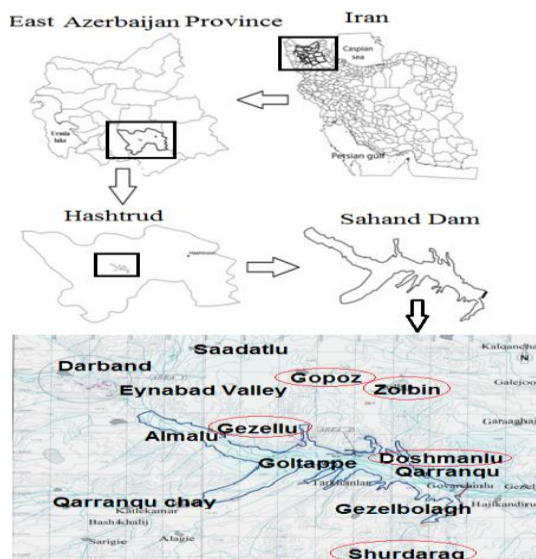


Figure 1: Location of the studied area

The major part of the region is characterized by a semi-arid and cold climate. The average annual precipitation (rain and snow) is 340 mm year^{-1} , the average relative humidity is about 55 %, and mean temperature in the coldest month (January) and warmest month (July) are respectively 6°C and 12°C (Bandab 2004; Bandab 2014).

Based on the collected data from site visiting, field investigations, and previous studies (Bandab 2004; Bandab 2014) regional hydrogeological setting is classified into: Upper Red Formation Deposits (URFD), pyroclastic deposits, and volcanic lava pile of Sahand volcano.

These formations have the highest development in the region and their age is from Miocene to Quaternary. Type of URFD is destructive and due to low depth of related sea, gypsiferous deposits and salt are seen frequently. For this reason, all surface runoff and springs discharged from this geological formation contain high content of dissolved salts and are saline. These formations are highly faulted and form highly unstable hill-slopes which leads to frequent land-slides. Due to water adsorption by gypsum, intense swelling of the earth (by 30 to 40 cm) is observed in some locations, e.g., Shurdaraq village¹⁹.

Pyroclastic deposits and volcanic lava pile of Sahand volcano have covered a wide part of area. In Qarranqu River basin, Dacitic and quartz-andesite lavas are observed as single or mixed

scattered volcanic peaks. Pyroclastic deposits of Sahand have precipitated around the volcanic mass intermittently in form of alluvial conglomerate and volcanic ash. Travertine forming springs are also observed in the region for example around the Goltappeh village¹⁹.

Water sampling and analysis

In order to evaluate the water quality and hydrochemistry status in the basin, a total of 308 samples were collected and analyzed during the period 2002-2015. Water samples included 144 samples from surface and ground waters of the basin and 164 samples from the reservoir and discharging water from Sahand dam. It should be noted that a specific sampling and analysis strategy has been designed since 2007 that focused on geological formations where previous investigations had indicated that there were significant arsenic anomalies.

The samples for heavy metals and arsenic analysis were acidified to pH less than 2 with nitric acid while non-acidified aliquots were used for major and minor ions analysis. All samples were filtered and collected in precleaned polyethylene bottles, labeled, and stored in a cool box at 4°C immediately after collection until analysis.

The quality characteristics (physicochemical parameters, major and minor constituents) and trace elements were determined by standard

methods and different laboratory analytical equipments²⁰. Arsenic and heavy metals of samples were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The accuracy of analysis was checked by calculation of ionic balances²¹ as: Ion balance percent = $\left\{ \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \right\} \times 100$

The mean calculated balances was less than 5% and furthermore, replicate samples, blanks, and re-measuring of standard solutions in each set of analysis confirmed the quality assurance of measurements. Finally, the obtained data were analyzed statistically using Statistical Package for Social Sciences (SPSS) software package (Version 16.0) and Spearman's rank correlation²² was conducted between various chemical parameters.

Results

A statistical summary for major constituents and trace elements of frequently monitored sampling points during the study period are presented in

table 1. The frequency distributions of measured parameters were checked for skew and kurtosis. As it can be seen, there is a wide variability in the electrical conductivities of sampled water in the basin which is a measure of water's dissolved salts (min = 256 $\mu\text{S}/\text{cm}$, max = 3650 $\mu\text{S}/\text{cm}$). The pH values of samples ranged from 6.9 to 9.10 with an average of 8.21, they demonstrate the characteristics of alkaline waters in the study area.

Correlation matrix of quality parameters of analyzed samples is shown in table 2. It is apparent from Correlation matrix of water quality parameters that there is a significant positive correlation between EC and specially Na^+ , Cl^- then Ca^{2+} , SO_4^{2-} , Mg^{2+} , HCO_3^- , and K^+ ions (Table 2).

Major ions' concentrations on the geological map are provided in figure 2. Based on the Pie charts of figure 2, where the radius of circles is in direct proportion with total amount of cations and anions, the distribution of major ions in the region does not follow a specific trend which indicates the presence of different scattered shallow aquifers and also unrelated surface waters.

Table 1: Analytical results of water quality and hydrochemical parameters

Parameter	Unit	Minimum	Maximum	Mean \pm SD
Fe	ppb	0.0	208.78	43.84 \pm 54.07
Mn	ppb	2.7	211.37	36.48 \pm 39.34
As	ppb	0.0	1440.00	265.22 \pm 171.68
Zn	ppb	11.97	217.65	40.66 \pm 44.34
Cd	ppb	ND	ND	ND
Pb	ppb	9.18	34.11	4.34 \pm 13.63
Cu	ppb	4.66	14.60	3.01 \pm 9.61
PO_4^{3-}	mg/L	0.03	0.22	0.03 \pm 0.08
NO_3^-	mg/L	0.25	6.10	1.32 \pm 1.71
NH_4^+	mg/L	0.06	2.20	0.42 \pm 0.36
SiO_2	mg/L	14.46	120.48	26.25 \pm 53.56
F^-	meq/L	0.0	0.10	0.02 \pm 0.03
K^+	meq/L	0.04	8.70	1.39 \pm 0.79
Na^+	meq/L	0.42	25.96	3.43 \pm 4.22
Mg^{2+}	meq/L	0.3	14.24	2.70 \pm 2.11
Ca^{2+}	meq/L	1.35	8.48	1.20 \pm 3.02
SO_4^{2-}	meq/L	0.12	13.48	1.56 \pm 1.54
Cl^-	meq/L	0.09	31.44	3.89 \pm 3.64
HCO_3^-	meq/L	0.95	12.80	1.70 \pm 3.10
CO_3^{2-}	meq/L	0.0	1.00	0.21 \pm 0.23
EC	$\mu\text{S}/\text{cm}$	256.0	3650.00	491.77 \pm 844.45
pH	-	6.90	9.10	0.45 \pm 8.21

Table 2: Correlation matrix of quality parameters of analyzed samples

Variable	Fe	Mn	As	Zn	Pb	Cu	PO ₄ ³⁻	NO ₃ ⁻	NH ₄ ⁻	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻	Cl ⁻	Hco ₃ ⁻	CO ₃ ⁻	EC	pH
Fe	1.00																		
Mn	0.62	1.00																	
As	-0.3	-0.37	1.00																
Zn	0.06	0.41	-0.12	1.00															
Pb	-0.19	-0.37	0.15	0.05	1.00														
Cu	0.42	0.01	0.17	0.45	0.48	1.00													
PO ₄ ³⁻	-0.21	-0.01	0.34	0.31	0.27	0.21	1.00												
NO ₃ ⁻	0.02	-0.09	0.00	-0.33	0.36	-0.03	-0.31	1.00											
NH ₄ ⁻	-0.14	0.05	-0.19	0.13	-0.17	-0.24	0.21	-0.59	1.00										
K ⁺	-0.26	0.27	0.05	0.46	-0.12	-0.14	0.43	-0.62	0.52	1.00									
Na ⁺	-0.33	0.11	0.32	0.44	-0.18	-0.03	0.41	-0.53	0.36	0.62	1.00								
Mg ²⁺	-0.52	0.00	0.00	0.29	-0.20	-0.32	0.28	-0.57	0.46	0.64	0.85	1.00							
Ca ²⁺	-0.25	0.16	0.28	0.37	-0.09	0.03	0.30	-0.36	0.24	0.49	0.95	0.81	1.00						
SO ₄ ²⁻	-0.22	0.20	0.18	0.45	-0.26	-0.05	0.46	-0.64	0.46	0.67	0.97	0.85	0.88	1.00					
Cl ⁻	-0.4	0.09	0.30	0.42	-0.16	-0.08	0.41	-0.55	0.39	0.67	0.99	0.89	0.94	0.95	1.00				
HCO ₃ ⁻	-0.18	0.18	0.30	0.29	-0.09	-0.01	0.13	0.04	0.02	0.20	0.79	0.58	0.88	0.68	0.75	1.00			
CO ₃ ⁻	-0.03	-0.38	-0.27	-0.37	0.18	-0.02	-0.28	-0.10	-0.13	-0.20	-0.61	-0.28	-0.61	-0.58	-0.54	-0.82	1.00		
EC	-0.35	0.11	0.29	0.41	-0.17	-0.06	0.38	-0.50	0.36	0.61	1.00	0.88	0.97	0.96	0.99	0.81	-0.59	1.00	
pH	0.10	-0.32	-0.21	-0.39	0.24	0.10	-0.15	-0.03	-0.14	-0.30	-0.71	-0.48	-0.72	-0.66	-0.65	-0.90	0.93	-0.71	1.00

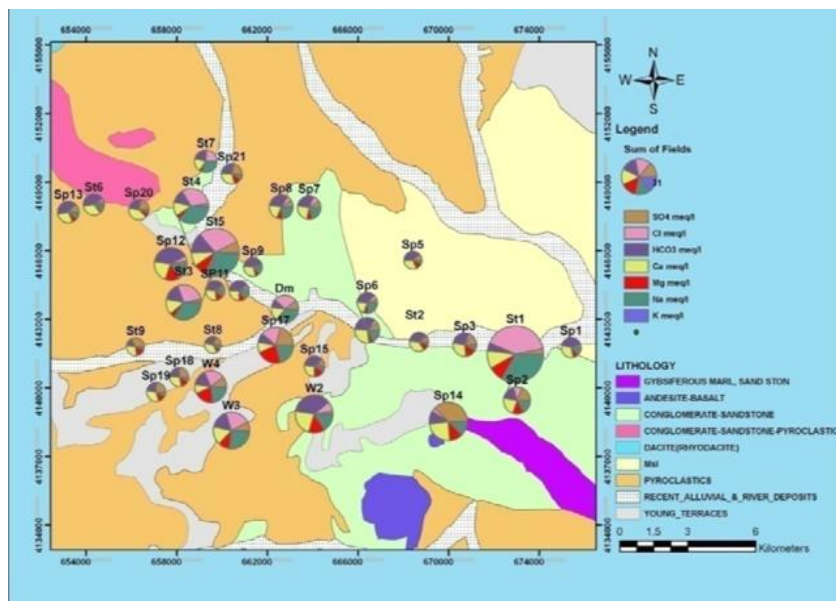
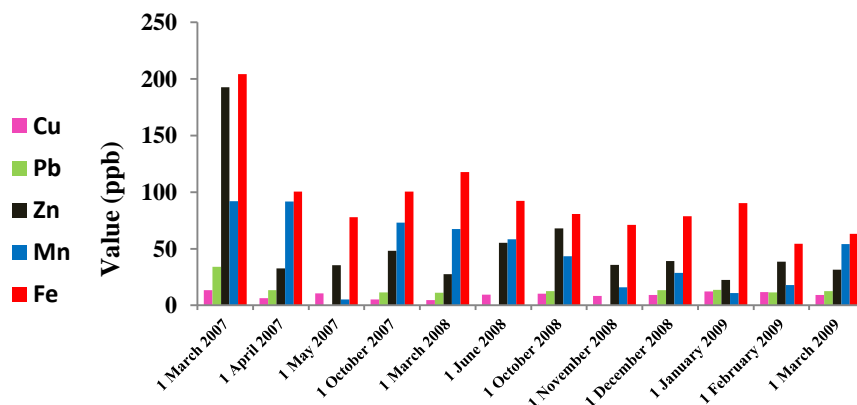


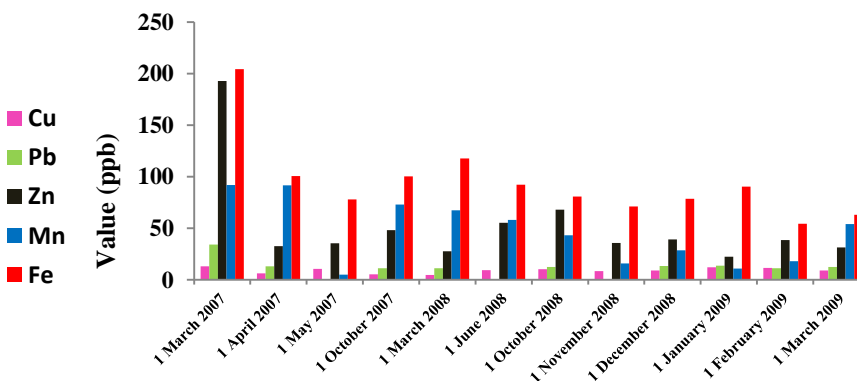
Figure 2: Major ions' concentrations on the geological map

Variation of trace elements' concentration inside the reservoir and in taken samples from outlet of reservoir are depicted in figures 3 a and b. Figure 4 represents fluctuations of arsenic concentration in

river, reservoir, and dam effluents in 2007-2015. Sometimes the arsenic levels in river water are much higher than the reservoir and vice versa.



a: Samples from reservoir effluent



b: Samples from reservoir inside

Figure 3: Variation of heavy metals' concentration; a: Samples from reservoir effluent, b: Samples from reservoir inside

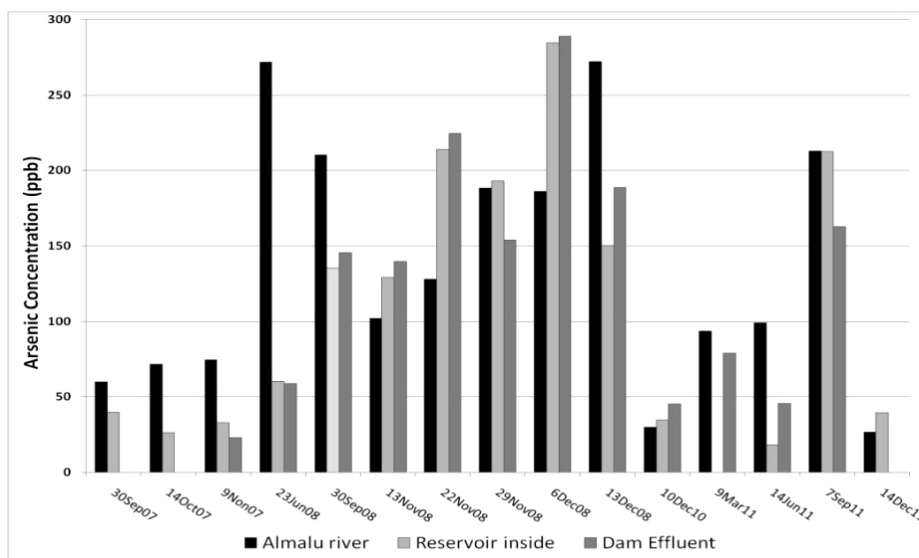


Figure 4: Fluctuations of arsenic concentration in river, reservoir, and dam effluent: 2007-2015

Figure 5 portrays petrographic studies in the region, realgar and orpiment inside the lime stones.

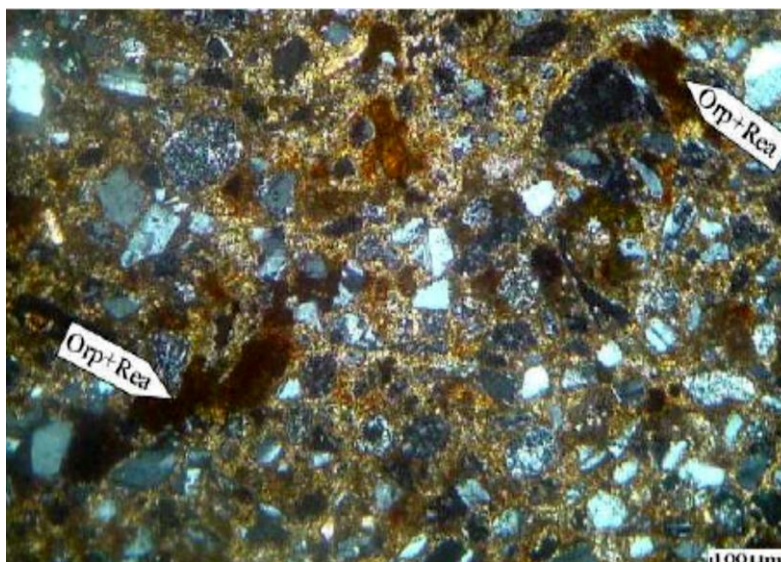


Figure 5: Petrographic studies in the region, realgar and orpiment inside the lime stones

Discussion

Hydrogeochemistry

As it can be observed from Table 1, regarding major ion variations, Sodium (Na^+) has the highest and potassium (K^+) has the lowest concentration range among the cations in water resources of the region. High amounts of Na^+ could be released into water as a result of gypsiferous compounds and salts' dissolution from URFD. Also, water samples show a wide variability in the concentrations of chloride (Cl^-)

due to leaching from the URFD.

Concentration of ions such as Na^+ and Cl^- are higher in surface waters (e.g., Almalu River and also Qarranqu River after Sahand dam) and some of the ground waters which originate from upper red geological formations, whereas springs which originate from the Sahand Mountains have a low TDS dominated by Ca^{2+} and HCO_3^- . It should be noted that water of Qarranqu River before joining to Almalu branch and also Almalu River before entrance to Eynabad Valley has a low content of

TDS. So, most of the spring samples except Eynabad valley springs are typically Ca-Mg-HCO₃ type water while samples from inside and effluent of Almalu River's reservoir are of Na-K-Cl-SO₄ type based on classification of chemical composition of sampled waters by a Piper diagram.

The obtained data revealed a large range of chemical composition in analyzed water samples of the basin.

Considering water quality in Sahand dam, it seems that Qarranqu and especially Almalu Rivers with mean annual discharge of 149×106 m³ have a significant association with water quality of the reservoir. The electrical conductivity values measured in Almalu River and reservoir ranged between "235–1,920 and 233–1,100" µS/cm, respectively, but there was no significant difference between the EC levels in the reservoir and river input ($p > 0.05$). However, there is a considerable fluctuation in level of EC so that during warm months with decrease of river flow, the values of EC increase significantly. In some cases, river's flow decreases to zero.

On the other hand, the behavior of EC is relatively similar in reservoir water and collected samples from outlet of reservoir, however some differences were observed that can be attributed to effects of some springs in the bottom of reservoir which directly discharge water to the reservoir.

Arsenic and trace elements

According to Table 1, concentrations of Fe and Mn were detected as 0.0-208.78 ppb and 2.7-211.37 ppb, respectively in sampled waters. Pb concentrations vary from 9.18-34.11 ppb and Cd was not detected in any of samples. The concentration of other metals including Zn and Cu except arsenic was below the recommended limits. Variation of trace elements' concentration inside the reservoir and in taken samples from outlet of reservoir is depicted in Figure 3 a and b.

The as content of the samples surpassed the drinking water guideline value of 10 µg/L²³ by a factor of about 11-13 fold during 2007-2015

(Figure 3).

The mean as concentration in water samples was calculated as 171.68 ppb and high levels of arsenic contamination with a maximum of 1440 ppb were detected in spring waters of Gopoz, Shurdaraq, Qezellu, Zolbin, Doshmanlu villages, and Eynabad valley (see Figure. 1 for approximate locations of villages). Among these potential sources of arsenic pollution, only Eynabad branch of Almalu River and water resources of Qezellu village have a direct connection with Sahand dam and it is likely that this branch is the main cause of water quality deterioration in the reservoir. There are numerous springs in Eynabad Valley with undesirable water quality and salt deposits around them which have arsenic contamination with levels as high as 700 ppb.

The fluctuation of arsenic concentration in both Almalu as well as inside and effluent reservoir are similar although no significant differences were observed between mean of concentrations ($p > 0.05$). Sometimes arsenic levels in river water are much higher than the reservoir and vice versa as shown in figure 4.

The maximum concentration of arsenic in Sahand reservoir is usually observed in autumn and early winter (especially in December). Seasonal variations can be attributed to sediments inside the reservoir and occurrence of anaerobic conditions, thermal destratification of water, and etc. More studies are required to determine the mechanisms responsible for arsenic cycling between sediments and the water column within the reservoir.

Arsenic anomaly source and mobilization

Generally, the most common sources of arsenic in the natural environment are volcanic rocks (specifically their weathering products and ash), marine sedimentary rocks, hydrothermal ore deposits and associated geothermal waters, and fossil fuels²²⁻²⁴.

Arsenic concentrations are typically high in regions with significant geothermal activity. Generally, the highest arsenic concentrations are

found in the fluids of geothermal reservoirs in volcanic rocks (typical range: a few to tens of mg kg^{-1})²⁵. Field surveys, microscopic studies, and geochemical investigations support that controlling agents and centralization of arsenic bearing ores in the studied region are related to magmatism, metamorphism, and tectonism processes¹⁹. The presence of large amount of hydrous minerals (e.g., amphibole and biotite) in volcanic rocks of the region indicates that local magma bodies are capable of producing geothermal fluids that could contain substantial amounts of arsenic. Additionally, different metamorphic processes including silicification, dolomitization, pyritization, and decalcification with different grades have taken place in the region that is likely to have affected the distribution of arsenic in rocks. It was also found that distribution of geological fractures and generally tectonic of the region are the most significant factors in the centralization of arsenic bearing materials. Fractures occur in limestone, marl, sandstone, and upper red conglomerate. In field studies, there were evidences of arsenic sulfide in seams, gaps, and fractures of these formations. According to the petrographical studies, realgar and orpiment, as two main ores of arsenic contain 70 and 61 percent arsenic, respectively (Figure 5). The fractures have been used as a passageway for movement of hydrothermal fluids under pressure. Although main faults have controlling role, yet this type of mineralization generally follow subsidiary faults and fractures.

As the primary source of arsenic in groundwater in western Quebec (Canada) is weathering of arsenic-bearing sulfides along the fault zone²⁶, in our study, regions with high arsenic contamination such as Gopoz village and Eynabad Valley were located at fault zones too. Gopoz village is located on the fault boundary and Eynabad valley has frequent small faults that are origin of springs with high arsenic contamination. Two springs of Gopoz village have formed a pond with elevated arsenic concentrations. Although this pond is unlikely to

affect water quality in Sahand reservoir, it is recommended to restrict access to the pond completely, the pond water should not only be avoided by human, but also by livestock potable purposes. Further, it is strongly recommended to prevent entrance of Eynabad valley contaminated springs to Almalu River¹⁹.

Keeping the above results in mind, it can be said that in the basin of Sahand dam, excessive high values of arsenic in water are significantly due to regional geologic formations.

Regarding adverse health effects of arsenic exposure in Gopoz village the results of a cross-sectional study in 2010 showed that the incidence of hyperkeratosis was 34 times higher among the exposure group (Arsenic concentration in drinking-water sources was 1031ppb) compared to the control group (As content was non-detectable in water sources), additionally, around 25 % of cases in the exposure group showed chromosomal abnormalities²⁷.

Although the arsenic contamination in the region is significantly geological in origin, the correlation analysis which provides useful information with respect to the genesis of any contaminant²⁸ can be helpful in further evaluation of probable arsenic release mechanisms. The obtained results showed a positive correlation between arsenic with PO_4^{3-} , Na^+ , HCO_3^- and Cl^- and there was no correlation between arsenic and nitrate ion (Table 1). The relationship between arsenic and bicarbonate is well documented because this ion can play an important role in mobilization of arsenic through the competition for adsorption sites and through the formation of arseno-carbonate complexes^{29, 30}. Arsenic-enriched sediments are deposited in surface water with low carbonate concentrations³¹. Subsequently, the sediments come into contact with sediment-ground water interface with high dissolved bicarbonate content, arsenic is then mobilized by displacement from the sediment surface. This process takes place better at high pH. Also, phosphate and nitrate act like bicarbonate and can lead to release of adsorbed arsenic³². Since arsenic correlates positively with

phosphate, sodium, and bicarbonate, it is possible that the above processes are contributing to the release of arsenic into the water of the studied region.

Conclusion

This study has investigated quality of water, hydrogeochemistry, arsenic contamination, and fluctuations in Sahand reservoir and its basin. High levels of arsenic contamination have been found in the studied region especially in Almalu River and inside Sahand reservoir. Eynabad branch of Almalu River is the main cause of deterioration of water quality in the Sahand reservoir. Springs of Eynabad Valley have high concentrations of arsenic. It was determined that centralization of arsenic follows direction and distribution of faults and tectonic of the region and is the control agent of distribution and centralization of arsenic bearing ores. The most likely sources of natural contamination of arsenic in the basin of Sahand dam are regional geologic formations and volcanic activities. Finding of the current study can be used for restriction of sources' pollution especially springs. It is strongly recommended that for consumption of Sahand reservoir water for drinking purposes, dilution with safe and less polluted water or treatment options should be considered in order to protect individuals' health. At present, a Water Treatment Facility (WTF) is operating to provide safe drinking water for Hashtud city. This facility just uses conventional treatment methods including coagulation, flocculation, sedimentation for turbidity removal, and disinfection with chlorine as final step for microbiological agents. Given that this treatment chain is not effective in removal of arsenic and other heavy metals, more effective and exclusive methods should be applied for providing safe drinking water.

Also, further research could be undertaken for better management of contamination.

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Conflict of interest

The authors are committed to declare that they have no competing interests.

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References

1. Bondu R, Cloutier V, Rosa E, et al. A review and evaluation of the impacts of climate change on geogenic arsenic in groundwater from fractured bedrock aquifers. *Water Air Soil Pollut.* 2016; 227(9): 296.
2. Banning A, Rude TR. Enrichment processes of arsenic in oxidic sedimentary rocks– from geochemical and genetic characterization to potential mobility. *Water Res.* 2010; 44(19): 5512-31.
3. Nemati S, Mosaferi M, Ostadrahimi A, et al. Arsenic intake through consumed rice in Iran: markets role or government responsibility. *Health promotion perspectives.* 2014; 4(2): 180.
4. Luo W, Lu Y, Zhang Y, et al. Watershed-scale assessment of arsenic and metal contamination in the surface soils surrounding miyun reservoir, Beijing, China. *J Environ Manage.* 2010; 91(12): 2599-607.
5. Schipper P, Bonten L, Plette A, et al. Measures to diminish leaching of heavy metals to surface waters from agricultural soils. *Desalination.* 2008; 226(1): 89-96.
6. Larios R, Fernández-Martínez R, Álvarez R, et al. Arsenic pollution and fractionation in sediments and mine waste samples from different mine sites. *Sci Total Environ.* 2012; 431: 426-35.
7. Mosaferi M, Yunesion M, Mesdaghinia A, et al. Arsenic occurrence in drinking water of IR

- of Iran: the case of Kurdistan Province. Fate of arsenic in the environment Dhaka: BUET-UNU International Symposium, International Training Network Centre, Bangladesh University of Engineering and Technology, United Nations University, Tokyo; 2003: Citeseer.
8. Tabelin C, Igarashi T. Mechanisms of arsenic and lead release from hydrothermally altered rock. *J Hazard Mater*. 2009; 169(1): 980-90.
 9. Takamatsu T, Watanabe M, Koshikawa MK, et al. Pollution of montane soil with Cu, Zn, As, Sb, Pb, and nitrate in Kanto, Japan. *Sci Total Environ*. 2010; 408(8):1932-42.
 10. Müller K, Ciminelli VS, Dantas MSS, et al. A comparative study of As (III) and As (V) in aqueous solutions and adsorbed on iron oxy-hydroxides by Raman spectroscopy. *Water Res*. 2010;44(19):5660-72.
 11. Luo X, Liu H, Huang G, et al. Remediation of arsenic-contaminated groundwater using media-injected permeable reactive barriers with a modified montmorillonite: sand tank studies. *Environmental Science and Pollution Research*. 2016; 23(1):870-7.
 12. Campbell K. Biogeochemical mechanisms of arsenic mobilization in haiwee reservoir sediments: California Institute of Technology; 2006.
 13. Reza AS, Jean JS, Yang HJ, et al. A comparative study on arsenic and humic substances in alluvial aquifers of Bengal delta plain (NW Bangladesh), Chianan plain (SW Taiwan) and Lanyang plain (NE Taiwan): implication of arsenic mobilization mechanisms. *Environmental geochemistry and health*. 2011; 33(3): 235-58.
 14. Cho KH, Sthiannopkao S, Pachepsky YA, et al. Prediction of contamination potential of groundwater arsenic in Cambodia, Laos, and Thailand using artificial neural network. *Water Res*. 2011; 45(17): 5535-44.
 15. Stahl MO, Harvey CF, van Geen A, et al. River bank geomorphology controls groundwater arsenic concentrations in aquifers adjacent to the red river, Hanoi Vietnam. *Water Resour Res*. 2016; 52(8): 6321-34.
 16. Tisserand D, Pili E, Hellmann R, et al. Geogenic arsenic in groundwaters in the western Alps. *J Hydrol (Amst)*. 2014;518:317-25.
 17. Mosaferi M, Yunesian M, Dastgiri S, et al. Prevalence of skin lesions and exposure to arsenic in drinking water in Iran. *Sci Total Environ*. 2008; 390(1): 69-76.
 18. Keshavarzi B, Moore F, Mosaferi M, et al. The source of natural arsenic contamination in groundwater, west of Iran. *Water Qual Expo Health*. 2011; 3(3-4): 135-47.
 19. Nadiri A, Asghari Moghaddam A, Sadeghi F, et al. Investigation of arsenic anomalies in water resources of sahand dam. *J Environ Stud (Northborough)*. 2012; 38(3).
 20. Association APH. Water environment federation standard methods for the examination of water and wastewater. Washington, Dc; 1994.
 21. Baig JA, Kazi TG, Arain MB, et al. Evaluation of arsenic and other physico-chemical parameters of surface and ground water of Jamshoro, Pakistan. *J Hazard Mater*. 2009; 166(2): 662-9.
 22. Smedley P, Kinniburgh D. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem*. 2002; 17(5): 517-68.
 23. Edition F. Guidelines for drinking-water quality. WHO chronicle. 2011;38:104-8.
 24. O'Reilly J, Watts M, Shaw R, et al. Arsenic contamination of natural waters in San Juan and La Pampa, Argentina. *Environ Geochem Health*. 2010; 32(6): 491-515.
 25. Birkle P, Bundschuh J, Sracek O. Mechanisms of arsenic enrichment in geothermal and petroleum reservoirs fluids in Mexico. *Water Res*. 2010; 44(19): 5605-17.
 26. Bondu R, Cloutier V, Rosa E, et al. Mobility and speciation of geogenic arsenic in bedrock groundwater from the Canadian Shield in western quebec, Canada. *Sci Total Environ*. 2017; 574: 509-19.
 27. Dastgiri S, Mosaferi M, Fizi MA, et al.

- Arsenic exposure, dermatological lesions, hypertension, and chromosomal abnormalities among people in a rural community of northwest Iran. *J Health Popul Nutr.* 2010; 14-22.
28. Pandey P, Sharma R, Roy M, et al. Arsenic contamination in the Kanker district of central-east India: geology and health effects. *Environmental geochemistry and health.* 2006; 28(5): 409-20.
29. Kim MJ, Nriagu J, Haack S. Arsenic species and chemistry in groundwater of southeast Michigan. *Environmental Pollution.* 2002; 120(2): 379-90.
30. Kouras A, Katsoyiannis I, Voutsas D. Distribution of arsenic in groundwater in the area of Chalkidiki, Northern Greece. *J Hazard Mater.* 2007;147(3):890-9.
31. Muñoz MO, Aróstegui JLG, Bhattacharya P, et al. Geochemistry of naturally occurring arsenic in groundwater and surface-water in the southern part of the Poopó Lake basin, Bolivian Altiplano. *Groundwater for Sustainable Development.* 2016.
32. Anawar HM, Akai J, Sakugawa H. Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater. *Chemosphere.* 2004; 54(6): 753-62.