EVALUATION OF NATURAL ARSENIC CONTAMINATION AND ROLE OF WATER BASIN HYDROCHEMISTRY (NORTHWEST, IRAN)

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ABSTRACT

Natural Contamination of surface and groundwater with arsenic is a widespread problem around the world. The problem is of most concern where contaminated water is used for drinking purposes. Sahand reservoir is an important reservoir in Northwest of Iran which supplies water for drinking and industrial purposes in addition to irrigation of 11000 hectares of agricultural lands.

The present study provides information on factors that affect the hydrogeochemistry of the Sahand reservoir basin and on the distribution of arsenic in surface water and groundwater in the basin based on available information and along with water samples analyzed during this study.

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 to be the main source of the natural genesis of arsenic in water in the region. There were a manifestation of arsenic sulfide in seams, gaps and fractures of limestone, marl, sandstone and an overlying ferruginous conglomerate. Concentrations of arsenic in Sahand reservoir varied seasonally with the maximum concentration of arsenic being observed in autumn and early winter season (especially in December). Seasonal fluctuations can be attributed to changes in geochemical conditions in sediments at the bottom of reservoir which requires more studies.

Keywords: Geogenic arsenic, water quality, hydrogeology, Sahand dam, Iran

1. Introduction

Natural contamination of water resources (both surface and groundwater) by arsenic is an important concern for many countries (Smedley and Kinniburg 2002). In spite of low average abundance of arsenic in the upper earths crust (1.5-2 µg/g), it can accumulate in rocks to concentrations several orders of magnitude higher than this value (Banning and Rude 2010). When water flow passes through arsenic rich deposits and stones, this toxic material can be interred to water and also changes in land and water use caused by human activities can cause arsenic and metals in soils to be transported from soils and sediments into surface and ground waters through runoff and leaching. Therefore, accumulation of As and metals in soils can affect the quality of water which can potentially affect terrestrial and aquatic communities and can directly and indirectly affect the quality and quantity of drinking water (Schipper *et al*. 2008; Luo *et al*. 2010). Over 200 different mineral arsenic forms can be present in natural soils (Larios *et al*. 2012). However, orpiment (As_2S_3), realgar (AsS) and arsenopyrite (FeAsS) are the most commonly encountered solid phases of As in the subsurface environment (Tabelin and Igarashi

2009; Takamatsu *et al*. 2010). One of the main processes controlling the distribution of arsenic in water is its reaction at water-mineral interfaces (Muller *et al*. 2010), likewise of arsenic amount in the geological source material, the environmental conditions control chemical and biological transformation of the material (Campbell 2007) and therefore arsenic mobilization mechanisms vary with location, depending on hydrogeological and redox conditions (Selim Reza *et al*. 2011).

Arsenic contamination of water resources in Iran was first recognized in the Kurdistan province in the West of Iran where a high concentration of arsenic >1mg/L in some villages have been reported (Mosaferi *et al*. 2003). Since that time a number of studies have been undertaken to investigate the occurrence of arsenic and possible health effects in this area. For example, in the study of Mosaferi *et al*. (2008) in 8 villages in Kurdistan province, 572 exposed subjects had been examined for skin lesions prevalence which 6.5% and 2.7% of them were suffering from hyperkeratosis and hyperpigmentation respectively.

Sahand dam with capacity of 135×106 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 and, in addition to supplying water for drinking and industrial purposes, provides water for irrigation of about 11000 hectares of agricultural land. 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 water in the reservoir. Due to the importance of this issue for water supplies in the region, present study was conducted in order to determine the extent and severity of the arsenic contamination problem, and 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 in order to assist with the management of the problem.

2. Materials and methods

2.1. The study area description and geology

The study area is located in the northwestern Iran in the south-eastern part of East Azerbaijan province and is 26km from Hashtrud County (UTM: X= 644000 to X= 677000 East longitude and Y= 4134000 to 4155000 North latitude). The area is a part of Hashtrud County that is 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 the provision of water for industrial and potable use. The Qarranqu River basin has an area of 820 km^2 and initiates from Sahand Mountain (height 3542m) and after 51 km reaches to dam site (height 1560m). Sahand dam has been constructed with soil and an impervious central core. The length, width and height of the dam are 405m, 10m and 35m, respectively. Six village and 320ha of agricultural land has been submerged by dam.

Based on the collected data from site visiting, field investigations and previous studies (Bandab 2004; Bandab 2007); regional hydrogeological setting is classified into: Upper red formation deposits (URFD) and pyroclastic deposits and volcanic lava pile of Sahand volcano.

Pyroclastic deposits and volcanic lava pile of Sahand volcano has covered a wide part of the region. 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 e.g. around the Goltappeh village (Nadiri 2011).

3. Results and discussion

3.1. Hydrogeochemistry

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 can be seen, there is a wide variability in the electrical conductivities of sampled water in the basin which is a measure of the dissolved salts content of water (min=256 μS/cm, max=3650 μS/cm). The pH values of samples ranged from 6.9 to 9.10 with an average of 8.21 demonstrating the characteristics of alkaline waters in the study area.

Table 1 Analytical results of water quality and hydrochemical parameters

Parameter or ion	Unit	Minimum	Maximum	Mean	Std. Deviation	Skewness	Kurtosis
Fe	ppb	0.0	208.78	54.07	43.84	0.9	1.64
Mn	ppb	2.7	211.37	39.34	36.48	2.46	9.01
As	ppb	0.0	1440.00	171.68	265.22	2.87	10.07
Zn	ppb	11.97	217.65	44.34	40.66	3.12	10.10
Cd	ppb	ND	ND	ND	ND	ND	ND
Pb	ppb	9.18	34.11	13.63	4.34	4.07	17.40
Cu	ppb	4.66	14.60	9.61	3.01	0.03	1.25
PO_5^{-3}	mg/L	0.03	0.22	0.08	0.03	1.16	3.64
NO^-_3	mg/L	0.25	6.10	1.71	1.32	1.08	1.04
NH_4^-	mg/L	0.06	2.20	0.36	0.42	3.01	9.96
SiO_2	mg/L	14.46	120.48	53.56	26.25	0.79	0.04
F^-	meq/L	0.0	0.10	0.03	0.02	0.76	0.07
K^+	meq/L	0.04	8.70	0.79	1.39	3.31	13.12
Na^+	meq/L	0.42	25.96	4.22	3.43	3.58	19.63
Mg^{2+}	meq/L	0.3	14.24	2.11	2.70	2.90	8.38
Ca^{2+}	meq/L	1.35	8.48	3.02	1.20	2.73	9.34
SO_4^{2-}	meq/L	0.12	13.48	1.54	1.56	5.66	40.66
Cl^-	meq/L	0.09	31.44	3.64	3.89	4.58	30.23
HCO_3	meq/L	0.95	12.80	3.10	1.70	3.40	15.24
CO_3^-	meq/L	0.0	1.00	0.23	0.21	0.53	0.33
EC	μS/cm	256.0	3650.00	844.45	491.77	2.93	13.16
pH	-	6.90	9.10	8.21	0.45	-0.82	0.44

It is apparent from Correlation matrix of water quality parameters there is a significant positive correlation between EC and specially Na^+, Cl^- then Ca^{2+}, SO_4^{2-}, Mg^{2+}, HCO^-_3, K^+ ions.

Considering water quality in Sahand dam, it seems that Qarranqu and especially Almalu Rivers with mean annual discharge of 149×106 m^3 have a significant association with water quality of the reservoir. The electrical conductivity values measured in Almalu River and reservoir inside ranged between "235–1,920 and 233–1,100" μS/cm, respectively which 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 and decreasing of river flow, the values of EC increase significantly. In some cases, river's flow decreases to zero.

3.2. Arsenic and trace elements

According to Table.1, concentrations of Fe and Mn were detected 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 sample. The concentration of other metals including Zn and Cu except arsenic was below the recommended limits.

The As content of the samples surpassed the drinking water guideline value of 10μg/L (WHO 2011) by a factor of about 11-13 fold during 2007-2011.

The mean As concentration in water samples was computed to be 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. Among these potential sources of arsenic pollution, only the 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 deterioration of water quality 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 of Almalu and reservoir inside and effluent are similar together and although no significant differences were observed between mean of concentrations ($p > 0.05$), sometimes the arsenic levels in river water are much higher than the reservoir and vice versa as shown in Fig. 1.

The maximum concentration of arsenic in Sahand reservoir is usually observed in autumn and early winter season (especially in December). Seasonal variations can be attributed to sediments inside the reservoir and occurrence of anaerobic conditions and thermal destratification of water and etcr.

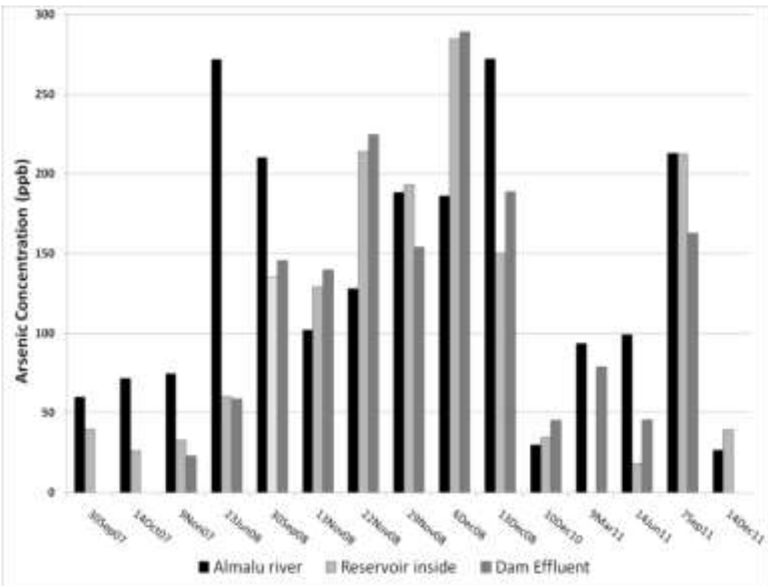

Figure1: Fluctuations of arsenic concentration in river, reservoir and dam effluent: 2007-2011

3.3. 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 fuels (Smedley and Kinniburg 2002; Reilly *et al*. 2010).

4. 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 of 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 concentration of arsenic. It was determined that centralization of arsenic follows direction and distribution of faults and tectonic of the region is control agent of distribution and centralization of arsenic bearing ores. At present, a water treatment facility (WTF) is operated in order to providing safe drinking water for Hashtrud 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. It is evident if this treatment chain will not be effective in removal of arsenic and other heavy metals, more effective and exclusive methods will need to be applied for providing safe drinking water.

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

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