

*Full Length Research Paper*

# Geochemical distribution of arsenic, antimony and mercury in surface waters and bed sediments from Aq-Darreh river, Takab, northwest Iran

Yousef Rahimsouri <sup>1\*</sup>, Abdolmajid Yaghubpur <sup>2</sup>, and Soroush Modabberi <sup>3</sup>

<sup>1</sup> Department of Geology, Faculty of Sciences, University of Urmia, Urmia 57153 -165, Iran.

<sup>2</sup> Department of Geology, Faculty of Sciences, University of Tarbiat Moalem, 49 Mofateh Street, Tehran 15614, Iran.

<sup>3</sup> School of Geology, University College of Sciences, Tehran University, Enqlab Street, Tehran, Iran.

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Aq-Darreh mining district is located in the Aq-Darreh river watershed, NW, Iran. The water and river-bed sediments of this area are very polluted due to the severe weathering and erosion of waste piles of Aq-Darreh Bala abandoned Sb mine and Aq-Darreh Au deposit. The concentration of As and Sb in water of Aq-Darreh river ranges from 3.2 to 159 µg/l and 1.32 to 54.00 µg/l respectively. Also the amount of As, Sb and Hg in the Aq-Darreh river-bed sediments ranges from 38.6 to 1087.4 mg/kg (As), 1.87 to 93 mg/kg (Sb) and 0.096 to 23.7 mg/kg (Hg). Detailed chemical analyses of water and bed sediments samples of Aq-Darreh river and its distributaries indicate that geochemical background of this area, and also mining activities are responsible for these high concentrations of toxic elements. According to the analytical results (As, Sb and Hg concentrations) and their comparison to world river average values it is concluded that Aq-Darreh river is amongst the heavily polluted water bodies of the world.

**Keywords:** Environmental geochemistry, water pollution, river-bed sediment contamination, Aq-Darreh mining district, Takab, NW Iran.

## INTRODUCTION

Aq-Darreh mining district (including Aq-Darreh gold deposit and Aq-Darreh Bala abandoned antimony mine) is located 38 km northwest of Takab, west Azerbaijan province, NW Iran (Figure. 1). Gold, As and Hg mineralization in these prospects were classified as Carlin-like type (Karimi, 1993) and some of them are currently mined without paying enough attention to environmental consideration. Aq-Darreh deposit is mined for gold and the waste rocks containing high concentration of potentially toxic elements, especially As, Sb and Hg are dumped as mine heaps.

Takab area has a semi-arid climate with moderate summers and very cold winters with an average annual temperature of about 9 °C. Annual precipitation is about 400 mm, falling mostly as snow (Modabberi, 2004; Modabberi and Moore, 2004a).

The main water source of the mine area is Aq-Darreh river flowing from northwest of the mine to the southeast (Figure. 1). More than 80 percent of the runoff of Aq-Darreh Au mine area reaches to Aq-Darreh river and the rest flows to Sarouq River by Qiz Qapan and Angurd streams that are flowing in the southeast of mine area (Figure. 2). The runoff of Aq-Darreh Au mine area joins the Sarouq River mostly via Aq-Darreh river that along with several other small stream waters from other prospects flows to the lake of Zarrineh Rud reservoir dam (Figure. 1). The annual discharge of Sarouq River to the Zarrineh Roud reservoir dam is estimated to be more than 225 million cubic meters (Modabberi and Moore, 2004a). The water in the Zarrineh Roud reservoir dam is used for agriculture and urban use of several cities in Kurdistan and East and West Azerbaijan provinces (Modabberi, 2004).

Mining activities in Aq-Darreh mining district has been taken place in two stages. The ancient mining activities (first stage) dates back to about 1000 years ago (Zavosh,

\*Corresponding authors: E-mail: rahimsouri@yahoo.com

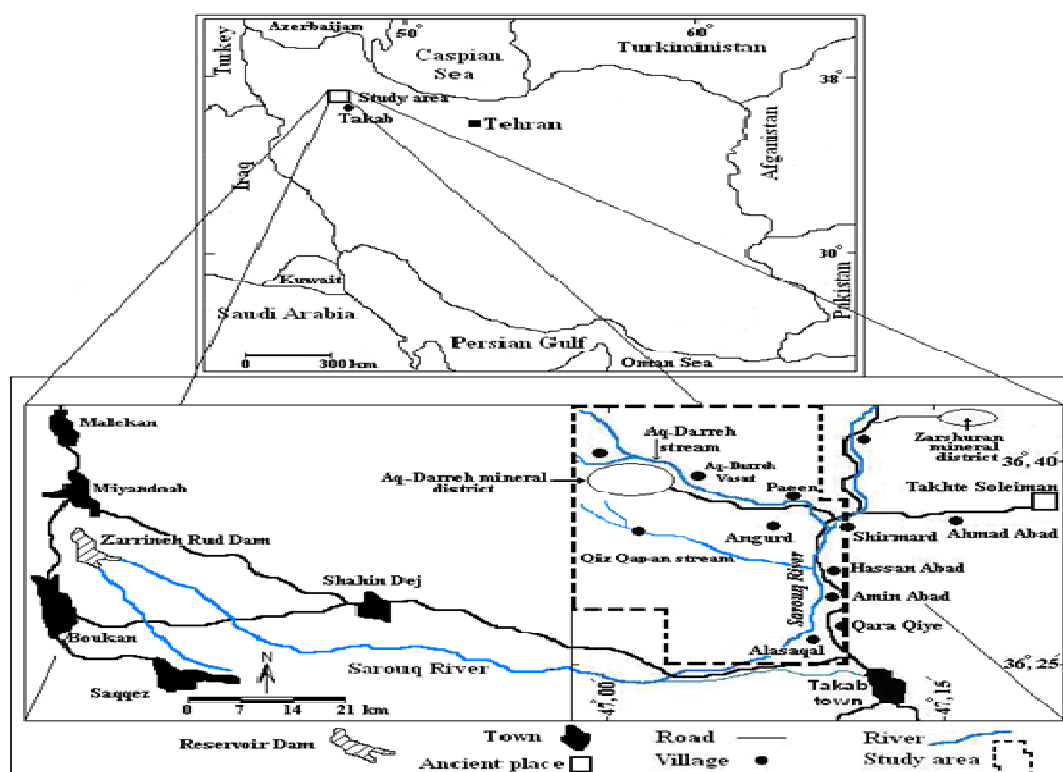


Figure: 1 Location map of the study area.

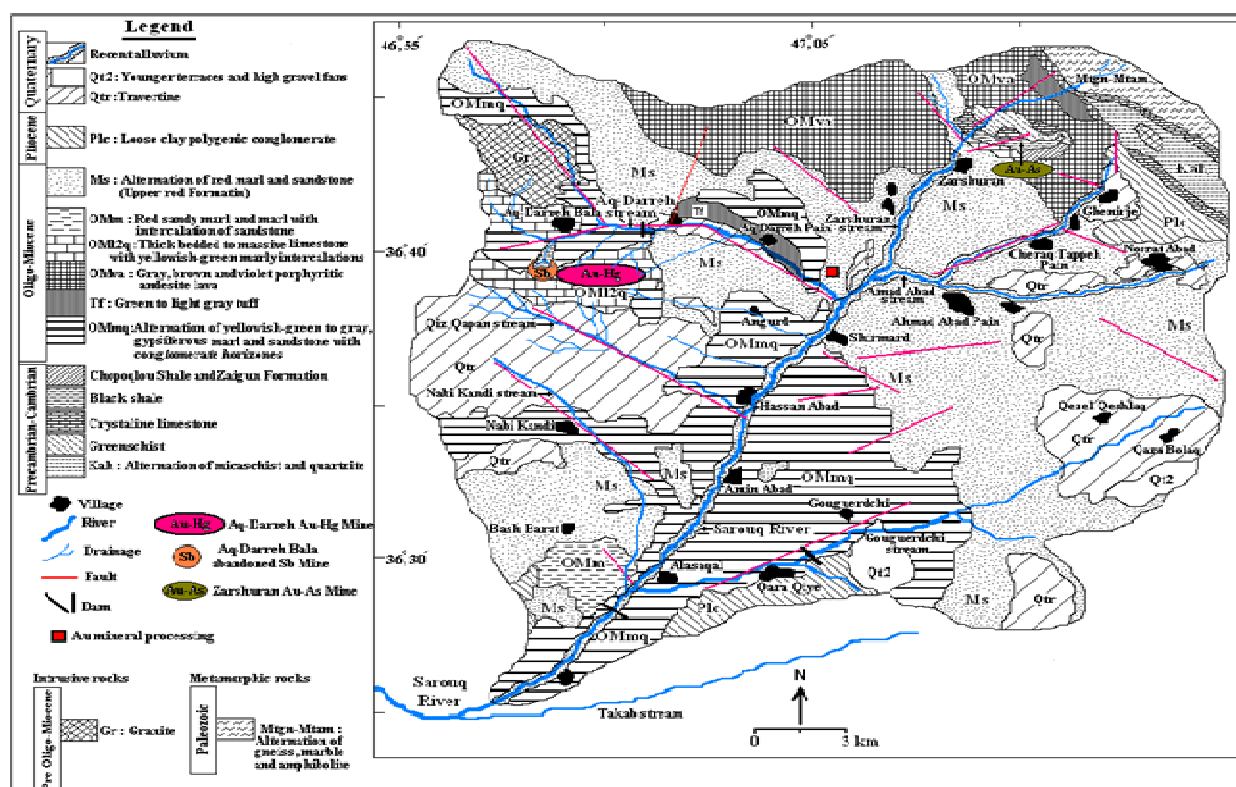


Figure: 2 Geological map of Aq-Darreh mining district and downstream environment.

1976), in an area of 6 km<sup>2</sup>. The new phase of activities (second stage) have been started in 1965 (Urdea et al., 1970). In 1990 the gold occurrence in Aq-Darreh area have been explored by the geologists of Iranian ministry of mines and metals (Kansaran, 1992). The total reserve of Au in the eastern and western parts of Aq-Darreh Au deposit is estimated to be about 11.5 and 2.16 million tons with an average concentration of 2.48 and 1.53 mg/kg respectively. The mineable reserves in the eastern and western parts are estimated to be about 9 and 2 million tons respectively (Baghosian and Shivaie, 2003). At present, more than 850000 ton of rocks containing some sulfide minerals and toxic elements including As and Hg with lesser amounts of Sb have been piled up as waste dump in the mine area, that should be carefully studied in terms of their potential environmental impacts (Yaghubpur and Rahimsouri, 2009).

## Geology

According to Stocklin (1968), the Aq-Darreh area is located in Sanandaj-Sirjan structural zone and based on Nabavi (1976), the area is a part of Khoy-Mahabad zone. It seems that Aq-Darreh area is located in the intersection between Alborz-Azerbaijan, Central Iran and Sanandaj-Sirjan structural zones (Babakhani and Ghalamghash, 1995).

Proterozoic, early Cambrian and Tertiary rock units crop out in the north of Takab. In the south of Aq-Darreh Bala Village (abandoned Sb mine valley) which is also the site of ancient mining activities, a black shale unit, 3 to 6 meters thick, crops out for about one kilometer long and it is apparently proterozoic in age. This shale is overlain by an Oligo-Miocene calcareous marl, marly tuff, and limestone containing some antimony-bearing siliceous veins. Different rock units in the Aq-Darreh river watershed have been studied (Figure. 2) and are briefly described here:

- *Tuff and hyaloclastic tuff breccia (Tf)*, thin to thick bedded with andesitic composition and porphyritic and vitrophyric textures.
- *Andesites (OMva)*, gray, brown or violet in color. The age of this rock unit ranges from 14.4±0.3 to 16.3±0.3 Ma according to Mehrabi et al. (1999). This rock unit extends from north to northeast of the Aq-Darreh river watershed.
- *Thick bedded to massive limestone (OMl2q)* forming high reliefs in the Aq-Darreh Au mine area. The age of this limestone has been postulated to be early-Middle Miocene based on their characteristic fossils (Babakhani and Ghalamghash, 1995). This unit extends throughout the Aq-Darreh Au mine area and it is the host rock of gold mineralization. Concentrations of gold in this unit ranges from 0.2 to 19.3 ppm and concentrations of potential toxic elements are As (0.17 to 19.5 %), Sb (0.022 to 1.7 %) and Hg (0.001 to 0.22 %) (Kansaran, 1992).

The ore minerals include arsenian pyrite or melnikovite, arsenopyrite, scorodite, jarosite, cinnabar, orpiment, realgar, stibnite, sphalerite, iron oxides (hematite, goethite and limonite), manganese oxides, barite and fluorite (Yaghubpur and Rahimsouri, 2009).

- *Gypsiferous marl with interlayers of sandstone and conglomerate (OMmq)* that according to Babakhani and Ghalamghash (1995) is also Early-Middle Miocene in age.
- *Red marl and sandstone (Ms)* with gypsum interlayers covering discordantly the andesite (OMva) and gypsiferous marl (OMmq) in the north and east of the study area. This rock unit is overlain by horizontal layers of *Quaternary travertine (Qtr)*.
- The rest of area is covered by recent sediments including gravel fans, surface soil and agricultural lands (*Qt2*) and recent alluvium (*Qal*).

In the northwest of Aq-Darreh Bala village a granitic intrusive body crops out (Aq-Darreh granite, *Gr*) which is an equigranular body composed of quartz, perthitic feldspars and few muscovite. Based on field observation and its relation to the surrounding rock units, it appears that the age of this granite is post-Cambrian and pre-Oligocene and it is probably Jurassic in age.

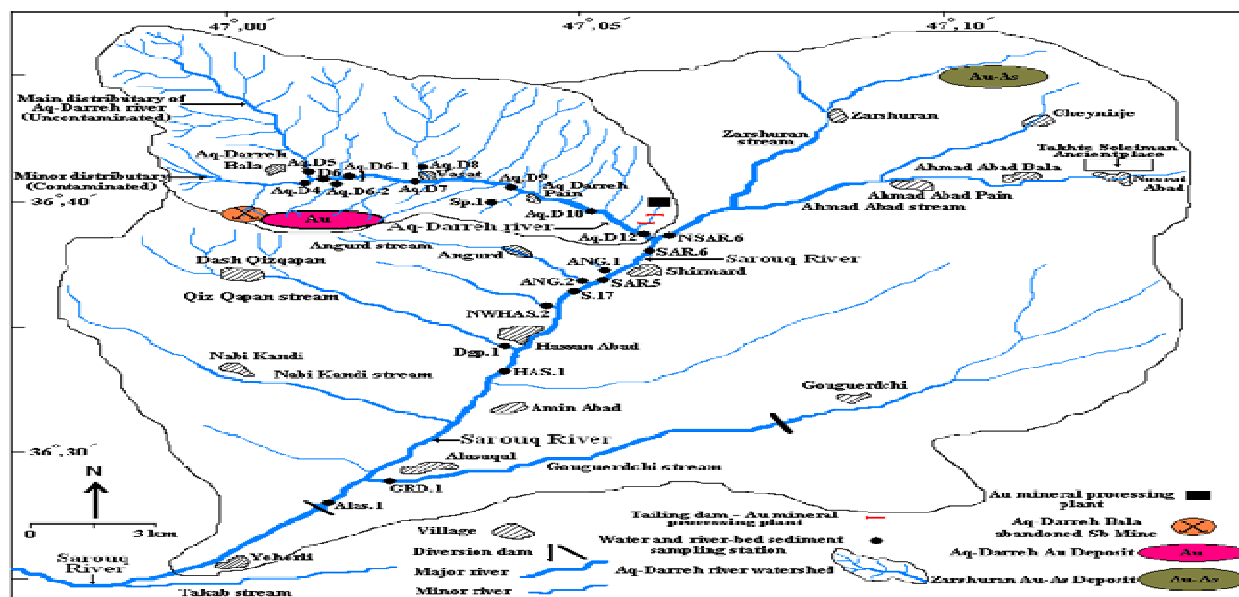
From the structural point of view, the area is composed of a syncline in the north and an anticline in the south of Aq-Darreh Au mine area with their axes trending northwest-southeast (Ghanati, 1995). Three fault systems trending NW-SE, NE-SW and N-S have been noted in the Aq-Darreh mining district. The main fault is trending northwest-southeast and it controls the course of the Aq-Darreh river (Figure. 2).

## MATERIALS AND METHODS

The geological map of the study area (Figure. 2) were prepared using satellite images (Google Earth, 2009-Cns/Spot Image, Imaginary date Apr. 6, 2004), 1:100000 geological map (modified after Babakhani and Ghalamghash, 1995) and detailed field work (rock sampling, structural geology and petrographical studies). One hundred twenty six thin and 148 polished sections from host, waste, and other rock units were studied to obtain mineralogical and petrological characteristics and 22 stations were selected for river-bed sediment and water sampling according to geological informations and location of the tributaries of Aq-Darreh and Sarouq rivers (Figure. 3).

Water samples were collected in June 2007. In all stations, field parameters including pH, Eh, TDS (total dissolved solids), EC (electrical conductivity), salinity and temperature of water were measured by Sension 156 multiparameter measuring instrument.

Two water samples were carefully taken with 250 CC open-mouth polyethylene bottles in each station.



**Figure: 3** Location of sampling stations in the study area.

**Table: 1** The accuracy and precision estimating results (in %) of As and Sb in water samples.

	As	Sb
Accuracy	3.1	0.7
Precision	0.9	0.2

**Table: 2** The accuracy and precision estimating results (in %) of As, Hg and Sb in river-bed sediment samples.

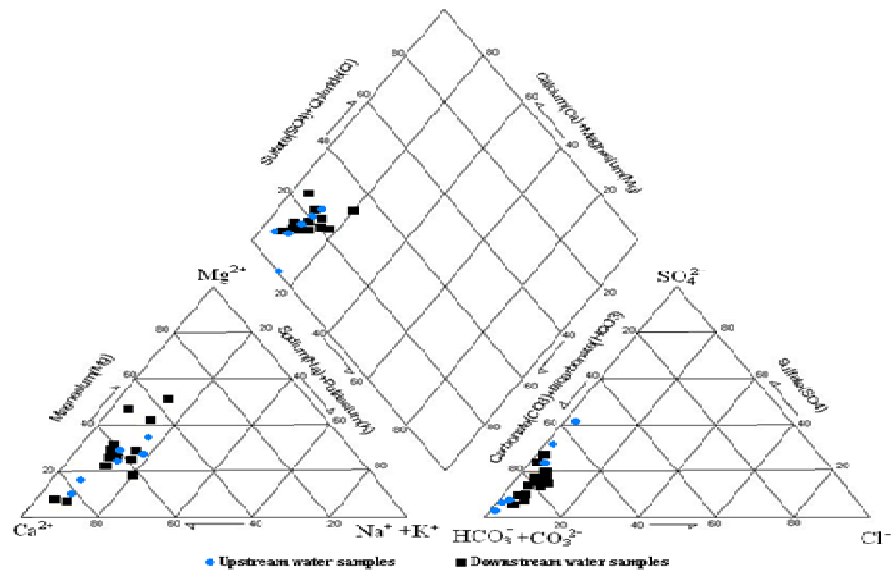
	As	Hg	Sb
Accuracy	6.4	13.2	6.1
Precision	4.9	11.7	3.2

River-bed sediment samples from each station were scooped and kept in 0.5 kg polyethylene capped containers. The water samples were kept below 4 °C and were analyzed for major cations and anions not later than 5 days after sampling. The first water sample divided into two subsamples, one of them acidified with nitric acid (Ultrapure, Merck) for major cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ) analysis and another, unacidified subsamples, were taken for major anions ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^{2-}$ ,  $\text{Cl}^{-}$ ,  $\text{SO}_4^{2-}$ ) analysis by ion chromatography. The chemical analyses were performed in the geochemical laboratory of Geological Survey of Iran.

Another water sample were taken for trace element analysis (total analysis). The bottles were filled and sealed in the field after adding 2.5 CC nitric acid as preservation agent. These samples were analyzed using ICP-MS in ACME laboratories in Vancouver, Canada.

Accuracy (A) of the analytical method for elements was estimated by calculating the absolute systematic error between the determined ( $X_a$ ) and recommended values ( $X_b$ ) of standard materials using equation:  $\%A = (|X_a - X_b| / X_b) \times 100$ . Standard solutions Wastewater D1 and D3 were used for estimating accuracy. All samples, replicates and standards were submitted to the laboratory in random order. Arsenic and Sb determined in standards differ on average by less than 1 % from their recommended values in the same concentration range (Table 1).

Precision was estimated by using duplicate analyses of selected samples according to the method introduced by Thompson and Howarth (1976). Arsenic and Sb determined in standards differ on average by less than 3 and 1 % respectively from their recommended values in the same concentration range (Table 1). Twenty-two river-bed sediment samples were taken in the stations corresponding to water samples. The sediments were then kept in the laboratory to be dried (room temperature) and then sieved with 180 micrometers sieve. Sediment samples (50 g) were sent to the ACME laboratories. 0.5 g of each samples were prepared and were analysed by ICP-ES/MS for 53 elements. Hg was determined with cold vapor atomic absorption spectrometry after aqua regia digestion at 95 °C. Standard materials G-1, DS 7 and SO-18 were used for estimating accuracy. Most elements determined in standards differ on average by less than 5 % from their recommended values in the same concentration range. Also estimating precision for As, Sb and Hg were calculated at less than 5, 4 and 12 % respectively (Table 2).



**Figure: 4** Piper diagram constructed by plotting the chemical composition of different water samples of the study area.

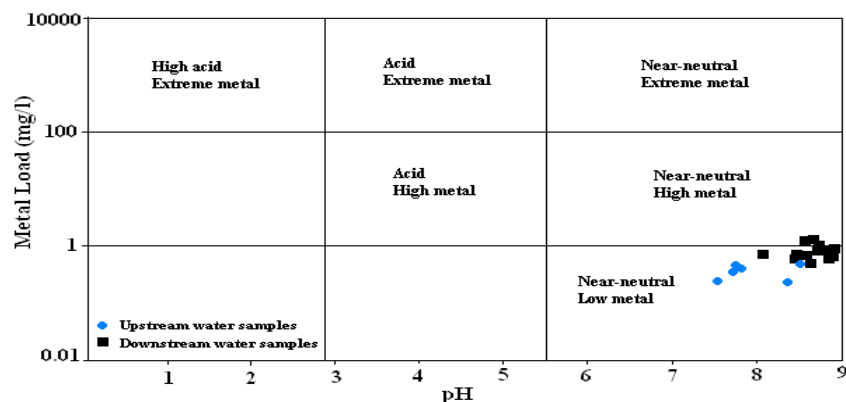
**Table 3** Physical parameters and chemical constituents (in mg/l for cations, anions and TDS) of water samples in the study area.

Station	pH	Eh (mV)	TDS	EC ( $\mu\text{S}/\text{cm}$ )	Salinity (0/00)	T ( $^{\circ}\text{C}$ )	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^{+}$	$\text{Na}^{+}$	$\text{CO}_3^{2-}$	$\text{HCO}_3^{-}$	$\text{SO}_4^{2-}$	$\text{Cl}^{-}$
Aq.D5	7.43	-21.3	184	330	0.2	21.3	73	4	1	4	176	12	23	4
Aq.D4	8.09	-26.6	554	1059	0.6	16.8	121	29	9	16	356	38	74	30
Aq.D6	7.76	-17.9	224	411	0.3	15.7	76	5	2	6	200	14	29	11
Aq.D6-1	7.86	-37.2	234	416	0.3	15.9	78	7	2	6	214	14	30	10
Aq.D7	8.46	-62.8	328	569	0.4	16.9	81	25	3	12	233	18	50	18
Aq.D8	7.62	-28.1	320	564	0.4	15.2	56	33	1	6	204	24	129	7
Aq.D9	8.37	-59.6	357	626	0.4	17.5	88	24	4	13	266	20	63	20
Sp.1	8.26	-57.5	184	318	0.1	16.6	64	10	1	4	169	14	22	4
Aq.D10	8.67	-72.4	332	596	0.2	17.8	82	24	4	14	246	17	73	20
Aq.D12	8.43	-71.1	298	548	0.3	19.5	85	22	4	15	209	21	67	20
NSAR.6	8.63	-67.7	399	621	0.4	21.2	86	26	7	27	286	24	111	32
SAR.6	8.65	-68.7	364	589	0.4	22.6	84	25	6	13	241	24	80	28
ANG.1	8.76	-86.9	249	450	0.2	23.8	42	36	2	17	288	21	12	6
ANG.2	8.62	-67.4	316	534	0.3	24.2	96	18	6	15	225	23	99	23
SAR.5	8.76	-72.1	361	612	0.3	23.8	88	23	6	23	242	24	84	27
S.17	8.72	-70.3	365	616	0.3	24.1	82	25	6	22	250	15	80	27
NWHAS.2	8.45	-57.3	469	857	0.5	23.9	112	20	2	39	251	17	200	6
Dgp.1	8.47	-59.4	467	789	0.5	19.7	116	31	3	23	313	15	165	12
HAS.1	8.80	-76.6	364	657	0.4	23.5	76	32	6	24	264	17	84	27
GRD.1	8.75	-83.8	302	593	0.3	23.0	60	34	5	18	245	9	91	14
Alas.1	8.78	-76.4	323	649	0.3	23.2	68	26	5	21	243	11	76	21

## ANALYTICAL RESULTS

The cations and anions of water samples are shown in Table 3, and plotted on a Piper diagram (Figure. 4). Piper

diagrams shows grouping of samples in one distinct field in the calcium-carbonate water facies, suggesting that downstream water of Aq-Darreh mining district were chemically similar to upstream ones.



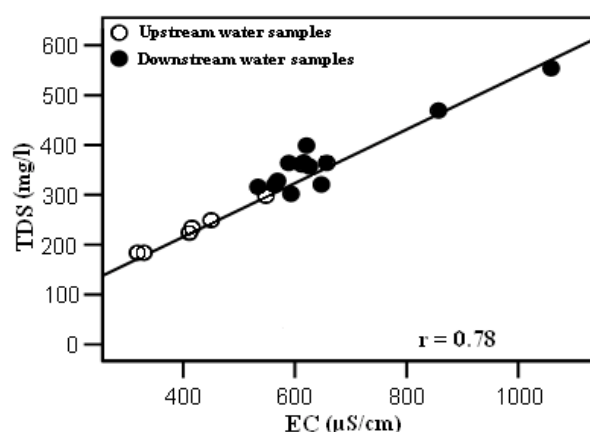
**Figure. 5** The relationships between pH and metal load (As+Cd+Co+Cr+Cu+Pb+ Se+Sb+ Sr +U+V+Zn) in mg/l (Ficklin et al., 1992 modified by Cabo et al., 1999; adopted from Milu et al., 2002).

**Table: 4** The total concentration of some trace and major elements (in mg/l for S and in  $\mu\text{g/l}$  for the others) in water samples in spring season (Jun. 2007), Hg values were less than 0.2  $\mu\text{g/l}$  (detection limit) in all water samples.

Element	As	Ba	Fe	Mn	Pb	S	Sb	Zn
Detection limit	0.5 $\mu\text{g/l}$	0.05 $\mu\text{g/l}$	10 $\mu\text{g/l}$	0.05 $\mu\text{g/l}$	0.1 $\mu\text{g/l}$	1 mg/l	0.05 $\mu\text{g/l}$	0.5 $\mu\text{g/l}$
Aq.D5	3.2	85.91	130	61.30	4.1	11	1.32	12.4
Aq.D4	159.9	224.91	2670	1046.75	4.1	37	54.00	47
Aq.D6	41.8	128.27	832	599.24	1.7	25	15.03	25.4
Aq.D6-1	46.3	119.13	522	362.80	3.8	18	6.26	10.2
Aq.D7	92.6	100.84	211	285.06	4.3	23	4.81	14.1
Aq.D8	3.9	74.61	699	77.24	1.5	53	6.48	16.4
Aq.D9	106.1	101.53	245	306.08	6.5	28	4.70	10.1
Sp.1	3.0	121.73	50	17.91	1.5	12	0.78	13.3
Aq.D10	89.5	118.59	451	226.27	3.8	26	4.38	8.5
Aq.D12	68.6	97.18	156	77.68	2.2	29	4.48	8.8
NSAR.6	54.2	94.16	161	114.80	2.7	44	1.82	4.3
SAR.6	58.7	90.87	83	99.10	4.0	35	2.63	5.9
ANG.1	3.6	218.29	<10	7.31	2.8	6	1.89	2.2
ANG.2	19.4	105.04	478	149.20	4.6	59	2.67	3.5
SAR.5	59.1	96.61	105	116.66	1.4	39	2.79	2.7
S.17	55.3	97.24	149	130.29	1.6	37	2.87	3.8
NWHAS.2	3.4	76.27	277	93.13	1.3	92	1.67	3.1
Dgp.1	34.0	115.70	213	150.13	2.7	69	1.84	2.5
HAS.1	52.1	100.76	73	91.46	1.8	39	2.80	3.5
GRD.1	15.1	260.62	5399	973.15	15.1	26	0.87	27.9
Alas.1	30.4	103.78	256	127.10	1.8	36	2.75	33.6

In order to determine the relationships between trace elements content and pH values, the Ficklin et al. (1992) diagram were used. Based on this diagram (Figure.5) almost all water samples were located in "Near-neutral, Low metal" field. The relationship between EC and TDS with a correlation coefficient of 0.78 is shown in Figure. 6.

The results of chemical analyses of water and river-bed sediment samples in Aq-Darreh and Sarouq rivers (Tables 4 and 6) indicate that among the trace elements, water and river-bed sediments samples of downstream Aq-Darreh mining district are enriched in As and Sb and As, Sb and Hg respectively, in compared with these



**Figure: 6** The relationships between EC and TDS in water samples.

**Table: 5** Pearson's correlation matrix between some trace elements in water samples of Aq-Darreh and Sarouq rivers. (a) Aq-Darreh stream

	As	Ba	Fe	Mn	Sb
As	1				
Ba	0.707**	1			
Fe	0.660*	0.994**	1		
Mn	0.641*	0.944**	0.946**	1	
Sb	0.685**	0.981**	0.992**	0.936**	1
b) Sarouq River					
	As	Ba	Fe	Mn	Sb
As	1				
Ba	- 0.818**	1			
Fe	- 0.870**	0.612*	1		
Mn	- 0.620*	0.706**	0.784**	1	
Sb	0.278	- 0.371	- 0.358	- 0.419	1

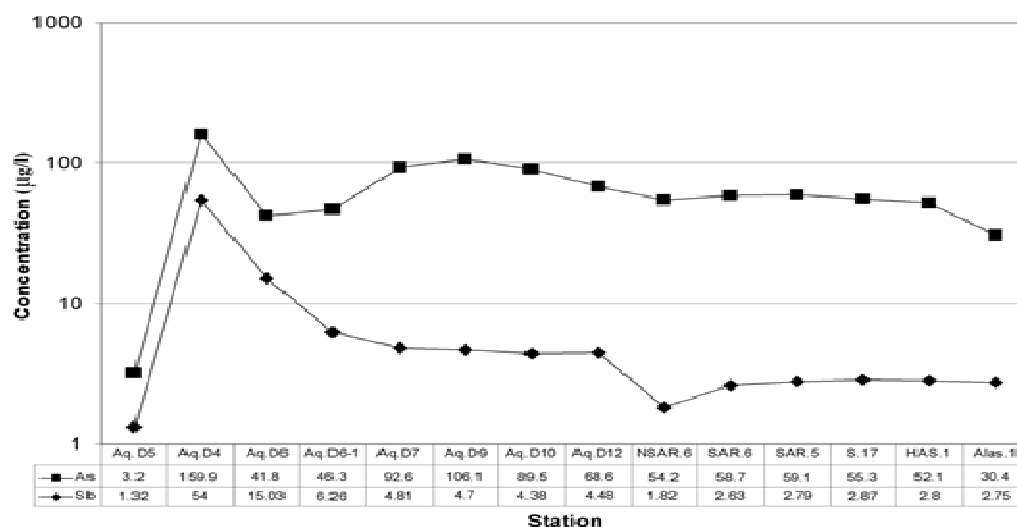
\* Correlations is significant at the 0.05 level

\*\* Correlations is significant at the 0.01 level

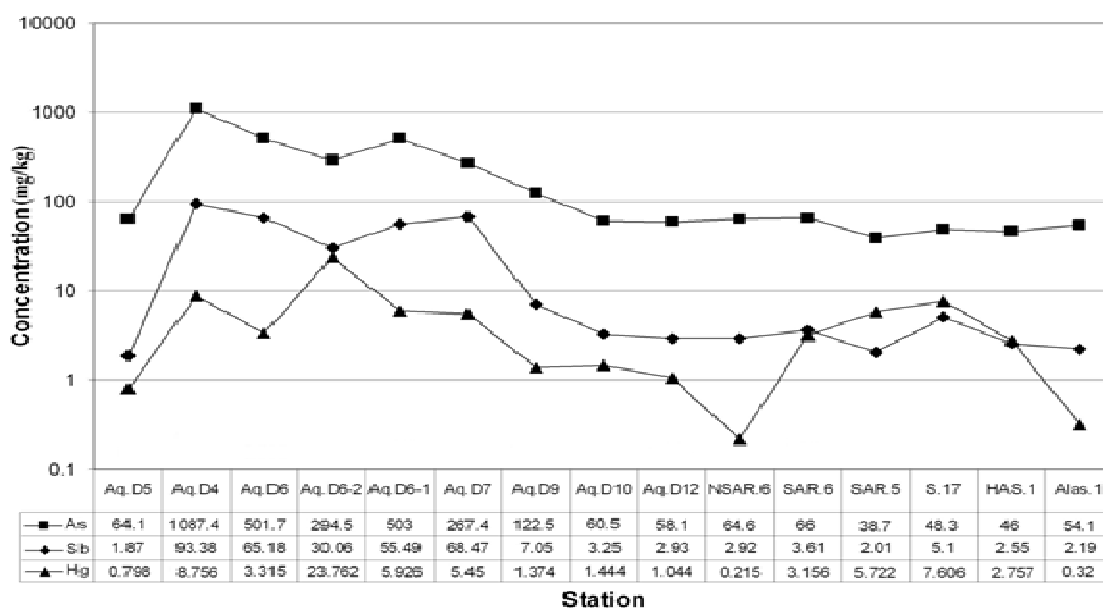
elements values in the world rivers (Smedley and Kinniburgh, 2002; Filella et al., 2002; ANZECC, 2000; Siegel, 2002). Concentrations of these elements in Aq-Darreh river watershed indicate significant differences in mineralized and extracted areas with the areas beyond the mineralization and mining district. The highest concentration of trace elements in water and river-bed sediment samples belongs to Aq.D4 station which is affected by Aq-Darreh Bala abandoned Sb mine. Variation of As and Sb concentration in water samples have been illustrated in Figure. 7, and variation of As, Sb and Hg concentration in river-bed sediment samples have been shown in Figure. 8. The correlation matrix between some trace elements in water and river-bed sediment samples of Aq-Darreh and Sarouq rivers were shown in Tables 5 and 7 respectively.

## DISCUSSION

The Aq-Darreh river is consist of two distibutaries in the headwater, the main distributary with high and minor distributary with low water discharge. The chemical composition of water and river-bed sediments of main and minor distibutaries of Aq-Darreh river have been studied in stations Aq.D5 and Aq.D4 respectively (Figure. 3). The analytical results of water and river-bed sediment samples (Tables 4 and 6) do not show any indication of contamination in the main distributary, while, this results show high concentration of As and Sb in water and As, Sb and Hg in river-bed sediment samples of the minor distributary, reflecting the lithological characteristics of the latter comprising black shales and mineralized limestones which also indicates the abandoned Sb mine



**Figure:7** Variation of As and Sb concentration in water samples from headwater of Aq-Darreh river to Alasaqal station (Alas.1).



**Figure: 8** Variation of As and Sb and Hg concentration in river-bed sediment samples from headwater of Aq-Darreh river to Alasaqal station (Alas.1).

of Aq-Darreh Bala and Aq-Darreh gold deposit (Figure. 3).

In the station Aq.D6, locating downstream of the stations Aq.D4 and Aq.D5, concentrations of trace elements in water and river-bed sediment are decreased, obviously because of the high discharge of the main distributary compared to the minor polluted distributary (station Aq.D4). Concentration of As in water samples increases downstream (from station Aq.D6 to station

Aq.D9) because of the inflow of polluted distributaries by draining waste piles from the northern parts of Aq-Darreh gold deposit. Conversely, the concentration of Sb is decreased gradually from Aq.D6 to Aq.D10 station and inflows of the above-mentioned distributaries have not significant impacts on the Aq-Darreh river. It can be related to low concentration of Sb (compared to As) in Aq-Darreh gold deposit and also to lower mobility of antimony (Hale, 1981). The slight increase in Sb



**Table: 7** Pearson's correlation matrix between some trace elements in bed sediment samples of Aq-Darreh and Sarouq rivers. **(a) Aq-Darreh river**

	As	Ba	Fe	Hg	Mn	Pb	Sb	Zn
As	1							
Ba	0.695*	1						
Fe	- 0.366	0.015	1					
Hg	0.365	0.807**	0.012	1				
Mn	- 0.396	0.096	0.522*	0.142	1			
Pb	0.090	0.402	0.564*	0.141	0.743*	1		
Sb	0.885**	0.813**	- 0.059	0.282	- 0.067	0.479	1	
Zn	0.820**	0.824**	- 0.040	0.435	- 0.078	0.497	0.936**	1

**b) Sarouq River**

	As	Ba	Fe	Hg	Mn	Pb	Sb	Zn
As	1							
Ba	0.462	1						
Fe	- 0.025	0.677*	1					
Hg	- 0.457	0.487	0.650*	1				
Mn	0.793*	- 0.052	- 0.199	- 0.856**	1			
Pb	0.035	0.733**	0.520*	0.509*	- 0.331	1		
Sb	0.219	0.889**	0.490	0.561*	- 0.292	0.921**	1	
Zn	0.845**	0.055	- 0.119	- 0.820**	0.990**	- 0.308	- 0.226	1

\* Correlations is significant at the 0.05 level

\*\* Correlations is significant at the 0.01 level

concentration in Aq.D12 station can be related to the inflow of polluted water derived from a spring flowing downstream of the tailing dams (Yaghubpur and Rahimsouri, 2009). Confluence of Aq-Darreh river with Sarouq River increases the concentration of As and Sb in the station downstream the confluence (SAR.6 station) because of higher concentrations As and Sb of Aq-Darreh river (in Aq.D12 station) relative to Sarouq River (in NSAR.6 station) .

Variation in concentrations of As and Sb in river-bed sediment samples resembles the water sample trend. Some stations do not follow the uniform decreasing trend because of the local variations related to high-Sb soil around these stations (Yaghubpur and Rahimsouri, 2009).

In river-bed sediment, arsenic shows the highest correlation with Sb, Ba and Zn in Aq-Darreh river. While in the Sarouq River As has the highest correlation with Zn and Mn. Antimony has also the highest correlation with As and Ba in Aq-Darreh river. In contrast in Sarouq River Sb has the highest correlation with Pb, Ba and Hg (Table 7). Mercury has also the highest correlation with Ba in Aq-Darreh river, while in Sarouq River Hg show moderate correlation with Fe, Pb and Sb (Table 7). River-bed sediments indicate high amounts of mercury and heavy mineral studies in station Aq.D6-2 reveal the mineral cinnabar in the river-bed sediment samples (Yaghubpur and Rahimsouri, 2009). Cinnabar has a slight solubility in neutral to alkaline waters (Gray et al., 2002), so, Hg concentration is very low in water samples of Aq-Darreh river. Instead, river-bed sediment samples indicate higher concentrations of Hg.

Orange-red colored river-bed sediments covering the Aq-Darreh river in middle and downstream intervals is an indication of Fe oxyhydroxide precipitation which was supported by XRD and sequential leach analyses of the representative samples (Yaghubpur and Rahimsouri, 2009). According to Biddau and Cidu (2005) transportation of trace elements is limited in the aqueous phase by precipitation of Fe oxyhydroxides as ferrihydrite, since this mineral is capable of excavenging As and associated elements from water, resulting a reduction in their concentration in water samples. They can also desorb the elements adsorbed as a result of a change in chemical characteristics of water (Bibi et al., 2006 ; Navarro et al., 2008). The process of desorption is much slower than the adsorption (Biddau et al., 2005). In case of desorption, the river-bed sediments can themselves act as a potential source of contamination (Lee et al. 2003) and they increase the bioavailability of trace elements (Siegel, 2002; Smith and Huyck, 1999; Kelley, 1999; Anawar et al., 2006; Ashley et al., 2004; Lottermoser, 2003; Lu and Zhang, 2005).

It seems that As adsorption on Fe oxyhydroxides phases in headwater of Aq-Darreh river-bed sediments and the water pH of the Aq-Darreh river (a neutral to slightly alkaline character) precludes the mobility and/or availability of trace elements to downstream environment.

Comparison of the values of station Aq.D12 with mean As and Sb values in the world surface waters (0.83 µg/l and 1.1 µg/l respectively, Smedley and Kinniburgh, 2002 and Filella et al., 2002) indicate that As and Sb values in

**Table 9**  $I_{geo}$  classes with respect to sediment qualities (Müller, 1979).

$I_{geo}$	$I_{geo}$ class	Sediment quality
0-0	0	Unpolluted
0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately to highly polluted
3-4	4	Highly polluted
4-5	5	Highly to very highly polluted
5-6	>5	Very highly polluted

**Table: 10**  $I_{geo}$  classes for As, Sb and Hg at stations Aq.D4 to Aq.D12.

Station	$I_{geo}$ classes (As)	$I_{geo}$ classes (Sb)	$I_{geo}$ classes (Hg)
Aq.D4	>5	>5	5
Aq.D5	2	0	1
Aq.D6	5	5	4
Aq.D6-1	5	5	4
Aq.D6-2	4	4	>5
Aq.D7	4	5	4
Aq.D9	3	2	2
Aq.D10	2	1	2
Aq.D12	2	1	2

this area are 80 and 8 times more concentrated than the mean values of other areas and in this regard, the Aq-Darreh river is regarded as one of the most contaminated rivers in the world.

Aq-Darreh river-bed sediments are also highly polluted regarding As, Sb and Hg compared with the CCME (1999) and ANZECC (2000) standards. The geo-accumulation index (Müller, 1979) was applied to quantify metal accumulation in polluted river-bed sediments. It has been widely applied for evaluating the extent of metal pollution in different environments (Manjunatha et al., 2001; Upadhyay et al., 2006; Jeelani and Shah, 2006; Krishna and Govil, 2008).

The geo-accumulation index ( $I_{geo}$ ) is expressed as:  $I_{geo} = \log_2 (C_n / 1.5B_n)$ , where  $C_n$  = concentration of the element in the sediment fraction ( $< 2 \mu m$ ),  $B_n$  = geochemical background value in argillaceous sediment (average shale, Turekian and Wedepohl, 1961) of the element. The constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences. In Table 9, the different geo-accumulation index classes, along with the associated sediment qualities as proposed by Müller (1979) are given.

In Table 10,  $I_{geo}$  classes calculated for the heavy metals As, Sb and Hg deposited on the river-bed sediments of Aq-Darreh river for the stations Aq.D4 to Aq.D12

Calculation of geo-accumulation index for bed sediment samples of Aq-Darreh river indicates that bed sediments are highly to very highly polluted with As and Sb for a distance of about 8 km downstream of the Aq-Darreh Bala abandoned antimony mine and for a distance of 5.7 km downstream the Aq-Darreh gold mine (from station Aq.D4 to Aq.D7 station). Contamination of river-bed sediments to Hg is also traceable up to 5.4 km and 3.1 km downstream the Aq-Darreh Bala abandoned mine and the Aq-Darreh gold mine, respectively.

According to methods described by Kelley and Taylor (1997) and Galuszka (2007) for determining the geochemical background (mean or median values of undisturbed and outside of the mining area were selected as background samples), the As and Sb concentrations in water samples and As, Sb and Hg in river-bed sediment samples in stations Aq.D5 and Aq.D8 (undisturbed or unmined areas) have been considered for geochemical background of this elements in the study area (Table 11).

**Table: 11** Estimated values of geochemical background in Aq-Darreh river water and bed sediment.

Geochemical background				
Surface water (concentration)		River-bed sediment (concentration)		
As (ppb)	Sb (ppb)	As (ppm)	Sb (ppm)	Hg (ppm)
3.55	3.9	51.35	2.34	0.447

## CONCLUSION

Chemical analyses of water and river-bed sediment samples indicate that Aq-Darreh river system is highly contaminated regarding As and Sb concentration in water and As, Sb and Hg values in river-bed sediment samples. It has been suggested by many researchers (Earman and Hershey, 2004; Modabberi and Moore, 2004 b) that mining heaps derived from Carlin type deposits have a significant role in water and river-bed sediment contaminations in the downstream of the deposits. Considering the open pit method of mining in Aq-Darreh gold mine which has been started since 6 years ago, type of mineralization (Carlin) and also presence of sulfide-rich mining heaps containing higher amount of potentially toxic elements, a higher degree of water and river-bed sediment contamination is expected in near future. The presence of limestone units in the study area is buffering the pH values in stream water, maintaining the values near neutral and preventing the formation of acid mine drainage (AMD) in the mining area and in the downstream environment and it is suggested (Borba et al., 2003) that small amount of pollutants are transported to downstream in near-neutral pHs.

Significant difference of Hg concentration in water and river-bed sediment samples indicate that mercury is transported mainly as bed-load in Aq-Darreh river and this could be related to higher partitioning of Hg in sediment phase than aqueous phase (Modabberi, 2004).

According to the mineralogical studies (Yaghubpur and Rahimsouri, 2009; Rahimsouri et al., 2010) it is suggested that major source rocks for potentially toxic elements are black shales along the Aq-Darreh abandoned Sb mine and mineralized limestones around the Aq-Darreh gold mine has minor effect in environmental contamination of the area.

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