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Full Length Research Paper

Environmental geochemistry of Aq-Darreh Bala abandoned Sb mine and its impacts on water, sediment, and soil pollution in the Aq-Darreh River Watershed, Takab, NW Iran

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The abandoned antimony mine of Aq-Darreh Bala is located 42 km northwest of Takab city in northwest Iran. The host rocks of the stibnite-bearing silica veins are calcareous marl and a black shale unit rich in toxic elements such as As, Sb and Hg. Toxic elements are released through weathering and oxidation of this black shale unit into the surface water, and also in sediments, surface and agricultural soils causing contamination in plant, fruits and crops. The contaminated waters of Aq-Darreh Bala abandoned Sb mine area mix with unpolluted main tributary of Aq-Darreh river and the As and Sb concentrations in the downstream of confluence point rise to 9 (29.2 µg/l) and 4 (5.96 µg/l) times repectively and the As, Sb and Hg concentrations in river bed sediments rise to 0.1 (73.4 mg/kg), 4.3 (16.65 mg/kg) and 1.8 (1477 µg/kg) times respectively relative to unpolluted parts of the river. Toward the downstream, the runoff from the Aq-Darreh Au-Hg mining area flows in to the middle parts of Aq-Darreh river and incomparison to the upstream, the concentrations of As and Sb in water samples increase 13 (385.0 µg/l) times and decrease 0.15 (5.10 µg/l) time respectively. The concentrations of As, Hg and Sb in bed sediments of Aq-Darreh river(in middle parts) increase 6 (445.1 mg/kg) and 4 (6174 µg/kg) times for As and Hg respectively and decrease 3.3 (4.95 mg/kg) times for Sb. In this paper, it is attempted to illustrate that Sb contamination of Aq-Darreh river is affected by Aq-Darreh Bala abandoned Sb mine, while As and Hg contamination are due to the effects of Aq-Darreh Au-Hg active mine and its waste piles.

Keywords: Environmental geochemistry, abandoned Sb mine, water and soil pollution, Aq-Darreh mining district, Takab, Iran

INTRODUCTION

The abandoned antimony mine of Aq-Darreh Bala is located 42 km northwest of Takab in west Azerbaijan province, NW Iran. Takab area has a semi-arid climate with moderate summers and very cold winters with an average annual temperature of about 9ºC. Annual precipitation is about 400 mm, falling mostly as snow (Modabberi and Moore, 2004; Modabberi, 2004).

Aq-Darreh Au-Hg deposit that it considered to be a Carlin-Type Deposit (Daliran, 2008) is located 3 km east

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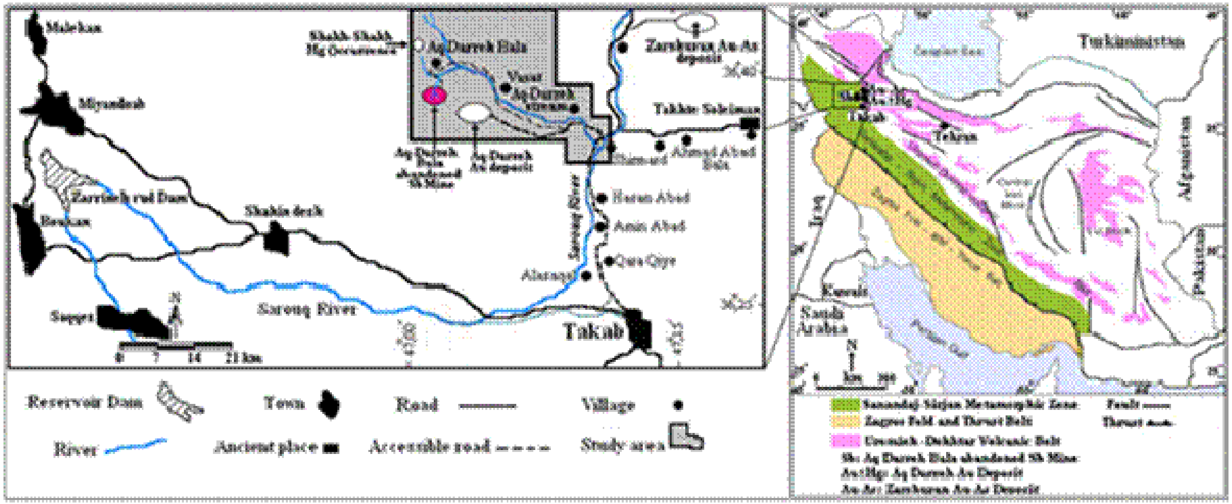

Figure 1. Location map of the study area in a simplified geological map of Iran (Modified after Stocklin, 1968)

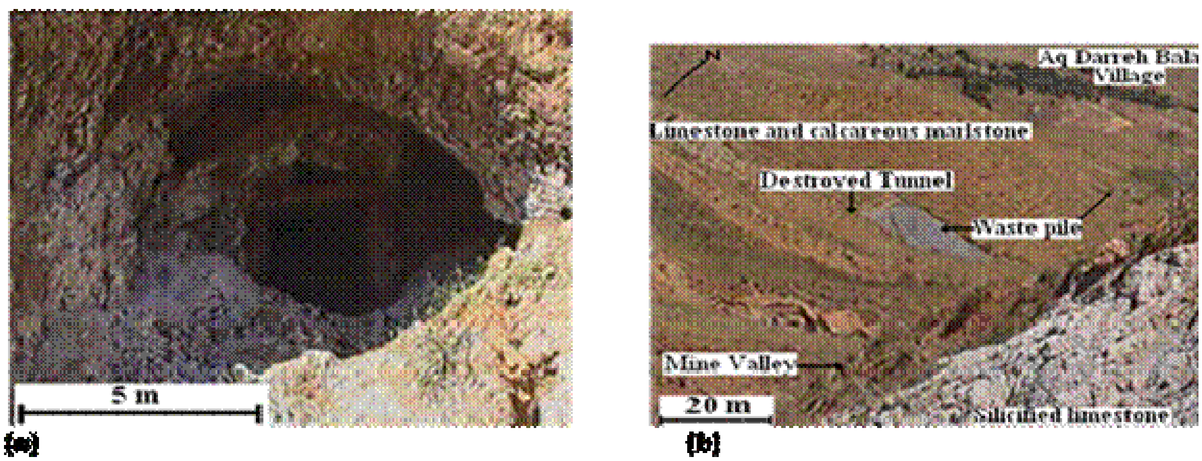

Figure 2. The Aq-Darreh Bala abandoned Sb mine; a) Entrance of main tunnel, b) location of main tunnel, its waste piles, and calcareous host rocks.

of this mine, and Shakh-Shakh Hg occurrence is also located 2 km northwest of Aq-Darreh Bala abandoned Sb mine (Figure 1).

Several ancient mine workings have been discovered in the south of Aq-Darreh Bala and Aq-Darreh Vasat Villages related to the abandoned mine (Kansaran, 1992). All of the tunnels and mine workings have been destroyed and the host and waste rocks including black shales and calcareous marl have been exposed to severe weathering and oxidation conditions (Figure 2).

Surficial oxidation of sulfide minerals of mine waste piles is a major cause of acid drainage and can increase concentrations of toxic elements downgradient from them (Munroe et al., 1999). Historic mines commonly abandoned with little or no rehabilitation of the mine sites, provision for potential metalliferous discharges from excavations exposed to oxidation. Consequently abandoned mines commonly have elevated, and locally very high, metalloid loads in their soils, discharge water, and in downstream waters and sediments (Baroni et al., 2000; Wilson et al., 2004). Sediments are potential sources of contaminants that may become mobilized, bioavailable, or more environmentally active in soil and aquatic systems, and sediments may be considered as a nonpoint source of pollutants in watershed (Leigh, 1997). According to certain changes in the physical and chemical properties, toxic elements in waste piles can be transported to, dispersed to, and accumulated in stream systems, surface and agricultural soils, plants and animals, and can then be passed up the food chain to human beings as a final consumer (Moore and Luoma, 1990; Jung, 2001; Kim et al., 2005; Chang et al., 2005;

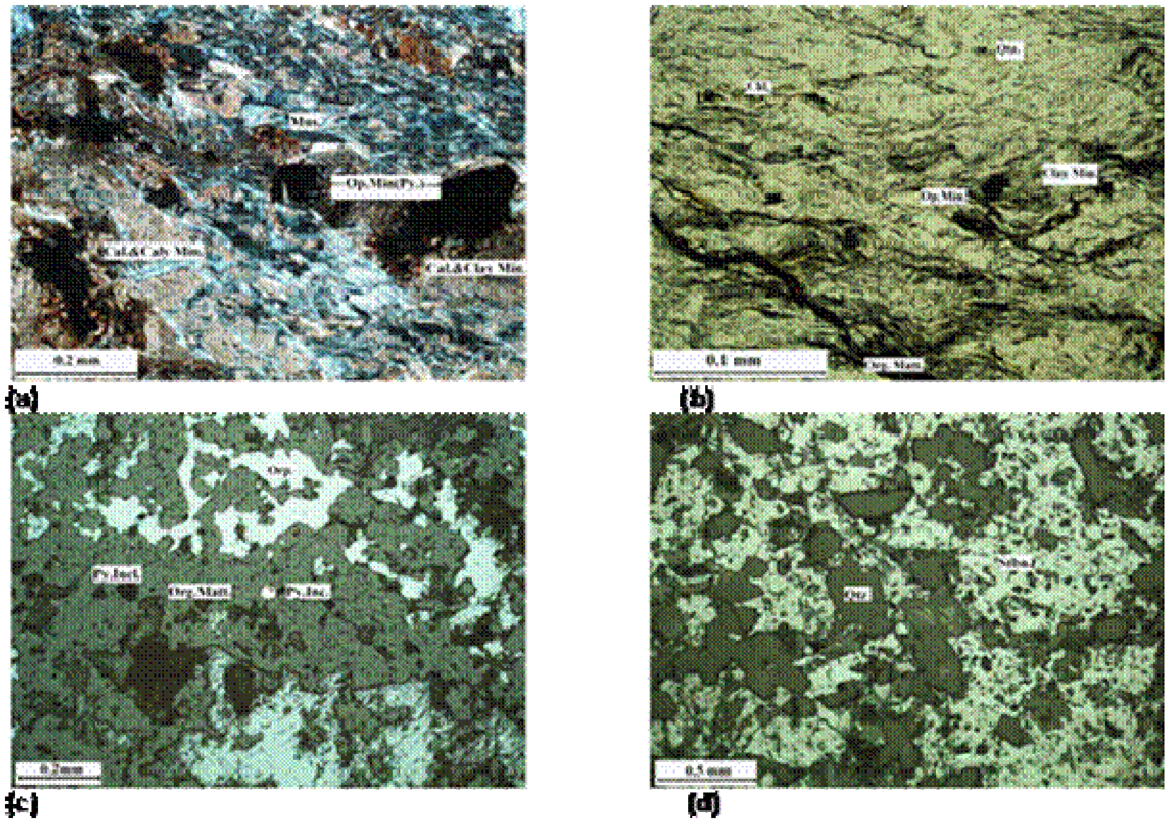

Figure 3. Microphotographs of black shale and hydrothermal quartz vein, **a)** black shale in transmitted polarized light, **b)** black shale in transmitted parallel light , **c)** black shale in reflected light and, **d)** hydrothermal quartz vein with Sb mineralization in reflected light.
(Fe.Oxd. : Fe oxides; Chl. : Chlorite; Mus. : Muscovite; Op.Min. : Opaque minerals; Orp. : Orpiment; Rea. : Realgar; Qtz. : Quartz; Stbn. : Stibnite; Py.Inc. : Pyrite inclusion; Py. : Pyrite; Org.Matt. : Organic matter; Cal. : Calcite; Clay Min. : Clay minerals)

Navarro et al., 2008). So, historic mining activities (abandoned mines) are often associated with environmental impacts especially heavy metal contamination and acid mine drainage (Gray et al., 2002; Jung et al., 2005; Navarro et al., 2008).

The purpose of this paper that is the first study on abandoned mines in Iran is to investigation the impacts of Aq-Darreh Bala abandoned Sb mine on water, sediment, and soil pollution in the Aq-Darreh River watershed.

Geology

The study area is located in Sanandaj-Sirjan structural zone (Stocklin, 1968) comparising a part of Orumieh-Dokhtar volcanic belt (Alavi, 1994). Babakhani and Ghalamghash (1995) believe that the northern part of Takab area is the site of junction between Alborz-Azerbaijan, Central Iran and Sanandaj-Sirjan zones (Figure 1).

The oldest rock unit is black shale exposed in the mine valley and partly in the mine adits, trending N290-310 and dipping 35º to 50º NE. It is composed mainly of clay minerals and quartz with traces of silt-size feldspar, carbonate cement, organic materials and opaque minerals (Figure 3a, 3b). Due to hydrothermal alteration, minerals such as orpiment and realgar and traces of stibnite, sphaleraite and iron oxides have been formed in parts of this rock unit (Figure 3c, 3d). The total carbon contents of the rocks are 7.21 to 16.08 % wt (Table 1).

A black shale unit is overlain unconformably by layers of yellow to cream calcareous marl with interlayers of sandstones and conglomerate. These layers are Oligo-Miocene in age based on their fossil contents (Babakhani and Ghalamgash, 1995). So, the age of black shale underlying these layers is older than Oligocene. The age of a similar and comparable black shale unit hosting gold and arsenic minerals in Zarshuran Au deposit, located 18 km northeast of Aq-Darreh abandoned Sb mine, is believed to be Precambrian (Mehrabi et al., 1999; Asadi et al., 1999; Asadi et al., 2000), but the age has not been determined by isotopic methods in Aq-Darreh black

Table 1. The total concentration of some trace elements (in mg/kg) and Fe2O3, MnO and total carbon (in wt %) in different rock units of Aq-Darreh river watershed

Elements	As	Ba	Cd	Fe_2O_3	Hg	MnO	Pb	Sb	Se	Tl	Zn	C (Total)
Detection limit Rock unit and Ore	1 mg/kg	1 mg/kg	0.1 mg/kg	0.04 %	0.1 mg/kg	0.01 %	0.1 mg/kg	0.1 mg/kg	0.5 mg/kg	0.1 mg/kg	1 mg/kg	0.01 %
Black Shale	1125-83182	292-568	1.3-3.5	2.21-4.76	15.7-41.6	0.08-0.11	46.2-241.4	43.6-786.2	0.8-1.3	6.1-32.7	32-2502	7.21-16.08
Calcareous Marl (Yellow to cream)	225-310	671-8276	1.3-7.6	0.62-1.15	3.1-3.4	0.05-0.31	15.3-18.6	31.6-48.5	<0.5-0.7	0.9-1.7	42-58	0.07-0.18
Marl *(Yellow to light green)*	98-312	51-88	2.8-3.5	1.78-2.24	3.6-8.9	0.02-0.03	14.7-62.8	29.2-215.6	<0.5-0.6	2.4-3.9	276-402	<0.01
Sb bearing Silica (vein)	286-507	263-1038	0.3-31.2	0.65-1.72	56.7-183.1	<0.01-1.09	48.6-9242.7	110361-218057	<0.5-3.6	0.5-83.2	105-23511	0.01-0.02
Tuff (Green to light gray)	76-691	52-86	116-243	1.96-2.73	8.3-38.6	0.13-0.18	33.2-51.6	56.6-93.5	0.6-1.1	2.7-18.2	51-63	<0.01
Andesitic lava (Oligo-Miocene)	167-726	308-411	0.2-0.62	3.05-3.26	0.2-1.9	0.11-0.15	18.1-26.7	82.2-106.1	<0.5	1.7-2.9	112-186	<0.01
Unaltered limestone	82-136	6-17	1.4-3.2	<0.04-0.06	<0.1-0.4	<0.01-0.07	6.7-18.2	1.4-2.8	<0.5-0.8	0.2-1.3	18-47	<0.01
Altered limestone	210-26411	36-5873	1.8-96.7	0.27-13.19	4.2-184.7	0.32-11.92	10.2-1137.2	12.6-342.5	<0.5-5.6	0.1-12.3	3-19241	<0.01
Silicified massive limestone (Gray)	52-1124	287-895	0.3-1.4	0.21-0.39	9.2-12.8	<0.01-0.03	8.2-101.3	12.9-54.3	<0.5	0.4-10.8	19-112	<0.01
Sandstone (URF)	14-49	36-79	<0.1-0.3	2.06-2.83	4.8-736.2	<0.01	7.3-32.2	2.3-11.2	<0.5	0.3-0.5	24-62	<0.01
Marl (URF)	15-46	41-80	0.2-0.4	1.77-2.11	2.6-113.9	<0.01-0.02	5.1-13.3	1.6-6.8	<0.5	0.1-0.3	13-21	<0.01
Travertine	308-11238	254-9305	0.6-1.1	0.96-8.07	11.2-296.8	0.83-10.41	5.3-892.4	13.6-402.5	<0.5-0.9	0.2-6.1	14-97	<0.01

shales. Antimony mineral (Stibnite) in this abandoned mine are found in hydrothermal quartz veins occurring in black shale and calcareous marl layers (Figure 3d).

In the eastern part of the study area there are several exposures of green to light gray andesitic tuff and gray marl (Tf) overlying the yellow to cream calcareous marl. This rock unit in overlaid by porphyritic texture andesitic lavas (OMva). A massive gray to brown color limestone host the gold mineralization in Aq-Darreh Au-Hg deposit which is lower Miocene in age (OMl2q). This rock unit covers the older rock units. The mineralized limestones contain high concentration of potentially toxic elements

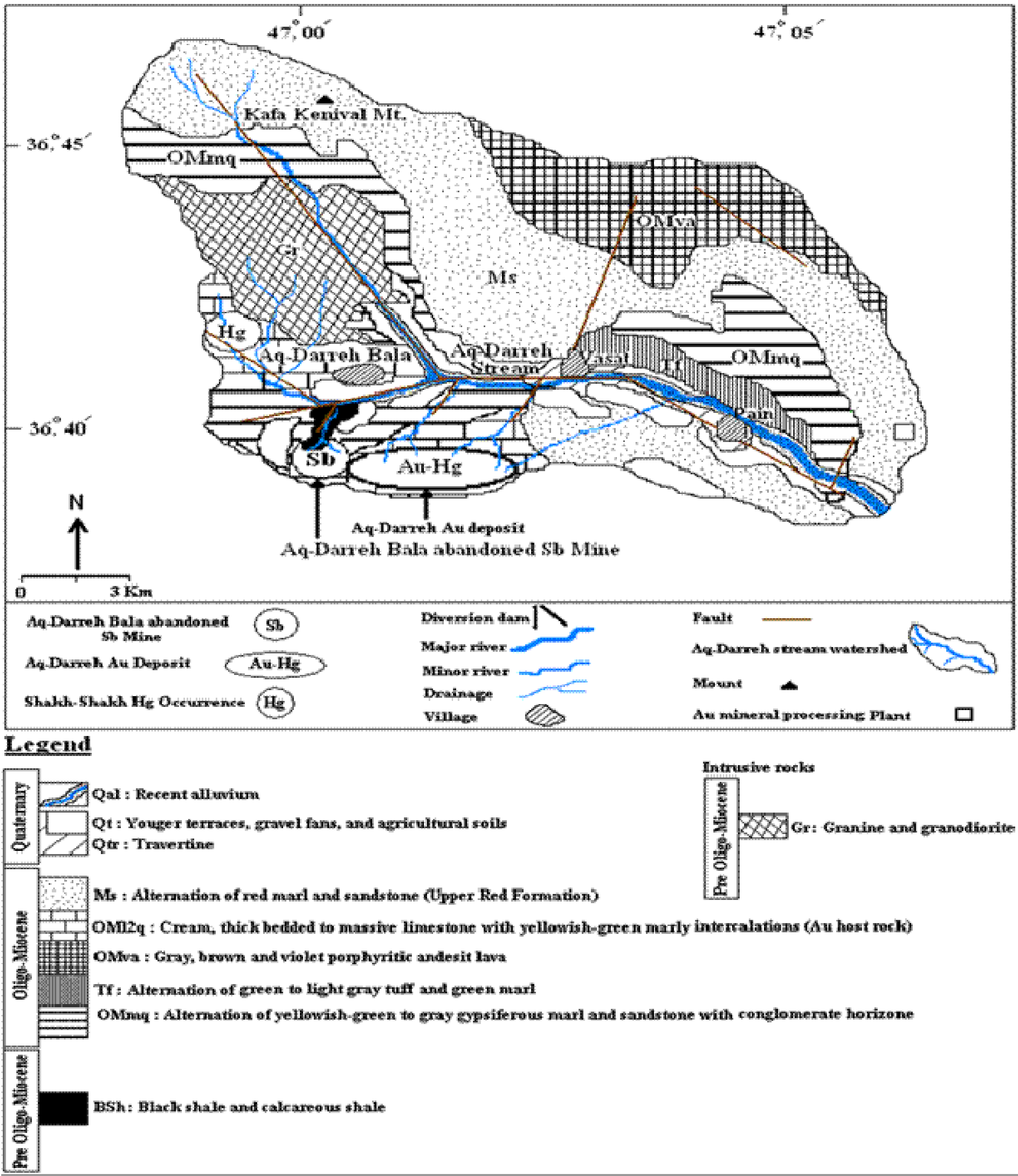

Figure 4. Geological map of the Aq-Darreh river watershed and the location of Aq-Darreh Bala abandoned Sb mine and Aq-Darreh Au-Hg mine

such as As, Sb, and Hg (Table 1).

In the study area, the upper Miocene red marl and sandstone (Ms) expose from northwest to southeast (Figure 4). The Quaternary alluvium, aragonite deposition of the hot springs (travertine) and terraces are the youngest rock units observed in the study area.

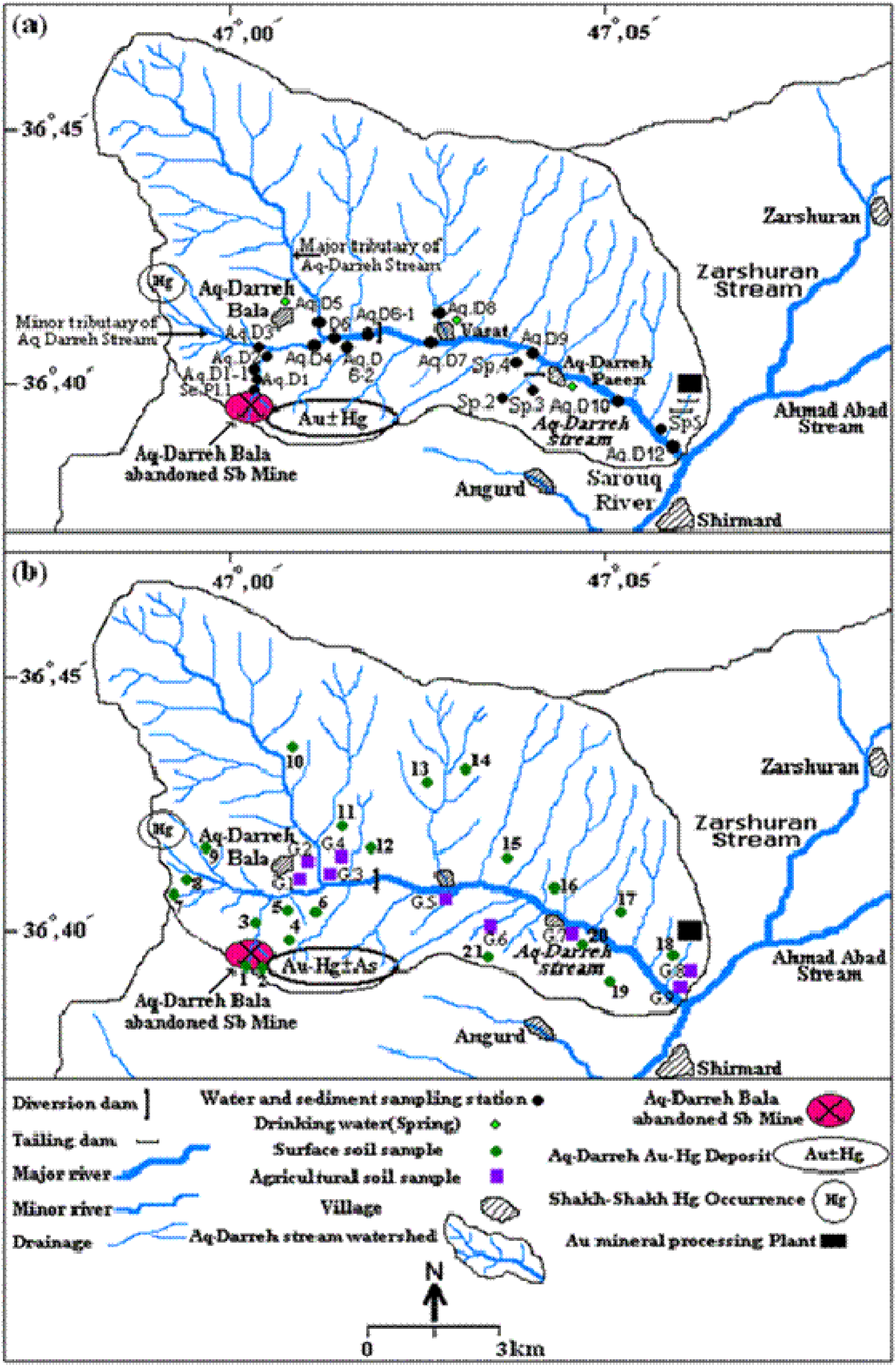

Figure 5. Location map of sampling sites; **a)** Water and stream bed sediment samples, **b)** Surface and agricultural soil samples (**Aq.D** : Aq Darreh; **Sp**. : Spring; **Se.Pl.1** : Sediment and plant samples; **1,2,…21**: Surface soil samples; **G.1-G.9** : Agricultural soil samples)

Table 2. Physico-chemical parameters of Aq-Darreh river, springs and drinking water samples of Aq-Darreh Villages

Station	pH	Eh (mV)	TDS (mg/l)	EC (µS/cm)	Salinity (‰)	T (°C)
Aq.D1	7.08	- 56.1	690	974	0.7	10.3
Aq.D1-1 (Sp.)	6.14	- 56.4	1007	1471	1.1	11.4
Aq.D2	7.93	- 55.1	841	1276	0.9	12.5
Aq.D3	7.56	- 11.6	345	537	0.4	12.8
Aq.D4	8.13	- 40.2	813	1271	0.8	13.8
Aq.D6	7.76	- 22.3	408	644	0.4	14.1
Aq.D6-1	8.21	- 42.7	435	719	0.4	15.2
Aq.D7	8.19	- 43.5	752	1166	0.8	13.2
Aq.D9	8.32	- 48.6	709	1122	0.7	14.1
Aq.D10	8.43	- 55.4	559	867	0.6	12.9
Aq.D12	8.68	- 67.1	522	771	0.5	10.9
Sp.Aq.D.B	8.06	- 53.7	187	325	0.1	12.4
Sp.Aq.D.V	8.11	- 51.4	192	318	0.1	11.3
Sp.Aq.D.P	7.86	- 43.6	211	343	0.2	12.2
Sp.2	8.02	- 50.3	181	309	0.1	10.7
Sp.3	7.98	- 52.1	193	322	0.1	11.1
Sp.4	8.04	- 49.4	197	304	0.1	10.6
Sp.5	7.74	- 31.4	898	1327	0.7	12.4

(Aq.D : Aq Darreh; Sp. : Spring; Sp.Aq.D.B. : Drinking water (spring) of Aq-Darreh Bala Village; Sp.Aq.D.V. : Drinking water of Aq-Darreh Vasat Village; Sp.Aq.D.P. : Drinking water of Aq-Darreh Paeen Village)

An altered granite to granodiorite intrusive body called Aq-Darreh granite (Jurassic in age according to Kholghi Khasraghi, 1991) is exposed in the north-northwest of Aq-Darreh Bala Village (Figure 4).

METHODS AND MATERIALS

Sampling of waters (surface and spring waters), river bed sediments, surface and agricultural soils and plants were performed in the study area. The sampling stations are shown in Figure 5. Eighteen water samples were taken from 11 stations and 7 springs along the Aq-Darreh river according to sampling methods introduced by Wild et al. (1998) and USEPA (2003), in November 2007. Prior to sampling in every station, the pH, Eh, EC, TDS, Salinity and temperature of water were measured by using Sension 156 multiparameter instrument. Two water samples were taken from each station in 250 CC polyethylene bottle washed carefully in the sampling station. For acidizing the water, 2.5 CC pure nitric acid (Merck quality) were added to the first sample in the sampling station and sealed for analysis of total concentration of major and trace elements (74 elements). The second water sample were sealed and sent to the laboratories where it has been filtered with 0.45 µ cellulose nitrate filter and 2.5 CC pure nitric acid was added in order to determine the concentration of the elements in dissolved phase.

Fifteen sediment samples were taken from Aq-Darreh river bed and kept in 0.5 kg polyethylene containers sent to the laboratory for analysis of trace elements. Twenty one surface soil samples and 9 agricultural soil samples were taken using sampling methods introduced by USEPA (1992). Also 6 samples of alfalfa, 4 samples of wheat grains, one sample of apple and one sample of equisetum species were collected, washed with stilled water and air-dried in room temperature. The analyses of water, sediment, soil and plant samples were carried out in ACME analytical laboratories, Vancouver, Canada. For quality control purpose three duplicate of the same sample were analysed and the precision is found to be 5 % for metals and 10-15 % for cations and anions. The location of different samples are shown in Figure 5.

Analytical results

The physico-chemical parameters of waters measured in the field are shown in Table 2 and the analytical data for

Table 3. Analytical data for unfiltered (U) and filtered (F) water samples from the the Aq-Darreh Bala abandoned Sb mine area, water springs and Aq-Darreh river (in mg/l for S and in µg/l for the others. All Hg values were less than 0.2 µg/l, Cr less than 0.5 µg/l, Bi, Sn, Ag and Th were less than 0.05 µg/l)

Element	As	Ba	Cd	Co	Cu	Fe	Mn	Ni	Pb	S	Sb	Se	Tl	U	V	Zn
Detection limit	0.5 µg/l	0.05 µg/l	0.05 µg/l	0.02 µg/l	0.1 µg/l	10 µg/l	0.05 µg/l	0.2 µg/l	0.1 µg/l	1 mg/l	0.05 µg/l	0.5 µg/l	0.01 µg/l	0.02 µg/l	0.2 µg/l	0.5 µg/l
Aq.D1.U	2168.0	294.43	0.75	16.33	25.8	16485	1847.00	44.3	94.5	96	676.98	4.4	4.81	13.31	12.1	292.2
Aq.D1.F	*1074.5*	*118.00*	*0.14*	*3.97*	*0.9*	*17*	*830.89*	*15.3*	*0.6*	*83*	*337.17*	*1.2*	*0.38*	*9.10*	*1.0*	*8.7*
Aq.D1-1.U (Sp.)	3753.0	101.13	0.28	26.82	4.9	58028	1090.00	64.6	8.5	159	319.84	1.6	1.87	8.26	5.6	34.5
Aq.D1-1.F (Sp.)	*187*	*37.95*	*0.13*	*23.11*	*1.9*	*15786*	*1030.37*	*56.6*	*1.1*	*149*	*8.63*	*1.3*	*0.03*	*6.80*	*<0.2*	*15.3*
Aq.D2.U	2427.0	193.31	0.37	13.23	16.0	21959	1588.00	35.6	40.9	97	364.54	3.2	2.86	9.91	7.4	135.9
Aq.D2.F	*205.0*	*84.99*	*0.23*	*4.64*	*1.0*	*51*	*610.44*	*17.7*	*1.4*	*90*	*191.87*	*1.0*	*0.26*	*7.09*	*0.3*	*5.4*
Aq.D3.U	13.3	190.21	0.15	0.43	1.1	83	142.27	0.4	0.5	29	7.12	<0.5	0.05	8.11	<0.2	3.3
Aq.D3.F	*9.6*	*183.34*	*<0.05*	*0.28*	*0.6*	*<10*	*94.25*	*<0.2*	*0.4*	*25*	*6.89*	*<0.5*	*0.02*	*8.09*	*<0.2*	*3.2*
Aq.D4.U	467.6	239.98	0.22	7.66	1.5	9341	2705.00	14.6	5.8	69	29.09	1.9	0.12	8.14	<0.2	21.4
Aq.D4.F	*45.4*	*193.02*	*0.09*	*5.87*	*0.8*	*26*	*2050.04*	*14.5*	*0.8*	*65*	*23.51*	*1.7*	*0.11*	*7.33*	*<0.2*	*3.4*
Aq.D6.U	29.2	158.30	0.15	3.00	3.9	1699	1181.00	5.6	2.4	34	5.96	1.1	0.03	2.59	<0.2	6.5
Aq.D6.F	*7.3*	*149.47*	*0.11*	*2.28*	*0.5*	*<10*	*1148.06*	*5.1*	*0.8*	*30*	*5.85*	*0.7*	*0.03*	*2.47*	*<0.2*	*1.7*
Aq.D6-1.U	34.3	167.07	0.26	2.34	1.8	990	1016.00	4.5	2.7	36	7.17	1.0	0.03	2.96	<0.2	5.1
Aq.D6-1.F	*17.2*	*148.16*	*0.07*	*1.30*	*0.8*	*<10*	*661.63*	*4.2*	*1.4*	*32*	*7.07*	*0.8*	*0.03*	*2.84*	*<0.2*	*1.2*
Aq.D7.U	385.0	117.97	0.30	0.99	4.2	390	945.00	3.3	3.2	72	5.10	1.9	0.04	2.31	<0.2	2.6
Aq.D7.F	*250.2*	*102.47*	*0.09*	*0.68*	*0.8*	*<10*	*396.03*	*2.3*	*1.3*	*70*	*4.67*	*1.6*	*0.03*	*2.01*	*<0.2*	*2.5*

Table 3. Continue

Aq.D9.U	264.5	131.26	0.22	2.20	2.6	778	836.00	3.9	3.6	74	4.39	1.8	0.04	2.01	<0.2	4.8
Aq.D9.F	*112.1*	*102.08*	*0.09*	*1.00*	*0.9*	*<10*	*249.42*	*3.7*	*0.4*	*71*	*3.34*	*1.5*	*0.03*	*1.74*	*<0.2*	*3.8*
Aq.D10.U	80.2	113.32	0.09	0.71	2.5	593	254.59	2.3	0.9	73	3.47	1.5	0.04	1.93	<0.2	2.5
Aq.D10.F	*55.1*	*94.82*	*0.08*	*0.44*	*0.9*	*<10*	*70.50*	*1.5*	*0.7*	*66*	*2.90*	*1.3*	*0.03*	*1.68*	*<0.2*	*1.5*
Aq.D12.U	50.9	97.91	0.11	4.16	1.4	266	86.64	1.8	0.8	81	3.40	1.6	0.05	1.83	0.6	1.9
Aq.D12.F	*43.9*	*90.35*	*0.09*	*3.64*	*1.2*	*58*	*45.35*	*1.6*	*0.6*	*79*	*2.89*	*1.5*	*0.03*	*1.11*	*<0.2*	*1.2*
Sp.2.U	3.1	115.68	0.09	0.21	0.7	171	41.54	<0.2	1.1	18	2.37	<0.5	0.01	0.73	<0.2	1.4
Sp.3.U	1.3	107.44	0.29	0.07	0.5	82	16.16	<0.2	3.6	16	0.89	<0.5	0.01	0.84	<0.2	<0.5
Sp.4.U	22.0	104.88	0.06	0.02	0.4	26	0.14	<0.2	0.4	3	0.56	<0.5	<0.01	0.47	<0.2	0.5
Sp.5.U	161.9	40.17	1.62	358.87	20.6	3069	1426.83	33.7	26.0	727	3.04	6.9	1.00	5.28	1.1	119.2
Sp.5.F	*112.7*	*12.61*	*0.42*	*296.39*	*10.7*	*88*	*1053.78*	*30.4*	*3.0*	*683*	*2.06*	*5.9*	*0.60*	*4.13*	*0.9*	*63.5*
Sp.Aq.D.B.U	7.0	253.49	0.08	0.76	3.3	34	556.26	0.2	0.5	4	1.12	<0.5	0.07	1.69	<0.2	10.0
Sp.Aq.D.V.U	11.8	14.10	0.08	0.13	3.4	167	13.38	0.6	2.8	13	5.01	1.6	0.01	0.02	<0.2	7.0
Sp.Aq.D.P.U	29.5	78.22	<0.05	<0.02	0.4	<10	<0.05	<0.2	0.3	5	0.73	<0.5	<0.01	0.58	<0.2	7.0

U: Unfiltered water samples, F: Filtered water samples, Aq.D.: Aq-Darreh, Sp.Aq.D.B.U : Drinking water of Aq-Darreh Bala Village, Sp.Aq.D.V.U : Drinking water of Aq-Darreh Vasat Village, Sp.Aq.D.P.U : Drinking water of Aq-Darreh Paeen Village

Table 4. The total concentration of some trace and major elements in sediment of river bed and some spring samples from the Aq-Darreh Bala abandoned Sb mine area and downstream

Element	**As**	**Ba**	**Cd**	**Co**	**Fe**	**Hg**	**Mn**	**Ni**	**Pb**	**S**	**Sb**	**Se**	**Tl**	**U**	**V**	**Zn**
Detection limit	0.1 mg/kg	0.5 mg/kg	0.01 mg/kg	0.1 mg/kg	0.01 %	5 µg/kg	1 mg/kg	0.1 mg/kg	0.01 mg/kg	0.02 %	0.02 mg/kg	0.1 mg/kg	0.02 mg/kg	0.1 mg/kg	2 mg/kg	0.1 mg/kg
Se.Pl.1	>10000	647.0	0.87	6.6	11.91	15394	5682	21.5	37.27	1.3	127.47	1.4	2.59	3.1	56	153

Table 4. Continue

Aq.D1	1732.7	445.4	1.30	8.0	2.13	15242	997	22.8	33.42	0.23	172.15	4.9	2.91	4.6	36	139
Aq.D1-1(Sp.)	4686.5	440.7	0.45	18.4	6.18	8396	2387	37.2	28.35	0.65	468.24	1.9	2.13	6.7	39	90
Aq.D2	621.6	105.0	0.12	3.8	1.15	1971	883	9.4	13.06	0.11	43.23	1.4	0.62	3.3	21	27
Aq.D3	885.9	853.7	0.86	25.5	1.32	10053	1047	22.0	34.78	0.12	48.18	0.9	0.65	6.5	37	89
Aq.D4	2437.4	523.6	0.58	18.4	3.42	3207	1232	26.7	25.75	0.31	60.06	1.4	1.54	4.0	37	173
Aq.D6	73.4	388.7	0.24	6.6	2.14	1477	946	11.3	32.79	0.25	16.65	0.8	0.12	3.5	39	36
Aq.D6-1	93.6	395.0	0.58	9.1	2.33	1884	1189	21.2	32.04	0.29	22.87	1.0	0.24	4.1	65	67
Aq.D6-2	130.8	529.0	0.53	12.9	3.47	9795	1932	32.4	33.66	0.14	28.03	1.2	0.31	3.7	63	64
Aq.D7	445.1	262.3	0.24	6.3	4.81	6174	3151	7.6	22.03	0.36	4.95	1.5	0.15	2.2	17	128
Aq.D9	304.4	362.6	0.86	10.3	4.22	1192	1477	20.7	86.18	0.20	11.54	0.7	0.27	2.8	66	97
Aq.D10	104.5	470.6	0.42	8.9	3.04	2236	1732	18.6	61.09	0.13	6.82	0.4	0.13	3.0	53	58
Aq.D12	92.2	376.3	0.81	10.6	3.17	1369	2134	23.9	54.73	0.09	7.78	0.4	0.28	2.9	69	77
Sp.2	59.5	410.1	0.33	10.9	3.26	4271	1431	24.1	28.15	0.07	3.79	0.4	3.01	2.0	79	59
Sp.4	132.9	342.9	0.36	11.7	4.17	369	2257	35.0	35.18	0.11	3.04	0.7	0.25	2.2	98	62

(Se.Pl.1 : Bedsediment sample with plant cover equisetum sp. in downstream Aq-Darreh abandoned Sb mine; Aq.D.: Aq-Darreh; Sp.: Spring)

Table 5. The concentration of some trace and major elements in surface and agricultural soil samples of the Aq-Darreh Bala abandoned Sb mine area and downstream

									a) Surface soil samples								
Element	**Al**	**As**	**Ba**	**Ca**	**Cd**	**Fe**	**Hg**	**Mn**	**P**	**Pb**	**S**	**Sb**	**Se**	**Tl**	**U**	**V**	**Zn**
Detection limit	0.01 %	0.1 mg/kg	0.5 mg/kg	0.01 %	0.01 mg/kg	0.01 %	5 mg/kg	1 mg/kg	0.01 %	0.01 mg/kg	0.02 %	0.02 mg/kg	0.1 mg/kg	0.02 mg/kg	0.1 mg/kg	2 mg/kg	0.1 mg/kg
SSO.1	0.73	364.7	238.4	10.01	0.91	2.01	387	802	0.064	296.16	0.22	102.21	0.9	0.57	0.8	76	146.3
SSO.2	0.88	1837.1	412.9	18.07	2.24	3.17	2401	2933	0.072	532.30	0.87	471.14	0.4	1.56	0.6	52	1293.4
SSO.3	3.07	8303.2	921.4	22.48	0.81	3.57	6245	987	0.070	131.70	0.27	358.43	0.8	2.94	7.9	93	362.1
SSO.4	1.62	552.5	415.7	11.92	0.77	2.27	621	933	0.068	192.41	0.34	134.52	0.5	0.78	0.6	66	111.7
SSO.5	2.48	321.7	405.3	9.70	0.76	2.02	436	1404	0.062	155.22	0.22	117.11	0.6	0.52	3.2	79	105.2

Table 5. Continue

SSO.6	3.03	433.5	392.7	9.41	0.83	2.11	584	1039	0.064	187.35	0.23	101.72	1.0	0.61	0.5	46	98.4
SSO.7	1.41	352.1	512.8	10.94	0.63	2.13	1402	636	0.060	116.10	0.22	492.17	1.0	0.62	0.7	63	105.4
SSO.8	2.09	152.4	212.3	5.67	0.55	1.17	142	474	0.049	96.63	0.11	94.51	1.2	0.31	0.8	72	93.9
SSO.9	3.52	114.2	209.4	6.01	0.51	2.54	185	532	0.049	87.11	0.26	102.31	1.1	0.29	3.2	112	102.7
SSO.10	2.61	64.9	198.3	7.37	0.61	1.81	242	536	0.053	112.45	0.23	57.41	1.0	0.48	3.8	89	128.4
SSO.11	3.33	82.1	183.8	8.26	0.59	1.93	257	704	0.055	138.12	0.38	64.10	1.1	0.42	2.5	91	142.1
SSO.12	2.17	312.7	204.5	12.11	0.85	2.70	626	3117	0.066	196.47	0.65	112.87	0.9	0.87	0.7	61	236.9
SSO.13	3.72	116.4	204.3	6.05	0.57	1.77	136	831	0.049	92.70	0.11	24.02	1.2	0.21	1.1	62	141.5
SSO.14	3.33	132.7	187.7	6.76	0.66	1.81	158	759	0.051	102.25	0.27	32.82	0.9	0.28	0.9	60	123.8
SSO.15	3.61	254.3	192.2	8.41	0.88	1.98	266	573	0.053	204.17	0.32	84.17	0.8	0.45	0.7	58	152.2
SSO.16	4.07	287.7	183.6	9.94	0.76	2.03	247	462	0.056	119.32	0.46	62.72	1.1	0.49	0.6	60	131.4
SSO.17	1.87	836.9	251.5	14.88	0.87	2.81	1142	2018	0.069	238.16	0.23	114.11	0.9	0.92	0.5	58	124.8
SSO.18	3.11	417.2	382.2	9.02	0.82	2.14	427	833	0.063	192.41	0.21	121.32	0.9	0.75	2.4	76	110.4
SSO.19	1.39	217.9	274.5	6.56	0.39	2.16	202	576	0.054	103.11	0.13	51.53	1.1	0.37	0.5	44	44.2
SSO.20	2.81	303.4	172.8	8.01	0.43	1.89	219	435	0.060	108.72	0.49	93.26	1.1	0.53	0.5	52	87.2
SSO.21	2.61	224.4	264.0	7.91	0.78	1.81	416	522	0.055	122.41	0.21	67.25	1.0	0.42	0.5	38	69.8

b) Agricultural soil samples

Element	**Al**	**As**	**Ba**	**Ca**	**Cd**	**Fe**	**Hg**	**Mn**	**P**	**Pb**	**S**	**Sb**	**Se**	**Tl**	**U**	**V**	**Zn**
Detection limit	0.01 %	0.1 mg/kg	0.5 mg/kg	0.01 %	0.01 mg/kg	0.01 %	5 µg/kg	1 mg/kg	0.01 %	0.01 mg/kg	0.02 %	0.02 mg/kg	0.1 mg/kg	0.02 mg/kg	0.1 mg/kg	2 mg/kg	0.1 mg/kg

Table 5. Continue

G.1	1.18	16.4	132.2	6.47	0.58	1.64	3315	714	0.061	29.07	0.02	1.24	0.4	0.39	0.7	52	99.8
G.2	1.49	92.8	185.4	6.68	0.33	1.98	1256	682	0.056	19.25	0.07	4.11	0.3	0.25	0.6	30	64.7
G.3	1.92	1396.7	387.3	17.59	0.72	3.17	6358	641	0.103	34.01	0.12	98.22	0.6	1.18	2.2	47	131.1
G.4	1.07	787.1	128.8	13.49	0.61	3.03	3218	689	0.091	22.05	0.04	14.61	0.3	0.31	0.8	41	68.5
G.5	1.21	358.2	228.6	12.93	1.11	2.79	4215	1283	0.082	119.73	0.10	72.53	0.5	0.89	0.9	50	124.4
G.6	2.32	82.4	76.8	6.11	0.67	3.72	787	677	0.079	11.17	0.03	1.64	0.2	0.16	1.0	28	17.2
G.7	0.95	47.6	81.4	6.48	0.32	3.10	2481	1124	0.053	34.20	0.05	11.20	0.4	0.33	0.9	48	72.2
G.8	1.05	949.4	288.6	16.26	2.61	3.11	3684	1262	0.096	31.38	0.09	13.72	0.6	0.76	0.9	62	134.1
G.9	0.99	168.2	178.4	12.38	0.63	2.17	2008	986	0.076	29.71	0.06	9.57	0.4	0.55	0.9	37	122.6

(SSO. : Surface soil sample, G. : Agricultural soil sample)

Table 6. The concentration of some trace and major elements in plant samples from the Aq-Darreh Bala abandoned Sb mine area and downstream

----	----	***Element***	**As**	**Ba**	**Cd**	**Co**	**Fe**	**Hg**	**Mn**	**Mo**	**Pb**	**S**	**Sb**	**Se**	**Tl**	**U**	**Zn**
Vegetation Type	*Soil situation*	*D.L* *Sample.Code*	0.1 mg/kg	0.1 mg/kg	0.01 mg/kg	0.01 mg/kg	0.001 %	1 µg/kg	1 mg/kg	0.01 mg/kg	0.01 mg/kg	0.01 %	0.02 mg/kg	0.1 mg/kg	0.02 mg/kg	0.01 mg/kg	0.1 mg/kg
Wheat	G.2	W.1	0.5	0.2	0.02	0.02	0.006	<1	12	0.71	0.66	0.04	0.03	0.1	0.02	0.02	11.3
Alfalfa	G.3	AF.1	2.4	36.1	0.03	0.02	0.009	37	41	1.99	1.31	0.21	0.09	0.2	<0.02	<0.01	66.1
Apple	G.5	AP.1	2.2	1.1	0.02	0.03	0.005	3	32	1.56	1.05	0.12	0.33	0.1	<0.02	<0.01	32.3
Alfalfa	G.5	AF.2	2.1	43.7	0.02	0.04	0.008	45	79	1.07	1.42	0.30	0.17	0.2	<0.02	<0.01	59.5
Wheat	G.6	W.2	0.8	1.2	0.02	0.02	0.008	6	35	1.09	1.07	0.10	0.09	0.1	<0.02	<0.01	40.7

Table 6. Continue

Alfalfa	G.7	AF.3	2.0	13.5	0.04	0.01	0.008	22	55	0.91	0.81	0.22	0.16	0.1	<0.02	<0.01	43.6
Wheat	G.8	W.3	3.1	1.5	0.02	0.03	0.007	8	37	1.74	1.19	0.15	0.29	0.2	<0.02	<0.01	58.1
Wheat	G.9	W.4	1.3	0.9	0.03	0.01	0.004	5	29	1.11	0.89	0.09	0.09	0.1	<0.02	<0.01	42.7
Alfalfa	SSO.3	AF.4	28.4	19.2	0.11	0.46	0.038	174	68	18.58	2.02	0.48	3.39	1.0	1.58	0.10	105.2
Equisetum sp.	SSO.3	Equ.1	154.9	23.8	0.05	0.34	0.037	182	46	4.98	2.02	1.61	3.25	0.7	3.59	0.05	43.8

unfiltered (U) and filtered (F) water samples are presented in Table 3. The analytical results of water, sediment, surface and agricultural soils and plant samples in Aq-Darreh river watershed are shown in Tables 3 - 6.

DISCUSSION

Based on the analytical results of water, sediments, soils and plants samples (Tables 3 - 6) it is obvious that the water, sediments, soils and plants of Aq-Darreh river watershed in downstream of mineralized and mining areas have relatively high concentration of toxic elements such as As and Sb. The variations of As, Sb and Fe concentration in unfiltered water (total concentration) and filtered water (dissolved phase concentration) in the study area are shown in Figure 6. The As, Sb and Hg concentration in sediment, some of the soils (especially agricultural soils) and plant samples in the vicinity of mining areas are relatively high. XRD and heavy mineral studies in stations such as Se.Pl.1, Aq.D1, Aq.D3 and Aq.D6-2 reveal the mineral cinnabar in sediment samples. Cinnabar has a slight solubility in neutral to alkaline waters (Gray et al., 2002), so, Hg concentration is very low in Aq-Darreh water samples. Instead, sediment and soil samples indicate higher concentrations of mercury.

In order to determine the relationship between trace element contents and pH values, the Ficklin et al. (1992) diagram were used. Based on this diagram (Figure 7) the water samples in the vicinity of mining areas were plotted in "Near-neutral, high metal" field and the water samples outside of mineralized and mining zones were plotted in "Near-neutral, Low metal" field.

The relationship between total concentration (unfiltered water sample) and dissolved phase concentration (filtered water sample) of As and Sb in water samples of Aq-Darreh river are shown in Figure 8. Based on Figure 8 it is obvious that the difference between the total concentration of arsenic in unfiltered water samples and its dissolved phase concentration in filtered water of each station is higher than Sb concentrations.

The variations of As, Sb, Hg, Zn, Pb, Ba, Fe and Mn in sediment samples of Aq-Darreh river bed are shown in Figure 9.

CONCLUSION

Field studies and analytical results of water samples indicate the high concentration of As in Aq.D1-1 station which is due to the spring water flowing through black shale into the valley of the abandoned Sb mine and also high concentration of Sb in Aq.D1 station is also due to leachates from the gangue and waste piles of the Aq-Darreh Bala abandoned Sb mine. It is apparent in Table 3, Figures. 5a and 6 the water samples in the vicinity of Aq-Darreh Bala abandoned Sb mine and Aq-Darreh Au-Hg mine are contaminated with As and Sb. The water that flows out of the Aq-Darreh Bala abandoned Sb mine (polluted minor tributary of Aq-Darreh river), in the downstream mixed with unpolluted waters of the major tributary of Aq-Darreh river (Fig. 5a). The total concentrations of As and Sb were 3.2 μg/l and 1.32 μg/l respectively in the water samples of the unpolluted major tributary of Aq-Darreh river before mixing with the polluted minor tributary of Aq-Darreh river, and the total concentrations of As, Sb and Hg in sediment sample of unpolluted major tributary of Aq-Darreh river were 64.1 mg/kg, 3.87 mg/kg and 798 μg/kg respectively

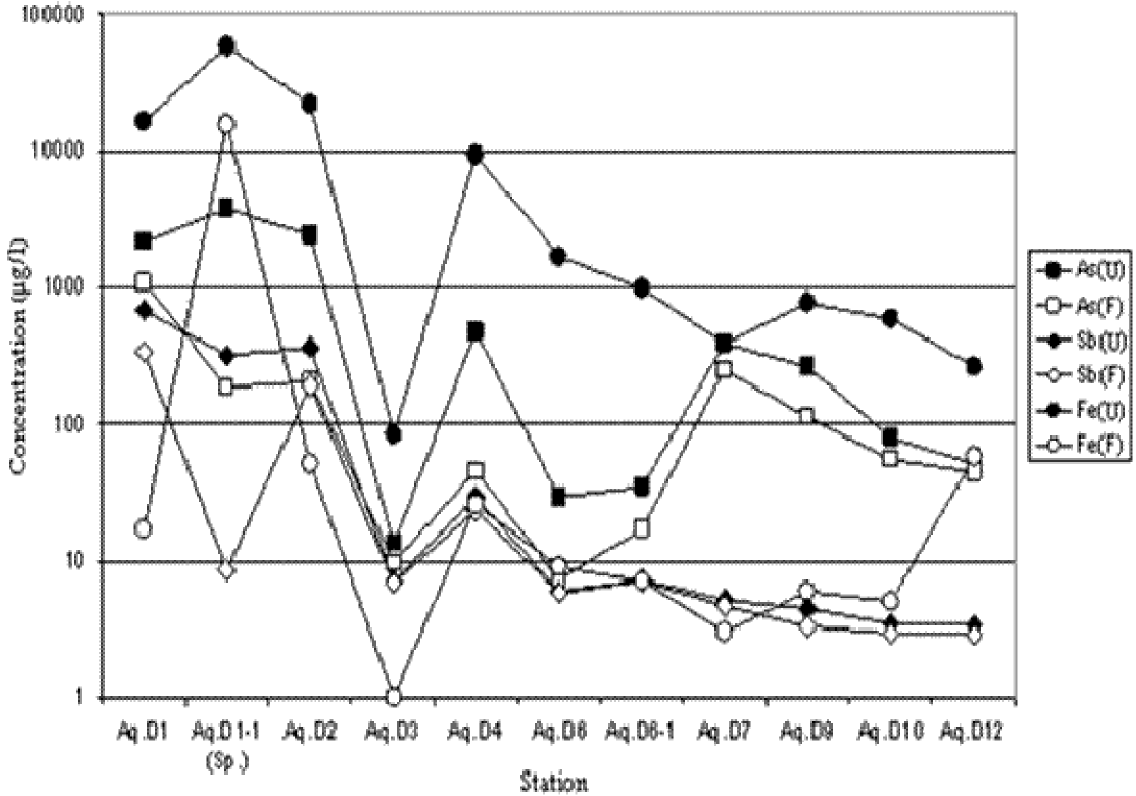

Figure 6. Variations of As, Sb and Fe concentrations in unfiltered (U) and filtered (F) water samples of Aq-Darreh Bala abandoned Sb mine area and Aq-Darreh river

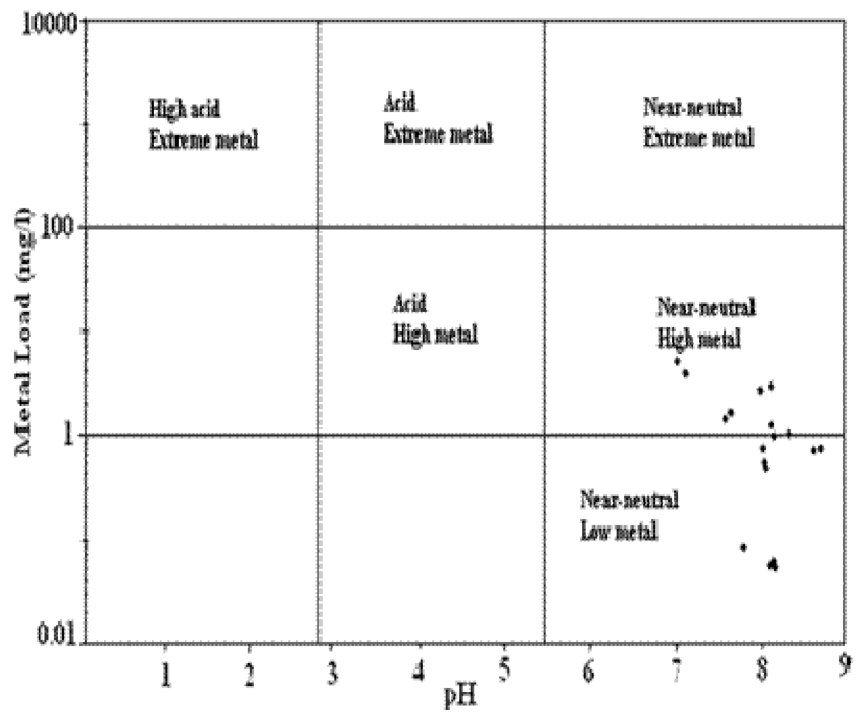

Figure 7. The relationship between pH and metal load (As+Cd+Co+Cr+Cu+Pb+Se+Sb+Sr+U+V+Zn) of water samples (Ficklin et al., 1992 modified by Caboi et al., 1999; adopted from Milu et al., 2002)

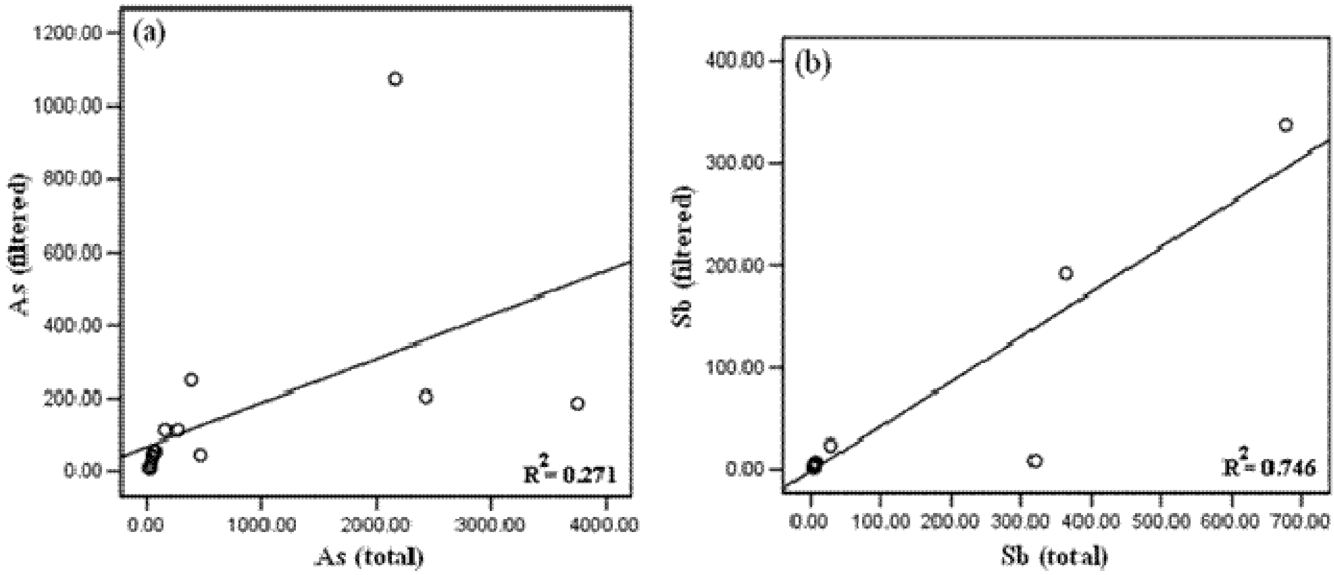

Figure 8. The relationship between unfiltered (total) and filtered concentrations of As (a) and Sb (b) in water samples of the study area

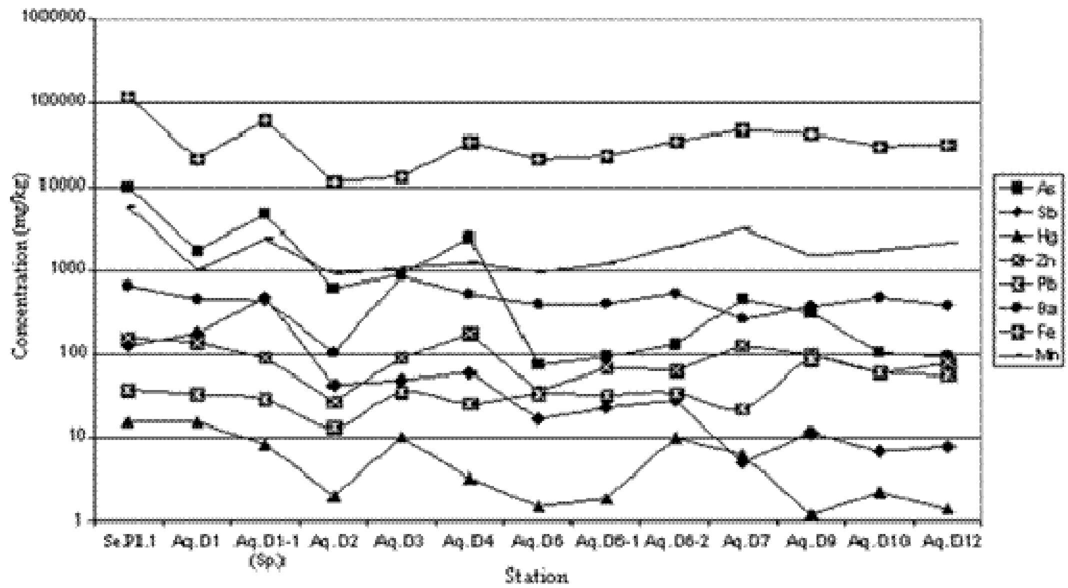

Figure 9. Variation of As, Sb, Hg, Zn, Pb, Ba, Fe and Mn in bed sediment samples of Aq-Darreh Bala abandoned Sb mine area and Aq-Darreh river

(Yaghubpur and Rahimsouri, 2009). Comparing these values with water and sediment samples in the station Aq.D6 indicates that after confluence of polluted and unpolluted tributaries of Aq-Darreh river in the station Aq.D6, the concentration of As and Sb in water increase 9 and 4 times respectively and the concentrations of As, Sb and Hg in the sediments increase 0.1, 4.3 and 1.8 times respectively. The water flowing from the main Au-Hg mining sites reaches to the middle parts of Aq-Darreh river and in the downstream station (Aq.D7), the concentrations of As and Sb in water reach to 385 µg/l and 5.10 µg/l respectively (Table 3). The concentration of As in the water samples compared with the upstream station(Aq.D6), increases 13 times and Sb decreases 0.15 time and the concentrations of As and Hg in bed sediments of Aq.D7 station increases 6 and 4 times respectively and while Sb decreases 3.3 times. Therefore, it is obvious that the cause of Sb contamination in Aq-Darreh river is the Aq-Darreh Bala abandoned Sb mine, while the As and Hg contaminations are due to Aq-Darreh Au-Hg minig activities.

Arsenic and Sb concentrations in the drinking water of Aq-Darreh Bala and Aq-Darreh Vasat Villages compared with USEPA (2000) and WHO (2004) standards indicate that these drinking waters are not contaminated. Drinking water of these two villages is supplied from springs Sp.Aq.D.B and Sp.Aq.D.V (Table 3). In the Aq-Darreh Paeen Village the drinking water is supplied from mineralized travertine in which the amounts of As is 3 times of safe water according to the above mentioned standards.

The potentially toxic elements As and Sb are very concentrated in spring Sp.5 (Table 3). The main reason for contamination of spring Sp.5 is leaching of contaminated water flowing from the tailing dams of Au mineral processing plant (Figure 5a).

Comparison of As and Sb water concentration of station Aq.D12 (Table3) with mean As and Sb values in the world surface waters (0.83 µg/l and 1.1 µg/l respectively, according to Smedley and Kinniburgh, 2002 and Filella et al., 2002) indicate that As and Sb values in this area are at least 60 and 3 times respectively higher than the mean concentrations of these elements in world rivers. Therefore, the water of Aq-Darreh river could be considered one of the very contaminated rivers in the world.

The amounts of As and Sb in surface soils are also very high in Aq-Darreh area. The mean concentration of As in surface soils according to Smedley and Kinniburgh (2002) and British standards (Clemente, 2008) are mentioned 7.2 mg/kg and 20 mg/kg respectively, while in some samples of Aq-Darreh mine area the concentration of As is more than 8000 mg/kg. Although the range of Sb concentration in surface soil is 0.05 to 2 mg/kg (Kabata-Pendias and Mukherjee, 2007), the surface soil samples of Aq-Darreh area indicate much more Sb in their composition up to 500 mg/kg. Therefore, the surface soils of Aq-Darreh mine area are highly contaminated and are not suitable for agricultural purposes especially of edible plants.

The analytical results of As, Sb and Hg in the agricultural soils of the study area compared to allowable amounts of 5.5-12 mg/kg and 5-10 mg/kg As according to Siegel (2002) and Smedley and Kinniburgh (2002) respectively, 0.05-2 mg/kg Sb according to Kabata-Pendias and Mukherjee (2007) and 6.6 mg/kg Hg according to Appletona (2007) and Conde Bueno et al. (2009) indicate that some of the agricultural soil samples of the study area are contaminated respect to As and Sb. Based on the chemical analysis of different rock units (Table 1) and mineralogical-petrographical studies it could be concluded that the weathered black shales and mineralized limestones are the source of these contaminations in surface and agricultural soils of the study area.

The allowable concentration amounts of As and Hg in wheat grain are reported 0.01-0.07 mg/kg and less than 0.1 to 29 µg/kg (mean 5 µg/kg) respectively (Skrbic and Cupic, 2005). The analytical results of wheat grains in whole area indicate high concentration of As and the plants of alfalfa and equisetum species in the study area are contaminated with the waters flowing from the Aq-Darreh abandoned Sb mine and therefore they have high concentrations of potential toxic elements of As, Sb and Hg. So, the plants of the area are not suitable for grazing the animals such as sheeps, cows and etc.

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