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Environmental impacts of natural contaminants and mining activities on the surface and agricultural soils in the Aq-Darreh river watershed, Takab, West Azerbaijan Province, NW Iran

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Abstract

The concentrations of potentially toxic elements (As, Sb, and Hg) and some trace elements in 36 topsoil samples and 18 agricultural soil samples were measured at the Aq-Darreh River watershed, NW Iran. Based on the results of the chemical analysis and comparing them with different standards, it seems that the soils of the Aq-Darreh River watershed are polluted with As and Sb. This pollution results from geochemical background (natural contamination) and mining activities. Geochemical background values in topsoil and agricultural soils were estimated for As (429.7 ppm and 98.8 ppm), Sb (79.02 ppm and 3.98 ppm), and Hg (356 ppb and 2596 ppb). This research also indicates that mining activities have played a significant role in soil pollution and increasing As, Sb and Hg concentration in topsoils and As and Sb in agricultural soils. Results of sequential leaches and XRD analyses of both soil types showed that most of the As concentration is bound to amorphous iron hydroxides in soils, while Sb and Hg are bound to resistant minerals such as stibnite and cinnabar. Clay and carbonate minerals have a lower adsorption of these pollutant elements in both topsoil and agricultural soils.

Keywords: Soil pollution; sequential leaches; geo-accumulation index; pollution sources; Aq-Darreh mining district; Iran

1. Introduction

The Aq-Darreh mining district (including Aq-Darreh Au deposit and Aq-Darreh Bala abandoned Sb mine) is located 38 km northwest of Takab, West Azerbaijan province, NW Iran (Fig. 1). The Aq-Darreh Au deposit is one of two known Au deposits within the Cenozoic-Recent hydrothermal system of the Takab region. This region hosts an active geothermal system where thermal springs locally precipitate exceptionally high amounts of Au and Ag, up to kg/t levels [1]. The Aq-Darreh Au deposit is hosted by carbonate-rich sedimentary rocks of Miocene age. This deposit has been compared with Carlin-type deposits [1, 2]. It has been suggested by some authors [3, 4] that mining heaps derived from Carlin-type deposits have a significant role in water and river-bed sediment contamination downstream of the deposits. Au occurrence in Aq-Darreh was explored by geologists of the Iranian Ministry of Mines and Metals [7].

Mining activities in the Aq-Darreh mining district has taken place in two stages. The ancient mining activities date back to about 1000 years ago [5] and the new phase was started in 1965 [6]. In 1990 the Au occurrence in Aq-Darreh was explored by geologists of the Iranian Ministry of Mines and Metals [7]. The Aq-Darreh Au deposit is currently mined without much consideration of the environment. The Aq-Darreh deposit is mined for Au and the waste rocks containing high concentrations of toxic elements (As, Sb and Hg) are dumped as mine heaps. At present, more than 850,000 tons of waste rock containing sulfide minerals, As and Hg with lesser amounts of Sb have been piled up as a waste dump in the mine area, which should be carefully studied in terms of their potential environmental impacts [2]. Pollution of water, river-bed sediments and plants in the Aq-Darreh River watershed has been reported by Yaghubpur and Rahimsouri [2]. This investigation focuses on the pollution of topsoil and agricultural soils. The Takab area has a semi-arid climate with moderate summers and very cold winters with an average annual temperature of about 9 ºC. Annual precipitation is about 400 mm, falling mostly as snow [8, 9].

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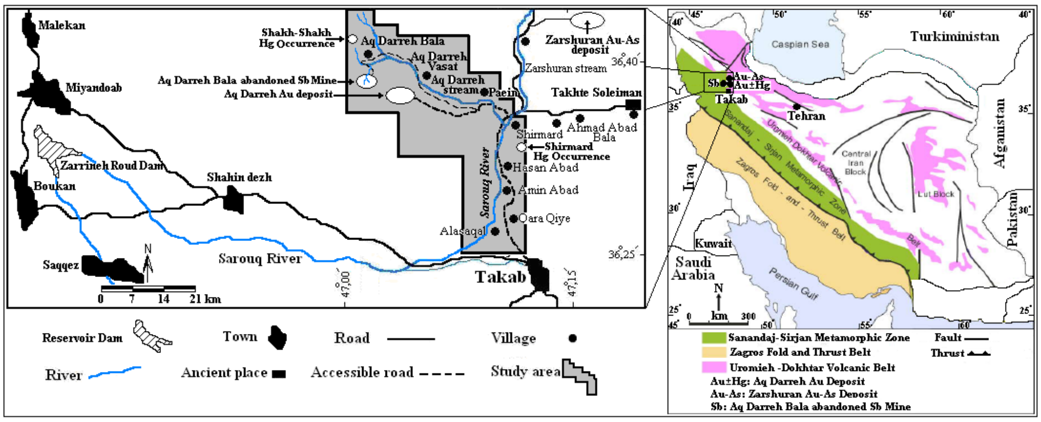

Fig. 1. Location of the study area in a simplified geological map of Iran [2]

The main water source of the mine area is the Aq-Darreh River flowing from the northwest of the mine to the southeast (Fig. 1). More than 80 % of the runoff of the Aq-Darreh Au mine area reaches to the Aq-Darreh River and the rest flows to the Sarouq River via the Qiz Qapan and Angurd streams [2], which flow in the southeast of the mine area (Fig. 2). The runoff from the Aq-Darreh Au mine area joins the Sarouq River via the Aq-Darreh River that, along with several other small stream waters from other prospects, flows to the Zarrineh Roud reservoir dam (Fig. 1). The annual discharge of the Sarouq River to the Zarrineh Roud reservoir dam is estimated to be more than 225 million m^3 [8]. The water in the Zarrineh Roud reservoir dam is used for the agriculture and drinking water of several cities in Kurdistan and East and West Azerbaijan Provinces [9].

2. Geology and mineralisation

The Aq-Darreh mining district is situated in NW Iran within the Uromieh-Dokhtar volcanic belt. This belt formed as a result of the northward subduction of the Neo-Tethys along the Zagros thrust fault [10]. According to Stocklin [11], the Aq-Darreh area is located in the Sanandaj-Sirjan structural zone and based on Nabavi [12], the area is a part of the Khoy-Mahabad zone. It seems that the Aq-Darreh area is located in the intersection between the Alborz-Azerbaijan, Central Iran and Sanandaj-Sirjan structural zones [13].

Proterozoic, early Cambrian and Tertiary rock units crop out in the north of Takab [13]. In the south of Aq-Darreh Bala Village (abandoned Sb mine valley) which is also the site of ancient mining activities, a Proterozoic black shale unit ($P\text{Є}_A$), 3-6 m thick, crops out for ~ 1 km [14]. This shale is overlain by an Oligo-Miocene calcareous marl, marly tuff, and limestone containing some Sb-bearing siliceous veins. Different rock units in the Aq-Darreh River watershed are illustrated in Fig. 2.

The area is composed of a syncline in the north and an anticline in the south of the Aq-Darreh Au mine area with their axes trending NW-SE [15]. Three fault systems trending NW-SE, NE-SW and N–S have been noted in the Aq-Darreh mining district (Fig. 2). The main fault is trending NW-SE, controling the course of the Aq-Darreh River.

Mineralisation in the Aq-Darreh Au deposit occurs in Miocene limestone. Massive mineralised limestone interbedded with white altered tuff and a Fe-Mn oxide/hydroxide horizon is the main unit widespread across the mining area. The unit varies from light to dark gray or brown colored, and it is a recrystalised limestone containing some secondary dolomite. This unit covers an area of about 0.3 km^2 in the Aq-Darreh mine area and is intensely weathered and has been altered by hydrothermal fluids [2].

Concentrations of Au in this unit range from 0.2 to 19.3 ppm and concentrations of toxic elements are As (0.17 to 19.5 %), Sb (0.022 to 1.7 %) and Hg (0.001 to 0.22 %) [7]. Minerals found in this deposit include arsenian pyrite or melnikovite, arsenopyrite, scorodite, jarosite, cinnabar, orpiment, realgar, stibnite, sphalerite, iron oxides (hematite, goethite and limonite), manganese oxides, barite and fluorite [2].

A jasperoid horizon covers the massive gray limestone which has resulted from hydrothermal alteration in the mine area. This unit forms layers and lenses ranging in thickness from 1-5 m. This horizon trends E-W in the Aq-Darreh mine area with a length of 800-1200 m and 120-400 m width. Generally, it is composed of microcrystalline silica and subhedral to euhedral crystals of pyrite with lesser amounts of orpiment, realgar, stibnite, and traces of galena and sphalerite [2]. The sulfides in jasperoid layers and lenses form up to 2 vol% of the rock. According to field and laboratory examinations, the jasperoid horizon can be divided into two groups based on the mineralisation [2, 16]: a) pre- and syn-depositional jasperoid, gray in color, and economically important, and b) post-depositional barren jasperoid with light gray color. The potentially toxic elements in mineralised jasperoids include As (0.05 to 14.1 %), Sb (<0.005 to 0.59 %) and Hg (0.004 to 0.19 %) [16].

3. Material and methods

In October 2007 two sets of samples including topsoil and agricultural soil samples (0-15 cm depth) were collected according to USEPA sampling techniques and strategies [17] from the Aq-Darreh River watershed (Fig. 3). The first set, composed of 36 topsoil samples (Sl) were taken randomly by a hand auger of 3 cm in diameter. The second set of 18 agricultural soil samples (AGS) was collected from the agricultural lands.

In order to have representative samples, soils were collected as composite samples by mixing of 3-8 sub-samples within a 1 m^2 area by hand auger, regarding the variation in grain size distribution and nonuniformity of topsoils and agricultural soils in the sampling sites.

The representative samples were dried at room temperature for 2 weeks and sieved to 180 µm. Samples sieved to <2 mm were placed in cleaned plastic bags and transported to the laboratory. All samples were analysed by ACME laboratories in Vancouver, Canada. Sample preparation is a 0.5 g soil sample of <180 µm size leached by 2-2-2HCl-HNO_3-H_2O method, after 1 hour at 95 ºC, the solution was analysed by ICP-ES and ICP-MS for 53 elements. International standards STD SO-18 and STD DS7 were used to control the accuracy and precision of the analysis.

The maximum errors for As, Sb and Hg were calculated at less than 5, 4 and 12 % respectively. The method proposed by Thompson Howarth, 1976 [18] was used to evaluate the error and precision of analysis by using repetitive samples.

Also, 2 topsoil and 2 agricultural soil samples were analysed by a sequential leach method which has been developed and used extensively in recent years [19-24]. These soil samples were analysed as follows in six stages:

Stage 1- **SLW** group: In this stage, samples are leached by distilled water in order to determine the water-soluble components,

Stage 2- **SLE** group: In this stage, samples are leached by 1 M sodium-acetate for extraction of cations adsorbed by clay minerals and carbonates,

Stage 3- **SLO** group: Samples are leached by 0.1 M sodium pyrophosphate for extraction of elements adsorbed by humic and fulvic materials,

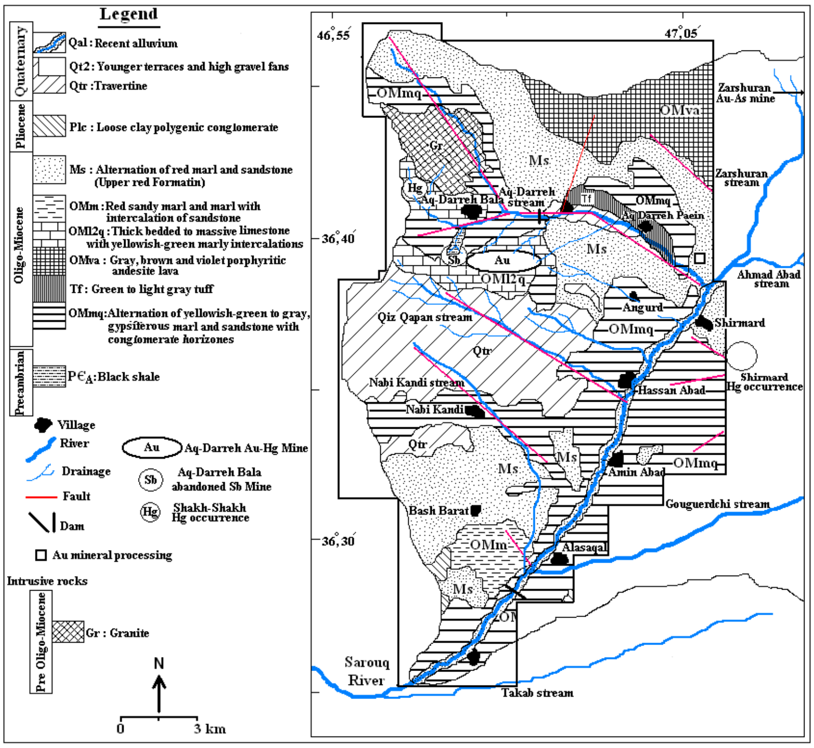

Fig. 2. Geological map and drainage basin of Aq-Darreh mining district and downstream environment [2]

Stage 4- **SLM** group: Samples are leached by 0.1 M hydroxylamine for extraction of elements adsorbed by amorphous Mn hydroxides.

Stage 5- **SLF** group: Samples are leached by 0.25 M hydroxylamine for extraction of elements adsorbed by amorphous Fe hydroxides and crystalline Mn hydroxides.

Stage 6- **Residual fraction**: That is calculated by subtracting the sum of the element concentration values in five groups from the total concentration of the toxic element.

Furthermore, because of the economic considerations, 11 samples from topsoils and 7 samples from agricultural soils from among all samples were analysed for mineral determination by XRD analysis in Kanpajouh mineralogical laboratory in Tehran-Iran.

4. Results and discussion

A summary of analytical results for As, Sb and Hg concentrations in the topsoil and agricultural soil samples of the study area shown in Table 1, and the spatial distribution of these elements is shown in Figs 4, 5 and 6. The results of total concentrations of As, Sb, and Hg in the selected topsoil and agricultural soil samples and the sequential leaching results of these elements are presented in Tables 2 and 3.

Previous studies [2] have indicated that water and river-bed sediment of the Aq-Darreh River are highly polluted regarding As and Sb concentrations in water and As, Sb and Hg values in river-bed sediment.

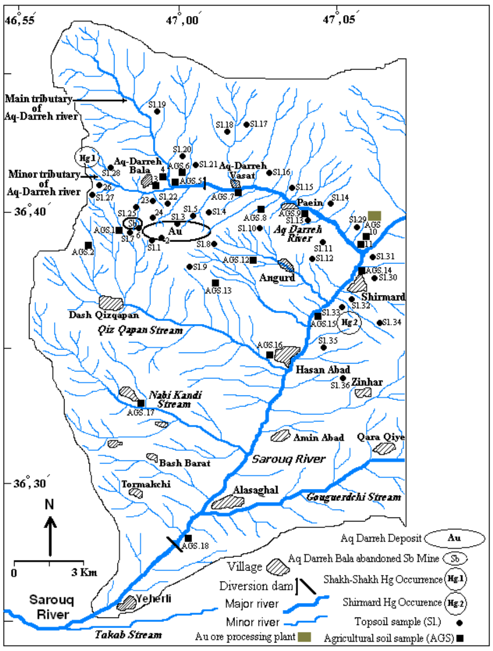

Fig. 3. Location map of sampling sites for topsoils and agricultural soils in the study area [2]

Table 1. Statistical summary of As, Sb and Hg concentration in topsoil and agricultural soil samples of the study area (all values in mg/kg)

Topsoils (n=36)				
Element	Mean	S.D.	Max.	Min.
As	1113.5	2287.27	9736.3 (sample Sl.1)	64.9 (sample Sl.19)
Sb	188.94	256.25	1247.01 (sample Sl.1)	24.02 (sample Sl.18)
Hg	2.368	4.084	15.355 (sample Sl.34)	0.136 (sample Sl.18)
Agricultural soils (n=18)				
Element	Mean	S.D.	Max.	Min.
As	257.9	349.57	1396.7 (sample AGS.5)	16.4 (sample AGS.3)
Sb	18.39	25.41	98.22 (sample AGS.5)	1.24 (sample AGS.3)
Hg	3.128	2.165	9.547 (sample AGS.15)	0.535 (sample AGS.17)

Table 2. Total concentrations and analytical results with proportion of toxic elements As, Sb and Hg in different groups of sequential leaches in the selected topsoil samples of the study area

	Sample	**Total Concentration**	**SLW group**	**SLE group**	**SLO group**	**SLM group**	**SLF group**	**Residual**
As	*Detection limit*	*0.1* ppm	*5* ppb	*100* ppb	*100* ppb	*100* ppb	*100* ppb	- ppb
	Sl.1	**9736.3**	104179 **(1.07 %)**	2327946 **(23.91 %)**	66209 **(0.68 %)**	703934 **(7.23 %)**	3918861 **(40.25 %)**	2615171 **(26.86 %)**
	Sl.25	**8303.2**	189313 **(2.28 %)**	1067791 **(12.86 %)**	19928 **(0.24 %)**	880969 **(10.61 %)**	3550449 **(42.76 %)**	2594750 **(31.25 %)**
Sb	*Detection limit*	*0.02* ppm	*1* ppb	*5* ppb	*5* ppb	*5* ppb	*5* ppb	- ppb
	Sl.1	**1247.01**	5861 **(0.47 %)**	74322 **(5.96 %)**	29180 **(2.34 %)**	43520 **(3.49 %)**	73574 **(5.90 %)**	1020553 **(81.84 %)**
	Sl.25	**358.43**	1864 **(0.52 %)**	29105 **(8.12 %)**	7204 **(2.01 %)**	14946 **(4.17 %)**	16954 **(4.73 %)**	288357 **(80.45 %)**
Hg	*Detection limit*	*5* ppb	*1* ppb	*5* ppb	*5* ppb	*5* ppb	*5* ppb	- ppb
	Sl.1	**11427**	12 **(0.11 %)**	534 **(4.67 %)**	116 **(1.02 %)**	365 **(3.19 %)**	301 **(2.63 %)**	10099 **(88.38 %)**
	Sl.25	**6245**	6 **(0.09 %)**	427 **(6.84 %)**	47 **(0.76 %)**	211 **(3.38 %)**	196 **(3.14 %)**	5358 **(85.79 %)**

According to the analytical results, the highest concentration of the As, Sb and Hg elements in topsoils of the study area are found in the Aq-Darreh mining district and downstream environment (Figs. 4, 5 and 6). The lowest concentration of As, Sb and Hg are seen in samples Sl.18, Sl.19, Sl.20 and Sl.28, also located outside of the mineralised and undisturbed areas. The highest concentration of As, Sb and Hg outside the mining area have been measured in topsoil samples Sl.34, Sl.33 and Sl.32, and could be related to the Hg anomaly located in south of the Shirmard Village (Fig. 3). The agricultural soil samples with high As, Sb and Hg concentrations are mainly located in mining areas and the lands downstream of the mine site. Low concentrations of As, Sb and Hg in agricultural soils partially belong to the lands irrigated by unpolluted waters (main tributary of the Aq-Darreh River and spring waters). The dry farmlands far from the mining areas also show low concentrations of potentially toxic elements. Pollutant elements, particularly As, may be transferred to cultivated lands by flood from the mines and ore processing plants [25]. The guideline levels (adopted from Smedley and Kinniburgh [26], Siegel [27], Kabata-Pendias and Mukherjee [28] and Appleton et al., [29]) and the concentration ranges of As, Sb and Hg elements in topsoils and agricultural soils of the study area are shown in Table 4. It can be found from Table 4 that both topsoils and agricultural soils are highly contaminated with As and Sb while Hg has a low concentration. The As-bearing minerals in the study area have been found to be arsenian pyrite, melnikovite and arsenopyrite and the most common Sb-bearing mineral is stibnite [2], therefore a higher concentration of As and Sb in soils is related to their higher solubility and lower stability against chemical weathering. On the other hand, cinnabar is a resistant mineral against weathering and this is why Hg has a lower concentration in soils. The results for topsoil and the agricultural soil samples of the study area compared with guideline values and permissible concentrations of toxic elements (Table 4) indicates As and Sb contamination in many soil samples. The topsoils and agricultural soils have low concentrations of Hg. Also, the geo-accumulation index (I_{geo}) [30] was used to quantify metal accumulation in the topsoil and agricultural soil samples of the study area. This index is expressed as: $I_{geo} = \log_2(C_n/1.5B_n)$, where C_n = concentration of the element in the soil fraction (<2 μm), B_n= geochemical background value of the element in argillaceous rocks or average shale according to Turekian and Wedepohl [31]. The constant 1.5 allows us to analyse natural fluctuations in content of a given element in the environment and very small anthropogenic influences. In Table 5, the different geo-accumulation index classes, along with the associated soil qualities as proposed by Muller [30] are shown. Calculation of geo-accumulation index for soils in the region indicates that As and Sb show contamination in classes 5 and >5 in all of the topsoil samples around the Aq-Darreh Au deposit and Aq-Darreh Bala abandoned Sb mine and downstream environment, while Hg is included in class 3 in the mentioned areas and also around Shirmard Hg occurrence (Figs. 3 and 6). The agricultural lands of Aq-Darreh Vasat and Aq-Darreh Paein villages, irrigated by the minor

Table 3. Total concentrations and analytical results with percents of toxic elements As, Sb and Hg in different groups of sequential leaches in the selected agricultural samples of the study area

	Sample	**Total Concentration**	**SLW group**	**SLE group**	**SLO group**	**SLM group**	**SLF group**	**Residual**
As	*Detection limit*	*0.1* ppm	*5* ppb	*100* ppb	*100* ppb	*100* ppb	*100* ppb	- ppb
	AGS.5	**1396.7**	16760 **(1.20 %)**	269144 **(19.27 %)**	87015 **(6.23 %)**	228081 **(16.33 %)**	640108 **(45.83 %)**	155592 **(11.14 %)**
	AGS.10	**949.4**	22406 **(2.36 %)**	463402 **(48.81 %)**	55160 **(5.81 %)**	114877 **(12.10 %)**	223014 **(23.49 %)**	70541 **(7.43 %)**
Sb	*Detection limit*	*0.02* ppm	*1* ppb	*5* ppb	*5* ppb	*5* ppb	*5* ppb	- ppb
	AGS.5	**98.22**	512 **(0.52 %)**	13180 **(13.42 %)**	6453 **(6.57 %)**	8191 **(8.34 %)**	11315 **(11.52 %)**	58569 **(59.63 %)**
	AGS.10	**13.72**	51 **(0.37 %)**	1173 **(8.55 %)**	662 **(4.83 %)**	508 **(3.70 %)**	849 **(6.19 %)**	10477 **(76.36 %)**
Hg	*Detection limit*	*5* ppb	*1* ppb	*5* ppb	*5* ppb	*5* ppb	*5* ppb	- ppb
	AGS.5	**6358**	10 **(0.16 %)**	179 **(2.82 %)**	88 **(1.38 %)**	100 **(1.57 %)**	116 **(1.83 %)**	5865 **(92.24 %)**
	AGS.10	**3684**	8 **(0.22 %)**	83 **(2.25 %)**	32 **(0.86 %)**	60 **(1.64 %)**	120 **(3.26 %)**	3381 **(91.77 %)**

Table 4. The guideline levels and the total and average range (in parenthesis) of As, Sb and Hg concentrations in topsoils and agricultural soils of the study area

Contaminant	Guideline levels in topsoils (ppm)	Guideline levels in agricultural soils (ppm)	Concentration ranges (ppm) in topsoils of the study area	Concentration ranges (ppm) in agricultural soils of the study area
As	0.1 – 55, mean = 7.2 [26]	5 – 10 [26]; 5.5 – 12 [27]	64.9 – 9736.3 (average = 1113.5)	16.4 – 1396.7 (average = 257.9)
Sb	0.05 – 2 [28]	0.05 – 2 [28]	24.02 – 1247.01 (average = 188.94)	1.64 – 98.22 (average = 18.39)
Hg	8 [29]	1 – 6.6 [29]	0.013 – 1.142 (average = 0.23)	0.071 – 0.954 (average = 0.312)

Table 5. I_{geo} classes with respect to soil qualities [30]

I_{geo}	I_{geo} class	Sample quality
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 6. Contribution of geochemical background and anthropogenic sources (in percent) on topsoil and agricultural soil pollution in the study area

Source	**Topsoils**			**Agricultural soils**		
	As (ppm)	**Sb** (ppm)	**Hg** (ppb)	**As** (ppm)	**Sb** (ppm)	**Hg** (ppb)
Total concentration (Average)	2803.4 (100 %)	355.22 (100 %)	3703 (100 %)	901.4 (100 %)	61.49 (100 %)	4752 (100 %)
Natural Contamination (Geochemical background)	429.7 **(15.33 %)**	79.02 **(22.25 %)**	356 **(9.61 %)**	98.8 **(10.96 %)**	3.98 **(6.47 %)**	2596 **(54.63 %)**
Anthropogenic (Mining activities)	2373.78 **(84.67 %)**	276.20 **(77.75 %)**	3347 **(90.39 %)**	802.67 **(89.04 %)**	57.51 **(93.53 %)**	2156 **(45.37 %)**

tributary derived from the Aq-Darreh River downstream of the Au ore-processing plant are also highly contaminated with As and Sb (classes 5 and >5). In these areas, the soils are classified in class 2 regarding Hg contamination, and Shirmard village soils falls into class 3.

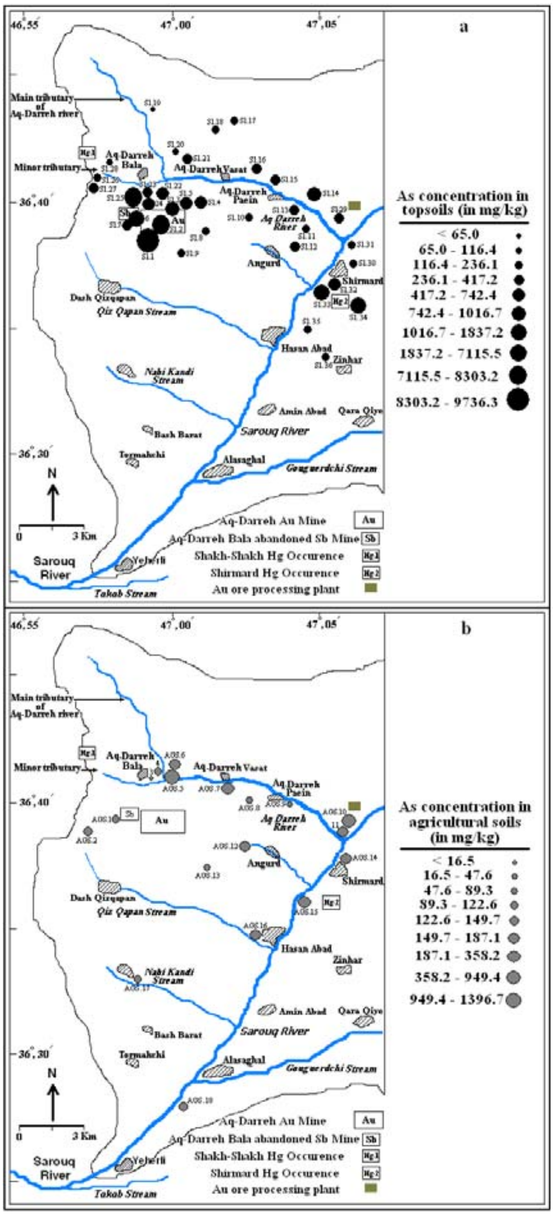

Fig. 4. Spatial distribution of As concentrations in the soil samples of the study area, (a) in topsoils, (b) in agricultural soils.

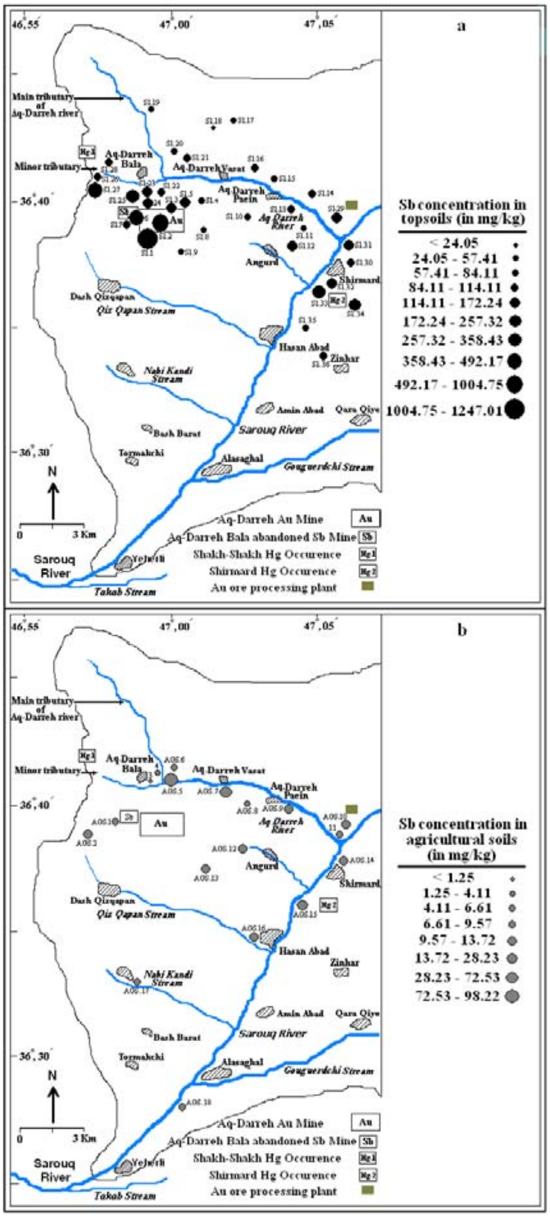

Fig. 5. Spatial distribution of Sb concentrations in the soil samples of the study area, (a) in topsoils, (b) in agricultural soils.

There is a strong positive correlation between As and Sb (0.858), Fe (0.766), Hg (0.626), S (0.548); between Sb and As (0.858), Fe (0.696), S (0.630), Hg (0.617); and also between Hg and Ca (0.774), Fe (0.758), As (0.626), Sb (0.617). Also, Fe shows a positive correlation with most of the trace elements in topsoils. These correlations indicate that As and Sb in topsoils are related to iron oxy-hydroxides mineralogical phases and also to As and Sb sulphide minerals. The correlation of Hg with these elements indicates that it is associated with carbonate, iron oxide and hydroxide minerals and sulphides containing As, Sb and Hg. The correlation between Fe and trace elements may be a relevant factor to take into account when determining background concentration levels and assessing the contamination extent of soil by trace elements, subject to anthropogenic activities [32]. The correlation between Fe and potentially toxic elements can indicate the fact that iron oxy-hydroxides (HFO) are the main transport agents for contaminants from mineralised and mining areas toward downstream sections i.e. soil environment [8]. The results of sequential leaching analyses of topsoils (Table 2) indicate that 40-43 % of the total concentration of As is bound to amorphous iron hydroxides and 12-24 % is bound to clay minerals (illite, kaolinite and montmorilonite) and carbonates.

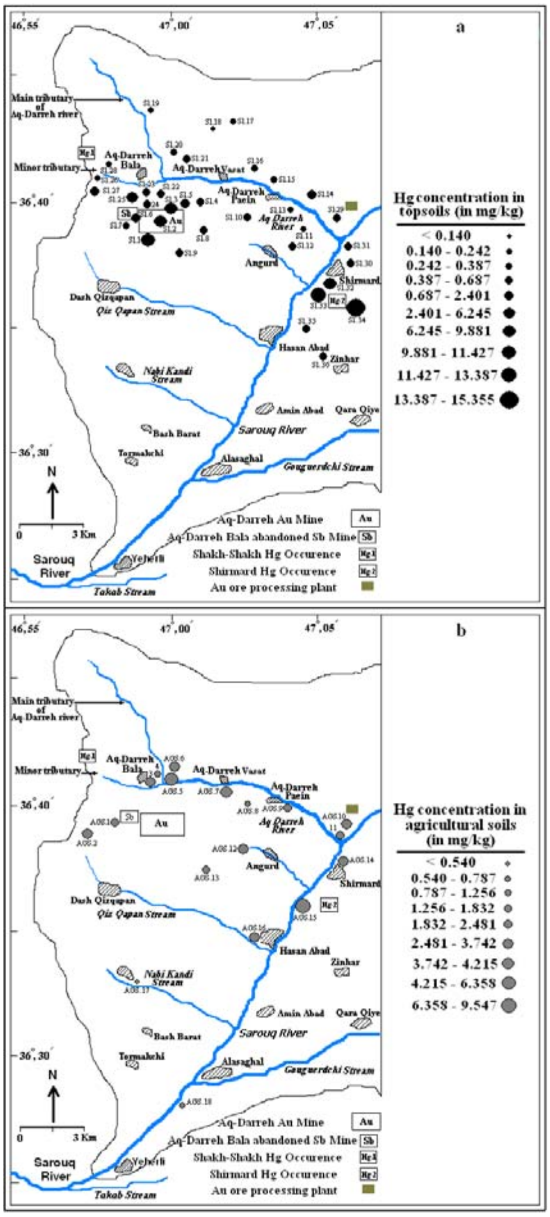

Fig. 6. Spatial distribution of Hg concentrations in the soil samples of the study area, (a) in topsoils, (b) in agricultural soils.

Antimony (Sb) shows 80-82 % of its total concentration is bound to the residual fraction (resistant minerals to weathering such as sulfides and oxides), 2-4 % of Sb is bound to amorphous iron hydroxides and 6-8 % is bound to clay and carbonate minerals. Similar to Sb, 85-88 % of the total concentration of Hg is bounded to residual fraction, 2-3 % of Hg concentration is bounded to amorphous iron hydroxides, 3-4 % of Hg is bounded to amorphous manganese hydroxides, and 4-7 % of the total concentration of Hg is bounded to clay and carbonate minerals. Sarkar et al., [33, 34] reported that Hg in soils is mainly bound to kaolinite and gibbsite.

The sequential leaching analyses of agricultural soils indicate that 23-46 % of the As total concentration is bound to iron hydroxides and 19-48% of As is bound to clay minerals and carbonates, while only 12-16 % of the total As concentration is bound to amorphous manganese hydroxides and 6% to organic materials.

Results of sequential leaching analysis (Table 3) showed that 60-76% of Sb total concentration is bound to residual fraction in agricultural soils, indicating the presence of stibnite in their composition. Sixty to 76 % of Sb concentration is bound to residual fraction, 8-13% to clay minerals and co-precipitated on carbonates, 6-11% to iron hydroxides, 3-8% to amorphous manganese hydroxides and the rest (5-7%) is bound to organic materials.

Ninety two percent Hg concentration is bound to residual fraction; 2-3 % to clay minerals and co-precipitated on carbonates, 2-3 % to iron hydroxides, 3-8 % to amorphous Mn hydroxides, and up to 1 % to organic materials.

Correlation coefficient results show sharp differences between agricultural soil and topsoil samples. In agricultural soils arsenic has positive correlations with Ca (0.770), Sb (0.643) and S (0.626); Sb has positive correlations with S (0.697), Hg (0.676) and As (0.643); and Hg have a positive correlation with Sb (0.676), Pb (0.593) and Mn (0.557). These differences are partially related to the mineralogical composition of agricultural soils compared to topsoils. From XRD analyses, agricultural soil samples are composed of calcite, clay minerals (illite, kaolinite and montmorilonite), quartz, geothite, and some amorphous phases, ferrihydrite and dolomite, while topsoil samples are composed of quartz, calcite, clay minerals (montmorillonte, illite, and kaolinite), and some goethite, scorodite, jarosite, albite, organic matter, barite, lepidochrosite, chlorite and gypsum.

Strong, positive correlations between As and P (0.785) may be due to super-phosphate fertilizers used in cultivated lands. It has been reported that phosphorous can increase the solubility of As in soils [35, 36]. A strong positive correlation between Sb and S may be due to stibnite (SbS_2) in topsoils.

Environmental pollution is generally the combination of natural contamination (geochemical background) and anthropogenic sources. In the study area, anthropogenic sources are mainly restricted to mining activities [2].

Background concentrations of elements in soil are highly dependent on the mineralogical composition of the parent material and on the weathering processes that have led to its formation [37-44], and also on soil particle size, clay and organic matter content [39, 45, 46]. Consequently, the natural concentration of elements in soil varies widely, making it inappropriate to use universal background levels for assessing the extent and risks of trace metal contamination in a specific soil type [32]. Therefore, although natural background concentrations in soil have been investigated in many countries and have laid the foundations for understanding natural element variation and in assessing soil contamination in many countries in Europe [47, 48], the USA [49, 50, 51] and China [52], it is still necessary to estimate local background concentrations and spatial distribution characteristics of elements in soil, and the factors affecting their evolution in a specific area.

Many studies adopt the geometric mean as the background value for elements in soil [38, 44, 53], because it is assumed to reflect the concentration trend of element distribution quite well [37, 44].

In the Aq-Darreh mining district, geochemical background values were measured by the methods introduced by Kelley and Taylor [54] and Galuszka [55]. According to this method, in order to determine the geochemical background, the mean or median values of concentration of elements in undisturbed or unpolluted samples which are located outside of the mining area were selected as background values. Hence the topsoil samples Sl.11 to Sl.21 and agricultural soil samples AGS.3, AGS.4 and AGS.6 (Fig. 3) were considered as the geochemical background of this area (Table 6). On the other hand, considering that topsoils and agricultural soils quality in mining and disturbed areas reflects a combination of both geogenic and anthropogenic sources [56, 57], subtracting the geochemical background values from the mean values measured in mining and disturbed areas gives rise to the concentration reflecting the anthropogenic source (Table 6).

Since the parent materials of the topsoil samples in the mining area and mineralised zones are the same and are composed of limestone, marl and some sandstone, the total concentration of potentially toxic elements in the samples Sl.1 to Sl.7 and Sl.22 to Sl.25 are considered to be both natural contamination and anthropogenic sources (Fig. 3). Geometric mean values of As, Sb and Hg concentrations in these samples were calculated as follows: For As: 2803 ppm, Sb: 355 ppm and Hg: 3703 ppb. Total concentration of toxic elements in agricultural soil samples AGS.5, AGS.7, and AGS.10 (Fig. 3) originate from natural contamination and anthropogenic sources, geometric mean values of As, Sb and Hg concentrations of these samples are 901 ppm, 61 ppm and 4752 ppb respectively. Based on these results the contribution of geochemical background and mining activities are listed in Table 6.

5. Conclusions

According to the guideline levels (Table 4) many topsoil and agricultural soil samples of the study area are polluted regarding As and Sb, While all soil samples have Hg concentration in permissible levels. All polluted agricultural soil samples are located in sites in which the lands had been irrigated by the Aq-Darreh and Sarouq Rivers or samples situated downwind of the Aq-Darreh ore processing plant (Fig. 3). The agricultural soil contamination in the AGS.11 site is considered to be caused by leakage of the tailing dams of the Au ore processing plant.

The results of XRD analysis of topsoil samples and the strong positive correlation between As, Sb and Hg with Fe and S indicate that the concentration of these elements is related to primary sulfide minerals which are weathered and oxidised to secondary minerals such as scorodite, jarosite and Fe oxy-hydroxides [2].

Due to the presence of calcite as a main phase in XRD analysis of soil samples it is concluded that acid-leaching of the soil is impossible and clay minerals such as montmorillonite, illite and kaolinite also prevented the leaching process [8].

According to the values calculated for I_{geo}, most of the soil samples are highly, to very highly, contaminated in As and Sb. However, Hg shows low contamination in most of the samples.

Natural contamination and anthropogenic sources contribution in the pollution of topsoil and agricultural soils (Table 6) indicates that mining activities have played a significant role in soil pollution and in increasing As, Sb and Hg values in topsoils and As and Sb values in agricultural soils. Hg in agricultural soils is due equally to geochemical background and mining activities. The higher impact of natural contamination of Hg in agricultural soils compared to topsoils is due to the higher density and content of Hg entered in cultivated farmlands. Also, the very low solubility of cinnabar in neutral to slightly alkaline waters [58] as is in the study area [2], concentrates Hg in soils and is not removed.

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