

## Effects of Abandoned Arsenic Mine on Water Resources Pollution in North West of Iran

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### ABSTRACT

**Background:** Pollution due to mining activities could have an important role in health and welfare of people who are living in mining area. When mining operation finishes, environment of mining area can be influenced by related pollution e.g. heavy metals emission to water resources. The present study was aimed to evaluate Valiloo abandoned arsenic mine effects on drinking water resources quality and possible health effects on the residents of mining area in the North West of Iran.

**Methods:** Water samples and some limited composite wheat samples in downstream of mining area were collected. Water samples were analyzed for chemical parameters according to standard methods. For determination of arsenic in water samples, Graphite Furnace Atomic Absorption Spectrometric Method (GFAAS) and for wheat samples X – Ray Fluorescence (XRF) and Inductively Coupled Plasma Method (ICP) were used. Information about possible health effects due to exposure to arsenic was collected through interviews in studied villages and health center of Herra City.

**Results:** The highest concentrations of arsenic were measured near the mine (as high as 2000 µg/L in Valiloo mine opening water). With increasing distance from the mine, concentration was decreased. Arsenic was not detectable in any of wheat samples. Fortunately, no health effects had been reported between residents of studied area due to exposure to arsenic.

**Conclusion:** Valiloo abandoned arsenic mine has caused release of arsenic to the around environment of the mine, so arsenic concentration has been increased in the groundwater and also downstream river that requires proper measures to mitigate spread of arsenic.

**Keywords:** Arsenic mine; Pollution; Water; Health; Hydrogeochemistry; Iran

### Introduction

Based on the definitions, environmental pollutants e.g. heavy metals, which lead to disease, are those substances that introduce in food, air, water, soil, or the home environment originally from human [1-3]. According to available data, the total

environmental burden of disease for high-income, developed countries may range from as low as 1 – 5% to as high as 15 - 22% [4]. Between pollution sources of the environment, mining activities has an important role in health and welfare of people

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who are living in mining area. Although mining activities have considerable effects in job creation and economic of a region, however such activities not only during operation phase, but also after mine closure can result in pollution of soil, water, plants etc. When the mining operation will end, activities in the region be terminated, but its effects remain, and if not controlled and reconstructed properly, environment of mining area can be influenced by related pollution e.g. heavy metals [3,5], therefore, it is necessary to take corrective measures to reduce related risks of mines [6].

From geological aspects, arsenopyrite is the most abundant ore mineral of the arsenic and arsenic can be achieved from roasting of arsenopyrite as well as smelter dust of some metals like as gold, copper, and lead [7]. Global resources of copper and lead contain approximately 11 million tons of arsenic. World total production of arsenic trioxide has been 59000 tons in 2007 [8]. Arsenic is highly toxic mineral that founds in the earth crust and can introduce to food chain via soil, water, and plants [9, 10]. Consumption of water contaminated by arsenic is one of the main sources of human exposure [11, 12]. It is reported that contamination of groundwater and drinking water by arsenic and related human health outcomes is a growing global concern [13]. Among arsenic species, inorganic As (v) and As (III) in water have highest toxicity comparing to organic species [9]. Chronic exposure to arsenic via drinking water causes different disorders like as skin lesions (hyperpigmentation and keratosis) [14,15], blood pressure [16], diabetes mellitus, internal and skin cancers [17], cardiovascular diseases [18], neurological disorders [14], pregnancy [19], metabolism [20], genetic [21] and etc. Considering toxicity of arsenic, attention to arsenic mines during operation phase and after closure takes more importance.

Valiloo arsenic mine has located in the North West of Iran (Heris city) (Fig.

1:a). Mining activities in which started since 1933 have been continued until 1997 [22]. The main objective of this study was to evaluate Valiloo abandoned mine effects on drinking water resources quality and possible health effects between residents who are living in mining area.

## Materials and Methods

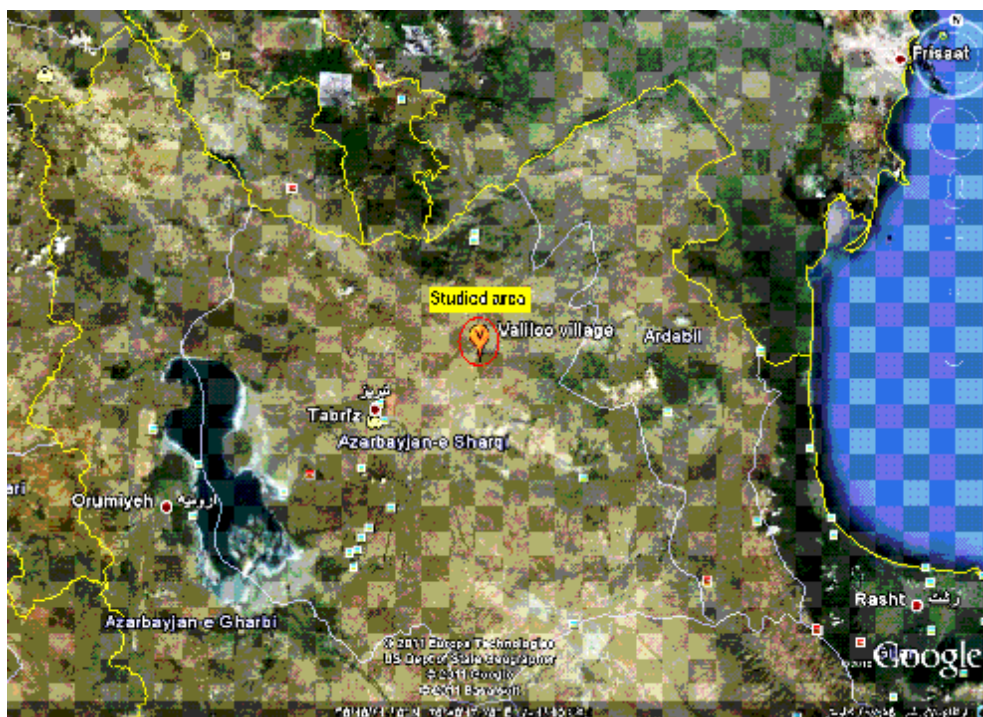
The study area, with surface over 95 km<sup>2</sup> is located in 103 km North East of Tabriz, Center of East Azerbaijan Province. This area is a part of geological map of Khajeh (Khoja) [22].

To evaluate impact of abandoned Valiloo arsenic (Zarnikh) mine, water samples was collected in mining area (around and downstream of it). The samples include sample from inside the mine opening, drinking water sources of villages around the mine and non-potable surface and groundwater as following: 5 samples from wells, 3 samples from surface water, 2 samples of mine drainage water and 4 samples of water distribution network especially in downstream of the mine (Fig. 1:b). Polyethylene acid washed containers with volume of 1 liter was used for sampling. Prepared samples were transferred to the environmental chemistry laboratory of faculty of health and nutrition at Tabriz University Of Medical Sciences during several hours and were analyzed for physical and chemical parameters (hardness, alkalinity, electric conductivity, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> according to standard methods for the examination of water and wastewater [23]. To determine the arsenic concentration of samples, Graphite Furnace Atomic Absorption Spectrometric Method (GFAAS) Buck scientific model was used.

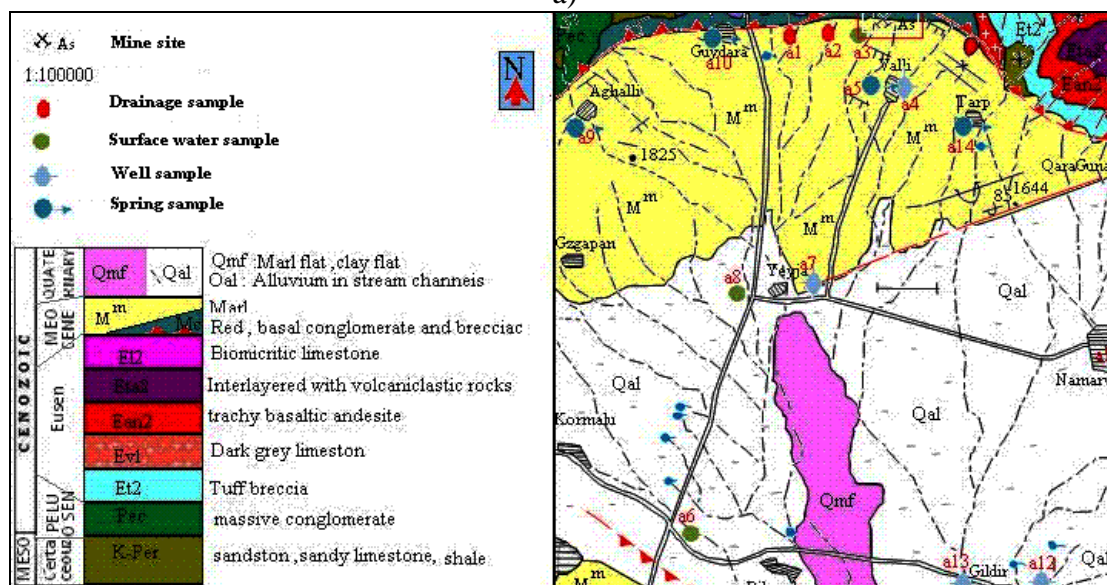
Results of water samples chemical analysis were processed by Hydrochem and Surfer-8 software and Piper and Wilcocks diagrams to determine the regional water quality and hydro geochemistry of aquifers.

In order to ensure the amount of arsenic in wheat cultivated in the region as a limited pilot study, composite samples of wheat from different parts of 4 fields, were collected and analyzed for presence of As and also Ba, Cu, Zn, Pb, Ni, Ce, La, Nb and Zr [24]. The samples were dried, powdered and finally analyzed with XRF [25] and ICP methods.

For collecting information about possible health effects due to exposure to arsenic e.g. skin lesions (hyperpigmentation and keratosis), local investigations were performed through interviews in studied villages and health center of Herra City.



a)



b)

**Fig. 1:** A: Location of study area on map of Iran (source: Google earth) , b: Sampling points on geological map of Khoja (1:100000)

## Results

According to our field observations for geological aspects, host rock minerals introducing arsenic in Valiloo region are sand stone, conglomerate, and red Miocene silt that suffered from alteration near mineral zones construction. In faults and fractures of Valiloo region, small or big streaks contain orpiment and realgar (arsenic bearing material) is frequently observed. Deposit of arsenic in Valiloo is epithermal sub-volcanic type.

Results of water samples analysis are presented in Table 1. Based on the table, hardness was measured from 100 to 1500 mg/L  $\text{CaCO}_3$ . For electric conductivity, range was measured from 271 to 4600  $\mu\text{s}/\text{cm}$  and for total dissolved solids (TDS) from 168 to 2852 mg/L. pH value was  $> 7$  in all of samples. The highest concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was in mine tunnel and For  $\text{Na}^+$  and  $\text{Cl}^-$  was in Yengjeh village water.

Arsenic concentration ranged from zero in some villages up to 2000  $\mu\text{g}/\text{L}$  in mine opening. Fig. 2 shows distribution of arsenic concentration in the studied region. As can be seen in figure, the highest concentrations of arsenic were inside and near the mine that with increasing distance from the mine, the concentrations were decreased.

Based on Wilcox diagram, most of water in the region was located in class  $\text{C}_2\text{S}_1$  that are almost suitable for agriculture. However, deep-well water (A13) in the southern region has significantly higher salinity, placed in the class  $\text{C}_3\text{S}_2$ . Surface water and water of mine tunnel have high salinity so are not suitable for agriculture. Consid-

ering sodium absorption rate (SAR), in 93% of samples, SAR was  $< 10$  that means excellent. However for EC, 33% of samples was unsuitable ( $2250 < \text{EC} < 2500 \mu\text{s}/\text{cm}$ ).

Most of waters in Valiloo district are bicarbonate Calcic type that have temporary hardness. Some samples are calcium chloride and calcium sulfate with permanent hardness and one sample was brine with high content of NaCl. Considering type of stone of piper diagram, it appears that Valiloo region waters are different and also have been affected by stone types. A group of water which include permanent hardness and rich in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  have located in region 1 of piper diagram and showing water have passed from rocks containing gypsum (sulfate). Other waters with temporary hardness, which are rich in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , are located in regions 2, 3 and 5 of piper diagram that originated from calcareous, dolomite stones.

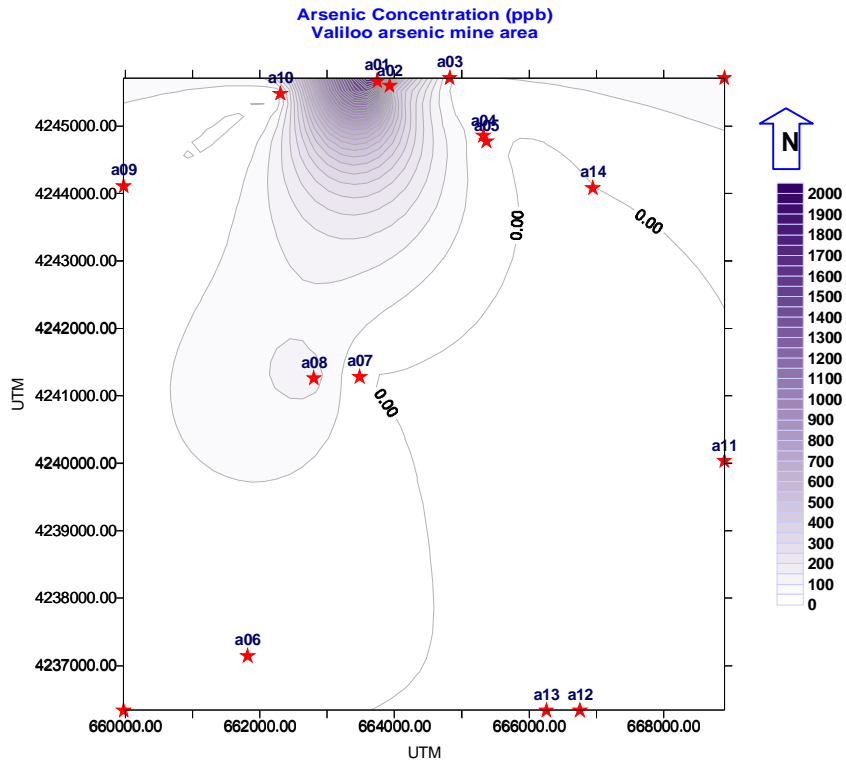
Waters of saline area are rich in  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , which located in region 6, 7 and 8 of piper diagram. Those waters have originated and passed from the Chile and brine rocks.

Fig. 3 illustrates that arsenic was not detectable in none of the wheat samples. However, other analyzed element concentrations were higher in comparison with standard levels.

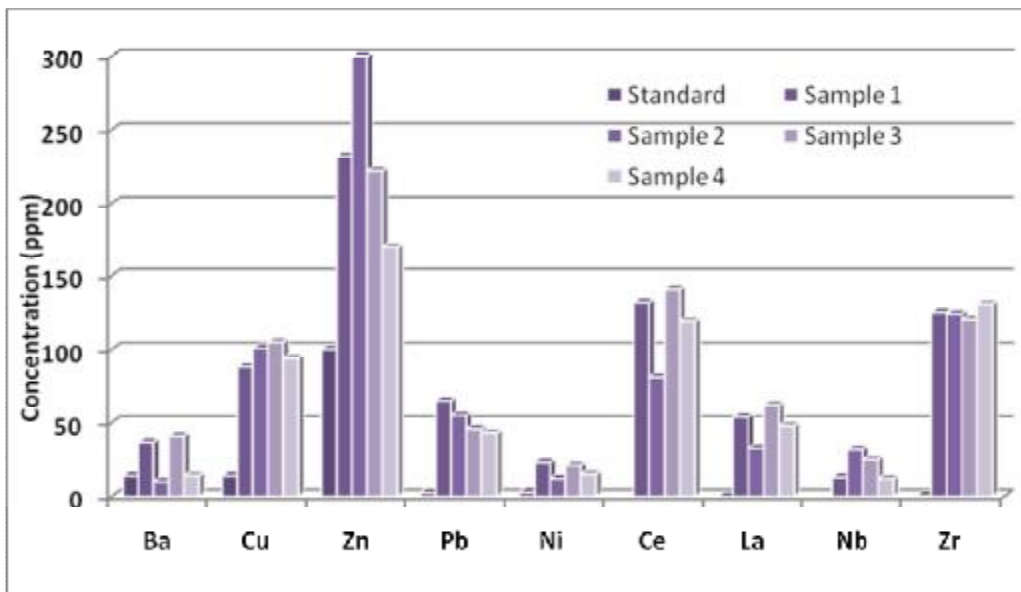
Fortunately, during the interviews with the residents of studied villages, none of persons complained from any routine arsenic-related health effects.

**Table 1: Quality of analyzed water samples in Valiloo abandoned arsenic mine area**

Sample Code	Location	U/IM		Cations (mg/l)						Anions (mg/l)						Hardness CaCO <sub>3</sub>	TDS (mg/l)	FC (µb/ho/cm)	pH	As (µg/l)
		X	Y	Ca	Mg	Na	K	HCO <sub>3</sub>	CO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	Cl	NO <sub>3</sub>	F	SO <sub>4</sub> <sup>2-</sup>	Cl					
A01	Mine opening 1	663743	4245665	304	179.82	180	18	263.5	20	1605	24	1.5	5	1500	1798	2800	8.4	2000		
A02	Mine opening 2	663926	4245395	38.4	73.87	110	3	278.16	24	340	54	29	1.5	400	793	1300	8.45	500		
A03	Sool darab Valley	664819	4245712	35.2	19.44	28	1.8	180.65	12	45.6	10	1	0.3	168	269	475	8.43	35		
A04	Valiloo village	663320	4244855	19.52	12.44	21	0.1	146.4	-	8.5	4	6.85	0.8	100	159	310	8.2	35		
A05	Valiloo well	665366	4244776	67.2	40.82	110	8	585.6	-	70	30	4.4	0.3	336	732	1200	7.9	10		
A06	Surface water near bridge	661815	4237144	27.2	143.85	450	22	366	-	818	440	1.6	0.4	660	1645	2650	8.13	9.5		
A07	Yengleh village	663482	4241279	36.8	118.58	450	8	414.8	28	598	452	15.88	0.3	580	1530	2500	8.5	0		
A08	River sample	662802	4241265	24	82.62	1150	4.5	683.2	80	1647	530	-	1.6	400	2852	4600	8.9	125		
A09	Agha-ali village	659975	4244108	48	51.5	19	3.5	366	20	47	20	2.59	0.1	332	354	571	8.48	3.5		
A10	Goydareh village	662304	4245480	28.8	33.04	15	1	209.84	20	21	10	2.66	0.07	208	244	294	8.3	0		
A11	Mamanvar village	668902	4240334	148.8	60.26	78	2	190.32	-	494	98	19.33	0.6	620	781.82	1261	7.96	0		
A12	Gildir viloge	660756	4236340	88	8.7	80	2	244	-	102	98	15.8	0.2	256	463	747	8	0		
A13	Deep well	660256	4236340	30	42	280	4	335.5	4.87	269.53	195.3	23.018	-	250	1152.7	1670.5	7.68	0		
A14	Laraf village	666919	4244082	36.8	11.66	11	0.5	170.8	-	11	10	6.18	0.01	140	168	271	7.9	0		



**Fig. 2:** Distribution of arsenic concentration in studied area



**Fig. 3:** Concentration of analyzed elements in composite wheat samples of Valiloo area in comparison with standard levels

## Discussion

Different researches in the world have been conducted for presence of arsenic in the environment [26], environmental

pollution, and health effects of different mines and mining activities. Many of these investigations have reported pollution of

soil, plants and water resources to arsenic and other heavy metals [27-33].

In the present study, we investigated probable water pollution and its health affects due to Valiloo abandoned arsenic mine. Study showed that in water which accumulated in tunnel of mine opening, high concentration of arsenic (200 folds higher than national drinking water standard [34] (MCL)), high TDS, hardness and EC was present. Also in groundwater around the mine, concentration of arsenic was as high as 50 folds > MCL. It is clear that if such water introduce to the surface water of region, arsenic pollution will be dispread to far distance. As a result, proper actions should be considered for preventing this contamination. Considering drinking water standards, springs around the Valiloo mine area are not potable.

In surface water current in valley between Valiloo village and mine as well as in water network of this village, concentration of arsenic was 35µg/L. However, in well water in Valiloo Village, concentration was about 10µg/L. In water sample of a river downstream the mine; arsenic concentration was 125µg/L. This high concentration was due to transfer of arsenic bearing minerals from mine area to downstream by runoff and dissolution of arsenic. Low hardness of Valiloo drinking water and presence of arsenic shows that water originated from volcanic rocks with low mineral making [35, 36]. Absence of arsenic in other analyzed water can be due to the role of natural iron compounds of soil in adsorption of arsenic as a natural barrier [37, 38].

Our study showed that water of villages, which placed in southern part of the region, had high concentration of magnesium sulfate and hardness comparing to the northern parts. Considering national drinking water standard [34], prolonged consumption of such water with mentioned quality can result adverse effects between residents. According to Herris City Health Center information, change of

drinking water quality in the region has occurred due to a shift of water supply form springs to wells. As a result, bladder and kidney problems and diarrhea has increased in the region. However, for better understanding of related problems organized research should be conducted by researchers. One of the limitations of present study was the lack of information about water quality over past years. Fortunately, according to performed investigations between residents of villages and health center through interviews, there were not disorders related to exposure to arsenic (e.g. hyperpigmentation and keratosis) between residents of mine area.

## **Conclusion**

According to the study, Valiloo abandoned arsenic mine has caused release of arsenic to the around environment of the mine and has increased arsenic concentration in groundwater and downstream river that requires proper actions to limit spread of arsenic. Although no adverse health effects related to arsenic were reported by residents during the study, however future studies should not be neglected.

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