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## A survey on heavy metals pollution in water resources of Kouh-e Zar Mining area (The West of Torbat Heydarieh, Iran)

Pouya Tahmasebi<sup>\*</sup>, Mohamad Hosein Mahmudy Gharai<sup>1</sup>, Fereshteh Ghasemzadeh<sup>2</sup>,  
Alireza Karimi Karouyeh<sup>3</sup>

<sup>1</sup>*Department of Geology, Ferdowsi University of Mashhad, Iran*

<sup>2</sup>*Department of Biology, Ferdowsi University of Mashhad, Iran*

<sup>3</sup>*Department of Soil Sciences, Ferdowsi University of Mashhad, Iran*

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### Abstract

Totally, eight samples of groundwater of the area were taken to test in order to studying the heavy metal pollution in Kouh-e Zar and eight heavy metal such as arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), Copper (Cu) Lead (Pb) and Zinc (Zn) were analyzed by ICP (Inductively Coupled Plasma- Optical Emission Spectrometer), wherein average of As and Cd in water resources were higher than the WHO standards. Then, the quality of water resources around the area was measured and assessed by qualitative indices of heavy metals MI, Cd, HEI and HPI. Five samples were non-potable water based on MI index and one sample of the studied area waters was in the category of high pollution based on Cd index. Cadmium and arsenic had a great role in MI and Cd indices high amounts. There are two main sources related to the presence of these two elements, one is interaction of water-rock and the other one is mining activities in the area, It is possible that over time and with increasing in concentrations of these elements in ground water, we have the environmental problems in the mentioned area. According to the point that long-term and continuous consumption of water resources containing heavy metals, will cause problems for human health, in this regard, it is recommended that more detailed examinations of the mining activity be done on the water resources of the region by sampling alternatively.

**\*Corresponding Author:** Pouya Tahmasebi ✉ [tahmasebipouya68@gmail.com](mailto:tahmasebipouya68@gmail.com)

## Introduction

“Heavy metal” is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4000 kg/m<sup>3</sup>, or 5 times more than water, and they are natural components of the earth’s crust (Hashim *et al.*, 2011). Heavy metal contamination is recognized as a major environmental problem and excessive use of heavy metals has led to rapid accumulation of these materials in the environment. Heavy metals are stable and persistent environmental contaminants since they cannot be decomposed or destroyed (Hassan *et al.*, 2010). Heavy metals can form toxic chemical species and contamination of environment by hazardous and toxic metals is harmful for human (Nriagu, 1988). Heavy metal concentrations in water resources depend on anthropogenic (mining and industrial and agricultural) activities and land resources (weathering and erosion of rocks) (Sargaonkar and Deshpande, 2003). Contamination with heavy metals such as cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) is a worldwide environmental problem (Muhammad *et al.*, 2011). Investigation of water contamination with HMs has become the prime focus of environmental scientists in recent years (Muhammad *et al.*, 2011). Water quality index (WQI) does not give the overall picture on the water quality just by itself (Chaurasia and Karan, 2014). In this regard different indices were used to assess heavy metal pollution of water resources. Four indices of water quality including, Cd (Contamination Degree), HPI (Heavy Metal Pollution Index), MI (Metal Index) and HEI (Heavy Metal Evaluation Index) were evaluated for water samples in this article. The mining areas soils have little stability and contain many heavy metals, as a result, their heavy metals can enter the water resources, the plant life cycle and food chains. So, study the water quality and degree of contamination of heavy metals in environment is necessary. This paper aims to assess the level of the mining activity on water resources of Kouh-e Zar Mining area using heavy metal pollution and metal indices and multivariate statistical methods.

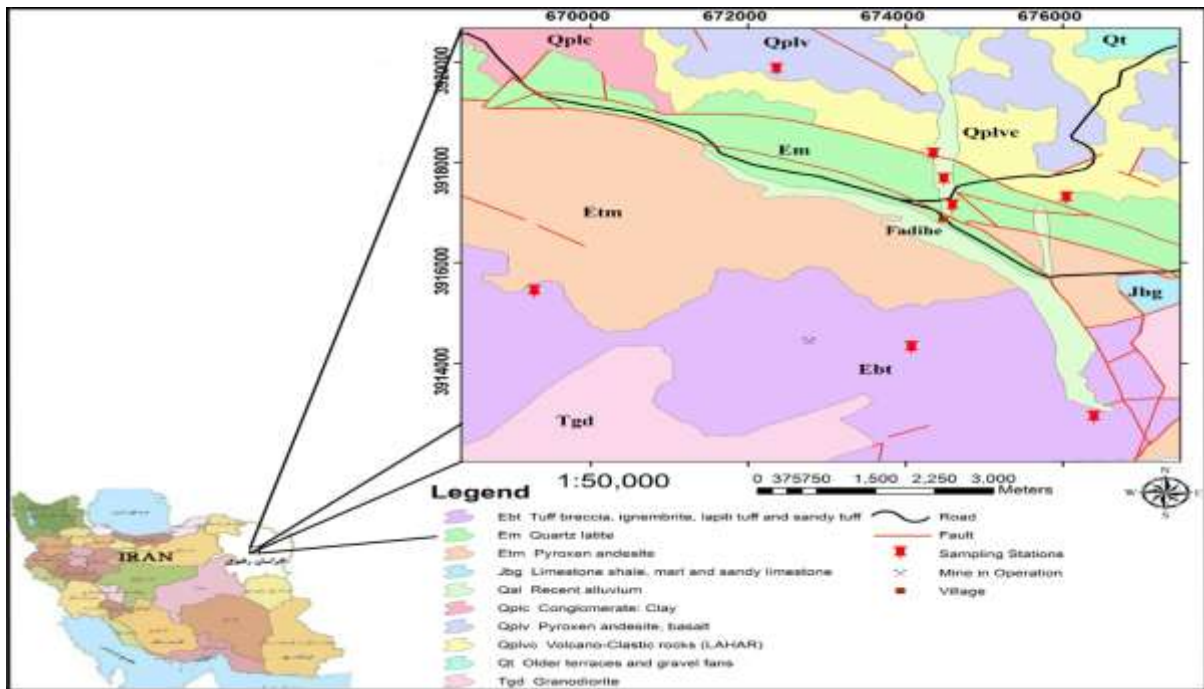
## Materials and methods

### *Geology of the study area*

Kouh-e-zar region is located in the central part of Khaf – Sangan volcanic – plutonic zone, in the 40 kilometers west of Torbat-e-Heydarieh in the Khorasan Razavi province. The vast explorations of the mentioned zone is caused the recognition of various Iron Oxide rich type of Cu-Au (IOCG) reserves, such as Kouh-e-Zar reserve (Mazlumi, 2008). The main drainages have an approximate north- south trend. The seasonal streams, are the most significant drain in this mountainous exploration zone, which join the Ghaleh Jugh Perennial stream and then enters into the Feiz Abad plain from the south side. Different types of Tuffs and felsic to intermediate lavas and also plutonic bodies with the composition range of Monzonite, Granodiorite and Granite are exposed in the area. Kouh-e-Zar area is located in in the northern mountains of Darouneh fault, with a E-W trend, which forms a distinguished narrow band in the north of mentioned fault (Fig. 1).

Transverse faults which are branched from Darouneh fault, compose the main structures of the area and play a significant role in the framework vein type and Hydrothermal breccia type of mineralization, which are related to the volcanic and plutonic rocks (Mazlumi, 2008). main drainages have an approximate north- south trend. The annual rainfall ranges from 300 to 350 millimeters, which reaches to 400 millimeters in the highlands of the north of area. The average of daily temperature ranges from 5 °C in the highlands of north of area to 17.5 °C in south of area and for the study area, it is estimated a bit more than 12.5 °C. The amount of annually evaporation from the evaporation basin, is estimated about 2400 millimeters. The study area is located in a semi dry and cool climate (Mazlumi, 2008).

In order to assess the heavy metal indices of the study area (surrounding areas of Kouh-e Zar), groundwater samples from various resources such as springs, wells and qanats were collected (Fig. 1).



**Fig. 1.** Geological map of Kouh- e Zar area (modified from Feyz Abad 1:100000 map) and location of water samples (Behroozi, 1987).

Samples were collected in duplicates-one for heavy metal and the other for anion analyses. Samples were filtered as soon as they were collected using cellulose nitrate filter with pores of 0.45 micron diameter. Polyethylene plastic bottles were used as sample containers. New bottles were cleaned with strong-metal free acid. The containers were rinsed with sample water prior to collection. Sufficient air space was allowed and sample stored upright. Teflon lined caps were screwed on tightly to prevent leakage. Water samples for cations and heavy metal analyses were acidified with metal free  $\text{HNO}_3$  to a pH of 1- 2. The samples were stored between 1 °C and 4 °C on cool ice packs from the field to the Lab. for analyses. To measure pH, temperature and electrical conductivity of the samples, respectively, during the sampling devices such as, thermometers, pH meters (Pen pH Meter, model: AZ 8686) and EC meters (Pen Cond. Meter, model: AZ 8351) were used. Eight water samples were collected in order to determine the concentration of heavy metals, physical and chemical properties of samples in water resources. The heavy metal cations (As, Pb, Cd, Ni, Cu, Zn and Cr) and trace elements were analyzed using an ICP- OES (Inductively Coupled Plasma- Optical Emission

Spectrometer) at central laboratory of Ferdowsi University of Mashhad, Iran. In order to investigate the relationships between measured parameters, the correlation matrix was drawn by the software SPSS- Version 20.

## Results and discussion

### *Calculation of water quality indices*

To investigate the water quality, four indices were used individually in this study. Contamination Degree (Cd), Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI) and Metal Index (MI) were calculated for the water samples of study area.

### *contamination degree (Cd)*

In this index water samples are classified by calculating the degree of contamination in water samples (Backman *et al.*, 1998). Contamination degree by combining several parameters affecting water quality, investigates suitability of drinking water samples for domestic consumption. Contamination degree has to be calculated separately for each sample based on the exceeded parameters from standard values. Index is calculated by the equation (1):

$$Cd = \sum_{i=1}^n Cfi \tag{1}$$

Cfi in this regard can be obtained from the equation (2):

$$Cfi = \frac{CAi}{CNI} - 1$$

(2)

Cfi: Contamination factor for the ith parameter

CAi: Measured value for the ith parameter,

CNi: Standard allowed value for the ith parameter,

In this study, the authors have used all measured heavy metals so that the contamination degree can be used for comparing with other indices. Although water samples with heavy metal concentrations below the permissible limit may not pose a threat to water quality but, the authors considers necessary to calculate the current condition of the water samples accurately and so, this makes it possible for future researchers to compare their results with the values of this investigation. To determine the quality of water samples by contamination degree, values are categorized into three groups, which include low contamination ( $Cd < 1$ ), moderate contamination ( $1 < Cd < 3$ ) and high contamination ( $Cd > 3$ ).

**Table 1.** standard values, ideal values and weight of metals in the study area.

Parameter	W	S	I	MAC
As	0.02	50	10	50
Fe	0.005	300	200	200
Cd	0.3	5	3	3
Cr	0.02	50	50	50
Cu	0.001	1000	2000	1000
Ni	0.05	20	20	20
Pb	0.70	100	10	1.5
Zn	0.0002	5000	3000	5000

It should be noted that because this is the first study in the mentioned area, data are not normalized. To calculate this index, measured values of eight heavy metals such as Pb, Zn, Ni, Cd, As, Cu, Cr, Fe have been used. Calculated values of this index for the samples are presented in Table 4.

*heavy metal pollution index (HPI)*

This index was first suggested in 1996 that represents the overall quality of water which is based on heavy metals (Mohan *et al.*, 1996). The index is calculated based on the weighting the parameters that the weight value is between zero and one, points the importance of the parameters. Weight of the samples can be considered as inversely proportional to the standard value for each element that have been calculated and considered for each parameter previously (Horton, 1965). This index is calculated by the equations (3 and 4):

$$Qi = \sum_{i=1}^n \frac{\{Mi(-)Ii\}}{(Si - Ii)} + 100$$

(3)

Mi: Measured value for the ith parameter,

Ii: Ideal value for ith parameter,

Si: Standard value allowed for ith parameter,

$$HPI = \frac{\sum_{i=1}^n WiQi}{\sum_{i=1}^n Wi}$$

(4)

Qi: Sub index calculated for the ith parameter,

Wi: weight assigned to the ith parameter.

The calculated the index, weight and ideal values for the elements Pb, Zn, Ni, Cd, As, Cu, Cr are given in Table 1.

**Table 2.** parameters measured in water samples from the study area.

S.ID	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Temp	pH	EC	Metal Load
ZW1	56.95	11.24	-	0.07	-	0.57	-	-	18	8.9	760	68.83
ZW2	3.78	-	3.33	1.23	5.43	-	2.08	-	15.9	7.8	760	15.85
ZW3	7.02	-	4.43	1.21	4.90	0.70	1.70	-	16.1	8.0	900	19.96
ZW4	5.39	0.27	6.82	4.64	6.77	3.15	14.93	25.52	11.2	7.9	840	67.49
ZW5	1.93	37.93	-	0.04	3.77	1.08	-	-	13.2	7.9	860	44.75
ZW6	20.46	0.10	15.62	4.53	3.46	0.51	5.29	24.21	5.8	8.3	1320	74.18
ZW7	16	-	-	-	-	-	-	-	7.1	8.9	407	16
ZW8	-	-	-	-	-	7	6.03	-	9.7	7.8	1219	13.03

Water quality based on heavy metal pollution index can be divided into three categories including: low heavy metal pollution (HPI <100), heavy metal pollution on the threshold risk (HPI = 100) and high heavy metal pollution (HPI > 100) (Mohan *et al.*, 1996). If the samples have heavy metal pollution index values greater than 100, water is not potable. Measured values of this index for the sample are presented in Table 4.

*heavy metal evaluation index (HEI)*

Heavy metal evaluation index is a way of estimating the water quality with focus on heavy metals in water samples (Edet *et al.*, 2003). The water quality index classify into three categories which include: low heavy metals (HEI <400), moderate to heavy metals (400 < HEI < 800) and high heavy metals (HEI > 800). The index is calculated from the equation (5):

$$HEI = \sum_{i=1}^n \frac{Hi}{Hmac}$$

(5)

Hi: Measured value for the ith parameter,  
Hmac: Standard allowed value for ith parameter

*metal Index (MI)*

This index expresses the overall quality of drinking water based on metal content like heavy metal evaluation index (Tamasi and Cini, 2004) and can be calculated by the equation (6):

$$MI = \sum_{i=1}^n \frac{Ci}{(MAC)_i} \tag{6}$$

Ci: Measured value for the ith parameter, MACi: Standard allowed value for ith parameter

According to this water quality index, water samples can be divided into three groups including: potable (MI <1), on the threshold of danger of drinking (MI = 1) and non-potable (MI > 1).

Both MI and HEI indices, measure with the use of the same equations, but the final classification varies. For the HEI index, the main problem related to the high amount defined for threshold risk (HEI = 400), which let the low and moderate contaminated samples to group with the high contaminated samples. In the case of index MI, that relies particularly on the quality of drinking water, classification considered less for a threshold risk (MI = 1).

It should be noted that the samples with lower metal index category are suitable for drinking but it is possible that a number of metals have enrichment in the water sample and with long-term usage it can create many problems for the human. Measured values of this index were similar to the HEI index values so are not recalculated. HEI index values are presented in Table 4.

The measured values for the eight metals with pH, temperature and electrical conductivity of the water samples taken at the stations shown in Fig.1, are

listed in Table 2. To investigate how the distribution of the measured parameters in water samples is, descriptive statistical data are presented in Table 3.

**Table 3.** descriptive statistics for the water sample parameters of the study area.

Parameter	Units	Min	Max	Mean	Std. Deviation
Temp	°C	5.8	18	12.13	4.44
pH	-	7.8	8.9	8.19	0.47
EC	µS/cm	366	1320	780.36	306.82
As	ppb	-	56.95	13.94	18.74
Cd	ppb	-	37.93	6.19	13.41
Cr	ppb	-	15.62	3.78	5.44
Cu	ppb	-	4.64	1.47	1.99
Ni	ppb	-	6.77	3.04	2.71
Pb	ppb	-	7	1.55	2.44
Fe	ppb	-	25.52	6.22	11.52
Zn	ppb	-	14.93	3.75	5.1

According to the calculated values, all samples pH are slightly alkaline by the mean of (8.17) which can influence the presence of heavy metals in the water samples. Average amounts of Cadmium and Arsenic of water samples (6.19 and 13.94 ppb, respectively), was more than the allowed standard limit for these

two metals (3 and 10 ppb, respectively), which shows the obvious importance of these two elements in the water pollution of the area. Other elements have been measured in low doses. Measured indices for the samples are given in Table 4.

**Table 4.** calculated indices for water examples of the study area.

No.	MI	HPI	HEI	Cd
ZW1	9.5	3.21	9.5	1.5
ZW2	0.52	0.07	0.52	-7.48
ZW3	0.87	0.13	0.87	-7.13
ZW4	1.21	0.21	1.21	-6.78
ZW5	13	7.46	13	5
ZW6	2.52	0.4	2.52	-5.68
ZW7	1.6	0.28	1.6	-7.4
ZW8	0.7	0.12	0.7	-7.3
Minimum	0.52	0.07	0.52	-7.48
Maximum	13	7.46	13	5
Mean	3.74	1.49	3.74	-4.41
Std. Deviation	4.77	2.64	4.77	4.85

According to HPI, the maximum amount of heavy metal pollution in the samples is for Fadihe village, located in 3 km upstream of mine, with a value of (7.46) and the lowest heavy metal pollution index is for the sample of Ghaleh Jugh spring, located in 2 km downstream with the value (0.07). Mean value for HPI in the water samples, is (1.49) which is classified as low heavy metal pollution.

According to HEI, the maximum estimated amount of metals in samples belongs to Fadihe village sample (13) and the lowest value is for the Ghaleh Jugh spring (0.52). Based on this classification for this index, the average index for samples is (3.74) so water samples are estimating at low heavy metals level. Index of MI (metal index) showed that 5 samples of water samples, not potable.



In order to investigate the relationships between measured parameters, the correlation matrix was drawn by the software SPSS (Table 5). Based on calculations performed, The amount of Arsenic is directly related to the pH. The presence of arsenic in water samples and the positive correlation with pH shows that the high amounts of arsenic in area water is because of the water-rock interaction and the

oxidation of As-bearing solid materials, and then more effect of pH on secondary manumission. Cadmium in water samples of the region, does not show correlation with other metals and parameters, and given that the two examples that have high levels of cadmium (ZW5 and ZW1) were taken from the Groundwater inside the Mine, As a result, it can be related to mining activities in the region.

**Table 5.** correlation matrix for the measured parameters and calculated indices.

	pH	EC	Temp	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe	HEI	HPI	Cd
pH	1													
EC	-.479	1												
Temp	-.098	-.260	1											
As	.806*	-.170	.282	1										
Cd	-.068	-.084	.254	.015	1									
Cr	-.131	.573	-.444	-.029	-.360	1								
Cu	-.228	.413	-.372	-.109	-.366	.890**	1							
Ni	-.638	.101	.189	-.477	-.022	.466	.639	1						
Pb	-.437	.484	-.242	-.345	-.124	-.183	-.031	-.219	1					
Zn	-.429	.341	-.299	-.314	-.379	.442	.758*	.494	.523	1				
Fe	-.122	.414	-.494	-.040	-.276	.831*	.965**	.481	.080	.786*	1			
HEI	.223	-.106	.325	.385	.927**	-.330	-.360	-.201	-.204	-.434	-.244	1		
HPI	.027	-.096	.284	.135	.993**	-.362	-.376	-.084	-.151	-.407	-.277	.966**	1	
Cd	.172	-.064	.363	.373	.928**	-.316	-.340	-.163	-.182	-.407	-.233	.997**	.965**	1

\*. Correlation is significant at the 0.05 level (2-tailed).

\*\* . Correlation is significant at the 0.01 level (2-tailed).

According to the relationship stated, calculated indices such as Cd, HEI and HPI were also directly affected by cadmium. Average amount of Cadmium in water samples (10) was more than the allowed standard limit for this metal (3ppb) and has a great impact on the high levels of these indices.

The results indicate that multiple sources of pollution in the water resources of the region. The two main sources, one associated with the dominant lithology in the region and another, mining activities in the region. High values of As element associated with lithologic units but high levels of Cd are associated with mining activities. These results are consistent with those obtained by Ameh and Akpah. (2011) for natural surface waters of River PovPov in Itakpe Iron-Ore mining area, Kogi State, Nigeria, and also by

Nazari and Razmara. (2014) for water resources in Pangi mining area, Torbat Hydarieh, Iran. Ameh and Akpah. (2011), concluded that the river is polluted by mining activities in the area and it is Non-potable. Nazari and Razmara. (2014), concluded that 5 water samples of the study area is Non-potabled, which the two effective factors in the water pollution of this area is included the lithology and Mining activities in the area. Yankey *et al.* (2013) with ground water quality survey of Tarkwa mining area in terms of heavy metal pollution, concluded that except one of water samples, the other samples had less pollution than the Critical value for HPI index. Hosseinpour *et al.* (2014), for evaluating the heavy metals pollution in water resources of around the Khorasan Steel Complex, used MI, Cd, HEI, HPI indices. The results of the survey suggested that the Amounts of heavy



metals pollution in the area is much less than the threshold limit.

Cadmium in water samples of the region, does not show Correlation with other metals and parameters, and given that the two examples that have high levels of cadmium (ZW5 and ZW1) were taken from the Groundwater inside the Mine, As a result, it can be related to mining activities in the region. The amount of Arsenic is directly related to the pH. The presence of arsenic in water samples and the positive correlation with pH shows that the high amounts of arsenic in area water is because of the water-rock interaction and the oxidation of As-bearing solid materials, and then more effect of pH on secondary manumission.

Copper concentration values are significant correlated with those of Cr ( $r=0.890$ ), Ni ( $r=0.639$ ), Zn ( $r=0.785$ ) and Fe ( $r=0.965$ ). Cr values are significant correlated with those of Fe ( $r=0.831$ ), and Zn values are significant correlated with those of Fe ( $r=0.786$ ). The determination coefficient ( $r^2$ ) of the metals indicated Fe and Cu to be more dependable to each of the medium than in the other metals ( $r = 0.965$ ). Hydrous oxides of Fe and Mn on particulate surfaces are significant carriers for Zn in aquatic systems (Howard and Vandenbrink, 1999). The relationship between Zn bound to the Fe oxides and present Fe ore deposits in the area, suggesting that Fe oxides may be the main carriers of Zn from lithologic units to the water resources.

### Conclusion

In order to assess the impact of mining activity and lithology of region on groundwater resources of Kouh- e Zar area, 8 groundwater samples were taken. Eight elements (Pb, Zn, Ni, Cd, As, Cu, Cr and Fe) in the samples were measured and were used in calculating Cd, MI, HEI and HPI indices. Based on the results, the maximum value for the indices were in the samples is for Fadihe village, located in 3 km upstream of mine (HPI = 7.46, HEI = 13, Cd = 5). According to the water indices, water samples of the

study area have been identified unsuitable for drinking and based on the correlation matrix, cadmium and arsenic has a great role in the quality of water samples. The results indicate that multiple sources of pollution in the water resources of the region. The two main sources, one associated with the dominant lithology in the region and another, mining activities in the region. According to the relationship stated, calculated indices such as Cd, HEI and HPI were also directly affected by cadmium.

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