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Accumulation of lead, antimony and arsenic in soil and water in Khunik gold prospecting area, Eastern Iran

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Abstract

Khunik gold prospecting area is located in the eastern part of Lut block, eastern Iran. Main rock units are andesite, agglomerate, latite, dacitic lava, rhyodacite, volcanic breccia and conglomerate. Geological and geochemical evidences indicate low to medium sulfide gold mineralization. Mining activates accumulate heavy metals in soil and water that are associated with harmful effects on human health. The object of this research is to evaluate the concentration of heavy metals in soil and groundwater resources and assess the effects of the mineralization zone. All investigated metals in soil samples are below world concentration except arsenic, antimony, and iron. Based on the assessment of pollution, high enrichment of silver, medium to high enrichment of antimony, arsenic, lead, and selenium in some samples were detected. The high correlation of silver, gold, and arsenic is due to the sulfide mineralization of gold in the Khunik area. Chemical analysis of water samples comparing International Standards confirms that water resources in this area have been polluted by heavy metals and it is not drinkable. MI and HPI values denote the dangerous pollution of groundwater, which has been described as serious in most sites.

Keywords: *Heavy metals, Pollution indices, Groundwater, Soil, Lut block..*

1. Introduction

Soil and water are a part of the biosphere that have an important role in controlling the transfer of elements and materials in the environment. Heavy metals migrate in soil, sediment, and groundwater derived from a variety of natural and/or anthropogenic sources. Mining, mineral processing, dumping of raw and waste materials are one of the main resources of metal pollution (e.g. Vural 2018; Sungur et al. 2020; Chen et al. 2021). In many parts of the planet, mainly around the mining area, heavy metal concentrations in drinkable waters are above than worldwide guideline values (Fernández-Luqueño et al. 2013).

Gold mining is one of the major problems of soil and water contamination and human health around the world (Dorleku et al. 2018; Dan-Badjo et al. 2019; du Plessis and Curtis 2021; Corredor et al. 2021). It is a source of some heavy metals that caused serious problems (Abdul Gafur et al. 2018), and exemplified by the heavy metal pollution in Ghana (Mensah et al. 2015; Hogarh et al. 2016; Kazapoe et al. 2022). Gold mining in Oman has contaminated the environment by Fe, Pb, zinc (Zn), cadmium (Cd), and manganese (Mn) (Abdul-Wahab and Marikar 2012). Small gold mines in Senegal create a high mercury contamination (Gerson et al. 2018). One important contributor of As to the environment is gold mines (Smedley and Kinniburgh 2002). High concentrations of As in soil have been reported in gold mining areas around the world. Sako et al. (2018) reported 278.6 mg•kg–1 As in gold mining soil. Kinimo et al. (2018) discovered that the As concentration in the Afema industrial mining area reached 294.4 mg•kg–1.

Mining is one of the most important industrial activities in the South Khorasan province of eastern Iran. Metallogenic belt in eastern Iran hosts different types of gold and copper mineralization. An environmentally and economically sustainable mining activities are essential for the long-term development of these metal resources. The geologically mapping for mineralization areas in eastern Iran is of high concerns, while the contamination of soil and groundwater might by caused by mining activities is not fully focused on.

The Khunik prospecting area is located at a semi-arid climate region, which is close to the Lut Desert, with an annual rainfall of approximate 150 to 200 mm. The diurnal temperature difference is very high, thus, the physical erosion in this area is intensive. The main object of this study is to evaluate environmental indices of soil, sediment, and groundwater, and to assess impacts of the lithology and mineralization on these resources in the Khunik prospecting area.

2. Geology and mineralization

The Khunik area is extended from 59°8' to 59°13' E and 32°21' to 32°26' N, which is located 106 kilometers southwest of the Birjand, South Khorasan province of eastern Iran (Fig 1B). This area is located at eastern part of the Lut Block, and near the intersection of this block with the Nehbandan-Khash flysch basin on the Sistan suture zone (Aghanabati 1998). The oldest stratum exposed in the southern part is the Paleocene-Eocene conglomerate (Rowshanravan et al. 2003). There are

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several outcrops of granitoid subvolcanic intrusions as dikes and stocks that intruded in volcanic rocks (andesite, agglomerate, andesitic tuff, and trachy andesite tuff). The subvolcanic rocks consist mainly of monzonite, quartz monzonite, quartz monzodiorite, monzodiorite, and diorite. Lava units have limited outcrops in central parts of the study area (Fig 1A). The drainage system has a north-south trend (Fig 1A). The study area is situated in the Lut Block which host various types of Cu-Au mineralization related to Tertiary subduction, e.g., Qaleh Zari IOCG Deposit, Maherabad porphyry-type Cu–Au, Sheikhabad high-sulfidation, and Hanich low sulfidation. Gold mineralization in the Khunik area is associated with sulfide minerals. The mineralization occurred as disseminated, veinlet, stock-work, and hydrothermal breccia. The mineralization zones mainly consist of pyrite, limited quantities of chalcopyrite, tetrahedrite, and galena. Geology, alteration, geochemistry, and fluid inclusions indicated a medium to low sulfide mineralization associated with the hydrothermal breccia (Omidvar 2004; Yazdi et al. 2015; Samiee et al. 2016)

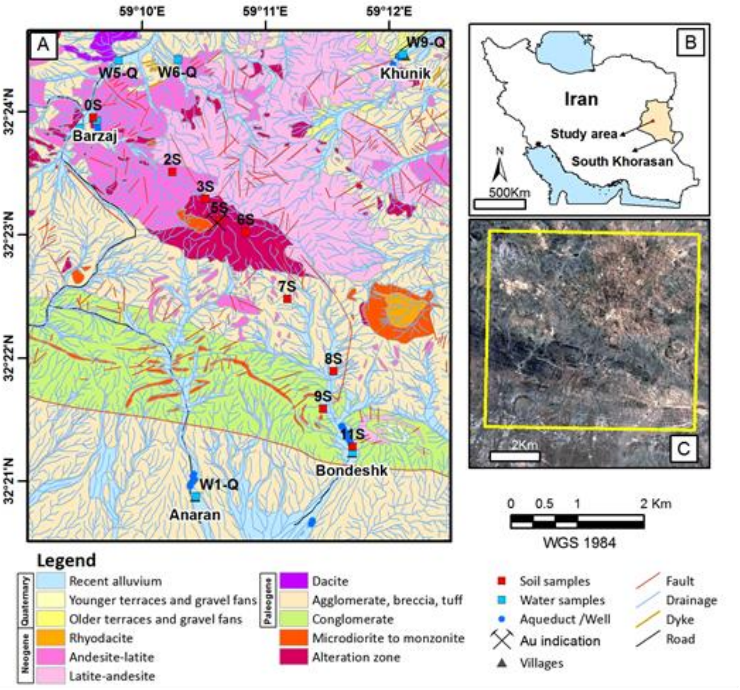

Fig 1. A) Geological map of study area (modified after Rowshanravan et al. (2003)).
B and C) Geographical location and satellite image of study area.

3. Materials and methods

3.1. Sampling and analysis

Ninety-two samples was collected from soil and stream sediment. Therein, 83 samples were collected by the geological survey of Iran. Nine fresh soil samples labeled as S0–S11 were collected in this study to ensure that samples are representative (Fig 1). Samples were taken from depths of 10 to 15 cm using a hand shovel, and then were homogenized, air-dried, and sieved to remove unwanted materials. Then samples were stored in polyethylene bags and sent to the ACME laboratory of Canada to determine the concentrations of Cu, Pb, Zn, Cd, As, Au, Ag, Sr, Sn, Se, Sb, Hg, Cr, Ni, and Co using an inductively coupled plasma mass spectrometry (ICP-MS) method (Table 1). The pH and EC of the soil samples were measured with a multimeter calibrated with a buffer solution (pH = 7).

A total of 9 groundwater samples were collected from aqueduct (Qanat), which is a system for transporting water from an aquifer to the surface. Two samples were taken from each location in two polyethylene containers, one for cations and the other for anions (bicarbonate, sulphate, chlorine etc.). Sampling protocols described by Standard Methods for the Examination of Water and Wastewater (APHA 1998) were followed. The containers were rinsed with the distilled water (At least 3 times) before samples were taken. The water samples were acidified with nitric acid (HNO_3) at collection sites, to keep it in oxidation state (pH ~2) and to prevent of heavy metals precipitation. Physical parameters, including pH, electrical conductivity (EC), temperature and Total dissolved solids (TDS) were measured in situ with a field multimeter (Table 2). The samples were kept in dark at 4°C before analyzing. Four water samples were sent to the ACME laboratory to determine concentrations of elements by an ICP-MS method (Table 3). Sampling and water analyses were completed during the months of May and June.

Table 1. Concentrations of heavy metals in soil samples (mg·kg^{-1}), average world shale (Turekian and Wedepohl 1961), and Dutch pollutant standard (2010)

Samples	Cu	Pb	Zn	Ag	Fe	As	Au	Cd	Sb	Hg	Se	Sn	pH	EC (µs/cm)
11S	33.74	13.81	70.50	0.05	34800	11.30	<0.01	0.16	1.01	0.15	0.30	0.70	8.95	395
9S	28.49	13.33	62.70	0.04	28900	9.90	<0.01	0.17	0.40	0.03	0.20	0.60	8.97	172.8
8S	36.22	13.23	76.20	0.03	39900	10.50	<0.01	0.15	1.45	0.04	0.30	0.80	8.95	201
7S	41.70	12.86	57.90	0.04	31400	10.70	<0.01	0.13	0.41	0.03	0.20	0.70	8.96	114
6S	36.40	43.16	60.30	0.09	40100	14.70	0.01	0.14	0.71	0.03	2.60	0.50	7.94	1721
5S	37.52	49.48	76.40	0.62	31300	22.50	0.63	0.34	8.17	0.06	1.40	0.60	8.90	344
3S	32.47	14.37	54.80	0.04	31000	11.40	0.02	0.12	0.60	0.02	1.00	0.50	8.89	102
2S	33.86	19.67	67.30	0.09	29500	11.30	0.01	0.17	0.51	0.03	0.30	0.60	9.04	246
0S	40.41	20.70	70.20	0.09	29900	12.30	0.04	0.21	1.06	0.03	0.60	0.50	7.94	1142
Max	41.70	49.48	76.40	0.62	40100	22.50	0.63	0.34	8.17	0.15	2.60	0.80	9.04	1721
Min	28.49	12.86	54.80	0.03	28900	9.90	<0.01	0.12	0.40	0.02	0.20	0.50	7.94	102
Average	35.65	22.29	66.26	0.12	32977	12.73	0.08	0.18	1.59	0.05	0.77	0.61	8.72	493
Median	36.22	14.37	67.30	0.05	31300	11.30	0.01	0.16	0.71	0.03	0.30	0.60	8.95	246
STDEV	4.06	14.01	7.79	0.19	4321	3.91	0.21	0.07	2.49	0.04	0.80	0.11	0.45	560
Average world shale	45	20	95	0.07	47200	13	-	0.3	1.5	1.4	0.6	6	-	-
Dutch standard	36	85	140	-	-	29	-	0.8	3	0.3	0.7	-	-	-

STDEV: standard deviation

Table 2. Physico-chemical parameters of the water samples

Samples	W1-Q	W2-Q	W3-Q	W4-Q	W5-Q	W6-Q	W7-Q	W8-Q	W9-Q	WHO
T (˚C)	17.2	17.2	18.7	17.6	18.8	18.6	18.7	19.2	18.3	12-25
PH	8.34	8.31	7.78	8.29	8	7.79	8.01	8.01	8.21	6.5-8.5
TDS (mg.Kg^{-1})	488	2350	2610	607	627	714	635	534	643	1000
EC (µs/cm)	698	3380	3740	3500	898	1022	908	762	956	400
Mg^{+2} (meq/Lit)	4.5	5.5	1.4	5.1	5.3	6.5	4.2	8.2	7.1	100
Ca^{+2} (meq/Lit)	2.2	2.5	13.3	7.2	7.7	9.1	8	1.4	6	75
Na^{+} (meq/Lit)	4	3.5	6.5	2.5	2.4	3	3.4	2.2	3	200
K^{+} (meq/Lit)	0.12	0.18	0.25	0.11	0.17	0.22	0.09	0.12	0.19	12
CO$_3^{-}$ (meq/Lit)	nd	nd	0.1	nd	nd	nd	nd	nd	0.2	100
HCO$_3^{-}$ (meq/Lit)	7.2	7.1	5.2	4.4	5.1	6	4.5	7.1	5.4	600
Cl^{-} (meq/Lit)	2.6	3.1	2.1	2.5	2.8	2.6	3	2	2.7	250
SO$_4^{-}$ (meq/Lit)	0.9	1.1	13.5	7.7	7.4	10.1	8	2.6	8	250
NO$_3^{-}$ (mg/Lit)	11.8	13.2	15.1	12.5	14.2	20.7	24.3	15.9	13.5	45
TH (mg.Kg^{-1})	332	396	733	611	646	775	607	474	650	100
SAR (meq/Lit)	2.19	1.75	2.4	1.01	0.94	1.07	1.38	1	1.17	-

Table 3. Metals' concentrations in groundwater samples (µg·L^{-1}) and the WHO (2017)

Sample	W1-Q	W2-Q	W3-Q	W9-Q	Min	Max	Average	Median	STDEV	WHO
As	1.3	2.3	0.9	1	0.9	2.3	1.38	1.15	0.64	10
Ba	30.55	32.37	19.12	22.88	19.12	32.37	26.23	26.72	6.28	1300
Cd	<0.05	<0.05	0.48	0.43	<0.05	0.48	0.46	0.46	0.04	3
Cr	1.7	1.1	0.9	1.3	0.9	1.7	1.25	1.2	0.34	50
Cu	3.9	5	15.3	10.4	3.9	15.3	8.65	7.7	5.27	2000
Se	2.9	3.3	2.7	2.7	2.7	3.3	2.9	2.8	0.28	40
Pb	24.3	20.4	275.7	471.2	20.4	471.2	197.9	150	217.86	10
Sb	2.13	2.28	2.2	1.97	1.97	2.28	2.15	2.17	0.13	20
Sn	<0.05	<0.05	<0.05	0.08	<0.05	0.08	0.08	0.08	-	1
Zn	25.6	14.8	237	235.3	14.8	237	128.18	130.45	124.76	3000
MI	2.8	2.5	28.0	47.6	2.5	28	20.2	-	-	-
HPI	279.8	250.6	2801.5	4760.1	250.6	2801.5	2023	-	-	-

MI: Metal index, HPI: heavy metal pollution index.

3.2. Evaluation on pollution

Pollution indices are broadly used to evaluate the degree of contamination. There are different types of pollution indices for the environmental quality assessment and for the determination of natural processes or anthropogenic activities. In this study, enrichment factor (EF), geo-accumulation index (I_{geo}), and contamination factor (CF) were used to assess the presence and/or extent of anthropogenic contaminants of heavy metals (Cu, Pb, Zn, Ag, As, Cd, Sb, Hg, Se, and Sn) in soil and sediment samples. MI and heavy HPI also adopted to assess the pollution in groundwater samples.

3.2.1. Enrichment factor (EF)

The EF is used to determine the levels of element contamination (Loska et al. 1997). It depends on the ratio of the each metal's concentration in the soil to its background (Eq. 1).

$EF=[C_n(Sample)/C_{ref}(Sample)]/B_n(Background)/B_{ref}(Background)]$ *Equation (1)*

Where C_n is the element's concentration in samples; C_{ref} is the concentration of reference element in samples; B_n is the concentration of element in the sample, and B_{ref} is the concentration of reference element in the background. Reference element is stable in the environment, and its concentration in the environment is not affected by human activities. Background elements (e.g. Al, Fe, Ba, Sc, Ti, Mn, and Br) are different, depending on soil types (Jiang et al. 1996; Emmerson et al. 1997; Dabiri et al. 2017; Kowalska et al. 2018). The natural concentration of Fe tends to be uniform (Daskalakis and O'Connor 1995). In the present study of enrichment factor, Fe is taken as the reference element.

Many authors prefer to express the metal contamination with respect to world average shale (Turekian and Wedepohl 1961) to quantify the extent and degree of metal pollution (Müller 1969). The enrichment has categorized into seven classes (Table 4).

Table 4. Classifications of geo-accumulation index, enrichment factor, contamination factor and modified contamination degree (Guo et al. 2014).

Degree of enrichment	EF
No enrichment	1>
Minor enrichment	1-3
Moderate enrichment	3-5
Moderately severe enrichment	5-10
Severe enrichment	10-25
Very severe enrichment	25-50
Extremely severe enrichment	50 <

Degree of contamination	I_{geo}
Unpolluted	0> =
Unpolluted to Moderately polluted	0-1
Moderately polluted	1-2
Moderately to strong polluted	2-3
Strong polluted	3-4
Strongly to extremely polluted	4-5
Extremely polluted	5 <

Degree of contamination	CF
Non-Contaminated	0
Non to medium contaminated contamination average	1
Medium contaminated	2
Medium to strong contaminated	3
Strong contaminated	4
Strong to very strong contaminated	5
Very strong contaminated	6

3.2.2 Geo-accumulation index

The (I_{geo}) introduced by Müller (1969) is calculated by Eq. (2).

$I_{geo}= Log_2[C_n/1.5B_n]$ *Equation (2)*

Where C_n is the concentration of element in soil samples; B_n is the concentration of element in the background (or world average shale); and 1.5 is a constant number for correction lithospheric effects. The accumulation has categorized into seven classes,

3.2.3 Contamination factor

In order to determine the pollution of a specific element, the contamination factor is calculated by a ratio of the element in sample to the same element in the background .The accumulation is categorized according to CF values into seven groups, from unpolluted (CF=0) to very strong contamination (CF=6) (Müller 1969) (Table 4).

3.2.4. Metal index

The MI is parameter used to assess the water quality.

$MI=\sum C_i/(MAC)_i$ *Equation (3)*

Where C_i is the element concentration; I is the i^{th} element in the sample and $(MAC)_i$ is the maximum allowable concentration of the element. If the MI was less than one the water would be drinkable; and if MI was equal to zero, the quality is on the verge of being considered risky (Tamasi and Cini 2004).

3.2.5. Heavy metal pollution index

This index evaluate the effect of each heavy metal on the overall quality of water in terms of its risk to human health (Mohan et al. 1996). It was calculated by Eq. (4).

$HPI=\sum(Q_iW_i)/\sum W_i$ *Equation (4)*
$W_i= k/S_i$ *Equation (5)*
$Q_i= 100\ V_i/S_i$ *Equation (6)*

Where, HPI is the heavy metal pollution index; W_i is the weight and Q_i is the quality rate of i component which could be calculated by Eqs. (5) and (6); k is constant of equation; V_i is the concentration; and S_i standard value (WHO) for i parameter. The higher HPI value, the greater harm to the health of people. Water quality based on HPI can be classified into three categories including: low (less than 100), the threshold risk (equal to 100), and high (more than 100). If a HPI is more than 100, the water is polluted by heavy metals and cannot be used for drinking.

3.2.6. Statistical analysis

Multivariate statistical analysis is adopted to interpret environmental data. The Pearson's correlation coefficient analysis and cluster analysis (CA) have used to recognize the geochemical behaviors and sources of different elements in this study.

4. Results and discussion

4.1. Soil quality

Physicochemical properties of soil control the mobility and pathways of pollutants (Jafari and Yazdi 2014; Carré et al. 2017). It is therefore important to assess soil physicochemical properties. The measured pH values for the soil samples vary from 7.94 to 9.04, indicating an alkaline nature (Table 1).

The soil samples show a wide variation of electric conductivity (salinity), ranging from 102 to 1721 μScm^{-1}. The electrical conductivity increases with the intensity of altered zone due to alteration processes and the formation of less soluble secondary minerals. The formation and alteration of these minerals are basically influenced by changes in the soil pH.

Concentrations of Cu, Pb, Zn, Ag, As, Cd, Sb, Hg, Se, Sn and Fe in soil and stream sediment is presented in Table 1. The Soil and sediment samples have a similar source due to dry weather condition. The variation in some metal concentrations in soil and stream sediment is shown in Fig 2. Fe content in soil and sediments varies from 28900 to 66500 and 26700 to 55000 $mg\cdot kg^{-1}$, respectively. Fe is a major element rather than trace element, and the higher concentration of Fe can relate to the Fe-oxides or sulphide minerals associated with ore deposits.

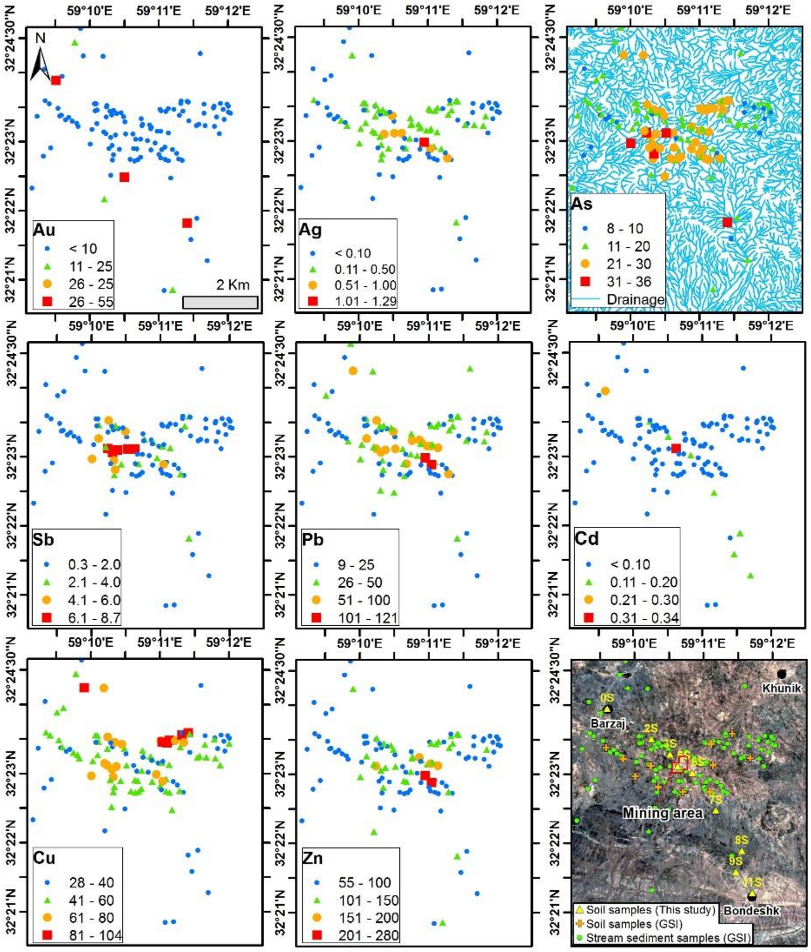

Fig 2. Variation of Au, Ag, As, Sb, Pb, Cd, Cu, and Zn ($mg\cdot kg^{-1}$) in the soil and sediment samples.

As varies from 9.9 to 35.9 in the soil samples and it accumulated between 6.7 to about 31.8 mg·kg^{-1} in the sediments (Fig 2), where it occurs in the Earth's crust at levels between 0.5 and 2.5 mg·kg^{-1} (Kabata-Pendias 2007 and 2010).

The concentrations of Sb in soil and sediment samples varies from 0.4 to 8.25 and 0.3 to 8.7 mg·kg^{-1}, respectively (Fig 2). The Sb concentration in most of the soil samples are less than the 2 mg·kg^{-1}. Generally, the Sb values are lower than the Dutch standard limit (2010), except for a few samples around the mineralization area.

The concentration of Pb in soil and sediment samples varies from 12.86 to 49.48 and 9 to 121 mg·kg^{-1}, respectively (Fig 2). The average concentration of Pb (31 mg·kg^{-1}) is higher than the world shale average (20 mg·kg^{-1}), and some values also are higher than the Dutch standard limit (2010) for soil (85 mg·kg^{-1}).

The concentrations of Cd are below the world shale average (0.3 mg·kg^{-1}) and Dutch standard limit (2010) value (0.8 mg·kg^{-1}), except for sample 5S near Au indication, that is higher than the World Shale Average (Fig 2).Copper (Cu) was detected in soil samples from 28.5 to 104 mg·kg^{-1}. The concentrations of Cu vary from 27.8 to 108.5 mg·kg^{-1} in sediment samples (Fig 2). The samples near mineralization area displayed Cu values higher than the surface reference soil and Dutch standard limit (2010) (Fig 2).

The concentrations of Zn in soil and sediment samples vary from 54.8 to 166 and 57 to 280 and mg·kg^{-1}, respectively (Fig 2). The average concentration of Zn in sample near the mineralization area is higher than the world shale average (95 mg·kg^{-1}, Turekian and Wedepohl 1961), and the Dutch standard limit (2010) for soil (140 mg·kg^{-1}). The location of high values of Zn match to high values of Pb (Fig 2), because of their paragenesis minerals. Selenium (Se) varies from 0.2 to 2.6 mg.kg^{-1} in the soil samples (Table 1), some samples near mineralization area exceeded the Dutch standard target values (2010). Generally, the distribution pattern of the metal concentrations followed the highest concentrations located near the prospecting area. The decrease in metal concentrations along the flow direction illustrated that the sediment transported in a few distance (Fig 2).

4.2. Pollution assessment

Assessing the level of enrichment in soil aids in the quantification of heavy metal pollution via anthropogenic activities and, geogenic and lithogenic sources (ur Rehman et al. 2018). Pollution indices are presented in Table 5. The calculated EF for all samples varies from 0.01 to 13.42 (Table 5). In general, the mean EF values are ranked as follows: EF (Ag) > EF (Sb) > EF (Pb) > EF (As) > EF (Zn) > EF (Cu) > EF (Au) > EF (Sr) > EF (Cr) > EF (Cd) > EF (Co) > EF (Hg) (Table 5).

Table 5. Statistics of EF, EC, and I$_{geo}$ for some elements in soil and sediment samples

Sample	**EF**			**CF**			**Igeo**		
	min	max	mean	min	max	mean	min	max	mean
Cu	0.7	2.79	1.30	0.66	2.31	1.13	-1.18	0.62	-0.47
Pb	0.51	6.71	1.81	0.45	603	1.55	-1.75	2.01	-0.27
Zn	0.63	3.28	1.17	0.61	2.95	1.02	-1.32	0.97	-0.63
Cd	0.55	1.71	0.72	0.40	1.13	0.53	-1.91	-0.40	-1.49
As	0.62	3.72	1.62	0.65	2.76	1.41	-1.22	0.88	-0.20
Au	0.01	2.38	0.04	0.47	157	1.71	-8.30	0.07	-6.08
Ag	0.87	13.42	1.25	0.49	1.73	0.93	-1.36	2.57	-0.89
Sr	0.36	1.94	.81	0.38	1.66	0.72	-1.99	0.14	-1.22
Sb	0.21	8.09	1.45	0.17	5.78	1.25	-3.17	1.95	-0.69
Hg	0.02	0.15	0.04	0.01	0.11	0.02	-6.71	-3.79	-5.61
Cr	0.87	1.82	1.18	0.76 76	1.49	1.03	-0.98	-0.01	-0.56
Ni	0.39	1.13	0.75	0.01	0.96	0.13	-1.83	-0.64	-0.20
Co	0.01	1.21	0.16	0.01	1.01	0.14	-1.45	-0.53	-1.09

The results show sample near mineralized area has severe enrichment of Ag and moderate to severe enrichment of Sb, Se and Pb. Some distribution maps are shown in Figure 3. The Inverse Distance Weighted (IDW) interpolation used for mapping these variables (Fig 3). Low neighborhood search radius values were more appropriate for IDW interpolation.

Assessment of CF (0.01-157) displays the soil samples changes from no contamination to very strong contamination. The most CF values reveal low to moderately contaminated (F< 2). Samples from mineralization zone have strong to very strong contamination of Au, Pb and Sb (Fig 3 and Table 5).

The soil is unpolluted with most the analyzed heavy metals since most of the I$_{geo}$ values were less than 2. Samples near mineralization zone has moderate to high contamination of Ag, and medium contamination of Sb, Se and Pb (Fig 3 and Table 5). Pearson correlation was worked out to identify the relationship between heavy metals concentrations in soil samples (Table 6). There is a high positive correlation between the As-Sb (0.930), As-Ag (0.961), Au-Ag (0.994), Au-As (0.943), Pb-As (0.909) and Pb-Se (0.821), which could be related to the mineralization source. There is also a significant correlation between Cd-Zn (0.656), and Cd-Pb (0.665) pairs (Table 6). The positively correlated ($p<0.01$) Au-As-Ag-Pb-Se elements is a characteristic of areas polluted by the gold mining area. The presence of Hg and Sn elements in the soil can attributed to their lithological origin (volcanic rocks), where the first group relate to primary mining activities. Cd, Zn and Cu maybe related to both origins. Based on statistical analysis, there are three broad element classes: (1) Au-As-Ag-Pb-Cd-Se mineralized association, mostly related to mining, (2) mixed origin (Cu), mostly related to gold mineralization and partly to lithology; and (3) natural origin (Zn, Hg and Sn).

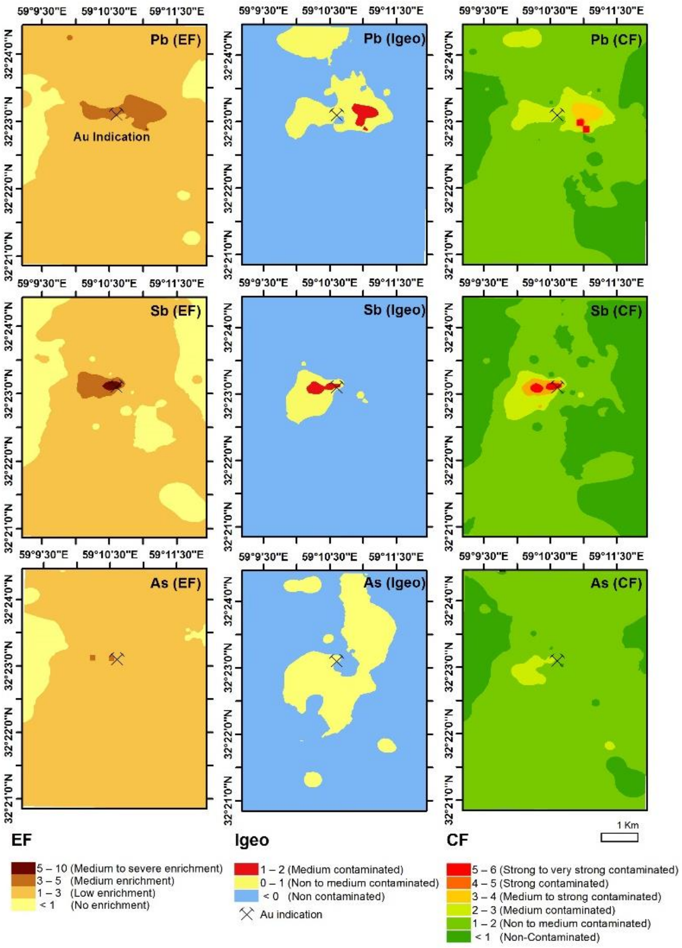

Fig 3. Pollution indices for soil and sediment samples in the study area.

Table 6. Correlation matrix of heavy metals in soil and sediment samples

	Cu	Pb	Zn	Ag	As	Au	Cd	Sb	Hg	Se	Sn
Cu	1.000										
Pb	0.235	1.000									
Zn	0.159	0.249	1.000								
Ag	0.199	0.784*	0.488	1.000							
As	0.267	0.909**	0.403	0.960**	1.000						
Au	0.198	0.737*	0.488	0.995**	0.944**	1.000					
Cd	0.190	0.665	0.656	0.934**	0.858**	0.930**	1.000				
Sb	0.205	0.716*	0.582	0.981**	0.930**	0.990**	0.924**	1.000			
Hg	-0.111	-0.097	0.396	0.033	0.026	0.044	0.100	0.107	1.000		
Se	0.120	0.821**	-0.164	0.354	0.585	0.308	0.166	0.288	-0.205	1.000	
Sn	0.086	-0.401	0.445	-0.115	-0.246	-0.079	-0.101	0.017	0.405	-0.572	1.000

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (2-tailed)

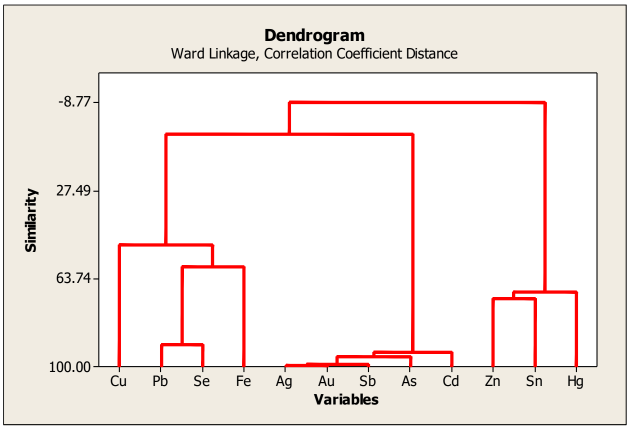

Fig 4. Dendrogram of element in soil and sediment samples.

Cluster analysis (Wards Method) also used to find the true groups that are assumed to exist. Wards method creates groups such that variance is minimized within clusters. The studied elements could divide into 3 groups. Au-As-Ag-Sb-Cd were highly correlated with each other, indicating the same origin of the metals in the soils. In addition, the results show that Cu-Fe, and Zn-Sn-Hg have the similar origin (Fig 4). The contaminated area has a horizontal trend, correspond to mineralized zone.

Medium to strong contamination of Pb is corresponding to the gold mineralization zone (Fig 3). These findings indicate that Pb can be a concern in future mining development. A similar pattern was also observed for Sb, which has medium to severe contamination (Fig 3). The amount of Cd was relatively low compared with As and Pb. The higher values of Cd are related to gold mineralization, but Cd compared with the other metals, is more immobile. As show medium contamination near Au mineralized area (Fig 3). For the reason of small-scale veinlet or disseminated mineralization, the most affected area is located close to the Khunik prospecting zone.

4.3. Water quality

The pH values of groundwater are 7.88 to 8.34, indicates the alkaline nature of water (Table 2). The pH of the samples is close to the limits recommended by WHO (2017) for drinking water that is about 6.5 to 8.5. Measured cations and anions in water samples (Mg^{+2}, Ca^{+2}, Na^{+}, K^{+}, CO_3^{-} , HCO_3^{-}, Cl^{-}, SO_4^{-2}, and NO_3^{-}) are within the allowable range of WHO (2017). However, Samples W2-Q and W3-Q have higher TDS and show moderately saline characteristic. All samples classify as very hard (TH: 332-775) waters.Piper chart (Piper 1944) has used to classify samples and determine the chemical type of waters. The samples are plotted in types of magnesium bicarbonate, calcic sulfate and magnesium sulfate (Fig 5). Based this results W2-Q, W3-Q and W4-Q are unsuitable for agriculture and W2-Q and W3-Q samples are unsuitable as drinking water.The measured concentration of the metals (As, Ba, Cd, Cr, Pb, Sb and Sn) in the groundwater were compared with the WHO (2017) limit for drinking water (Table 2). The arrangement of average frequency elements is Pb> Ba> Sb> As> Cr> Cd> Sn, which with the exception of Pb, have concentration lower than WHO standard (2017). The concentration of Pb in the study area varied between 20.4 and 471.2 μgL^{-1} with an average value 197.9 μgL^{-1} and all samples have a concentration more than 10 μgL^{-1} (suggested by the WHO 2017). Pb is toxic to human because it can cause gastrointestinal symptoms although no abnormalities were found on physical examination (Van Vonderen et al. 2000).

The MI values (2.5-47.6) are more than one, so the waters are not drinkable (Table 3).

Calculated HPI had a range 250-4760, exceed the limit of high pollution by HPI >100, which should be considered undesirable for drinking water (Table 3). The critical HPI even in samples far from the mining area, specify that groundwater is highly polluted with heavy metals. Pearson correlation analysis shows a high correlation between TDS and EC (0.767) and Na^{+} (0.736) (Table 7). There is a high correlation between calcium and sulfate (0.967), calcium and hardness (0.870) and sulfate and hardness (0.946).

Table 7. Correlation matrix of heavy metals in water samples of study area.

	pH	TDS	EC	Mg^{2+}	Ca^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	TH
pH	1.000										
TDS	-0.184	1.000									
EC	0.076	0.767*	1.000								
Mg^{2+}	0.217	-0.577	-0.537	1.000							
Ca^{2+}	-0.694*	0.326	0.341	-0.641	1.000						
Na^{+}	-0.317	0.736*	0.486	-.842**	0.539	1.000					
K^{+}	-0.532	0.620	0.323	-0.258	0.552	0.537	1.000				
HCO^{3-}	0.257	0.113	-0.201	0.372	-.727*	-0.035	0.037	1.000			
Cl^{-}	0.402	-0.028	-0.089	0.012	-0.144	-0.243	-0.181	-0.118	1.000		
SO_4^{2-}	-0.724*	0.203	0.244	-0.455	.967**	0.418	0.544	-.742*	-0.244	1.000	
TH	-0.750*	0.047	0.093	-0.179	.870**	0.150	0.542	-.693*	-0.176	.946**	1.000

5. Conclusions

This research evaluated the levels of pollution of soil and groundwater in Khunik prospecting area in South Khorasan province, east of Iran. Multiple methods used to evaluate the degree and extent of contamination and assess the effects of lithology and mineralization processes.

Based on contamination indices and statistical analysis, the distribution of the elements such as Au-As-Ag-Pb-Se have controlled by the gold mineralization and related alteration zone. On the other hand, the distribution of Zn, Hg and Sn has lithological sources. Statistical analysis demonstrates that Cu maybe mixed from both inputs. MI and HPI values signify the dangerous pollution of groundwater, which has described as seriously in most sites. Because of small-scale veinlet or disseminated mineralization, the most affected area is located close to Khunik prospecting zone. In fact this area, It is not an active mine yet but it needs from now to consider dangerous pollution of soil and water in future. Obviously, Soil and waters around Khunik area have high potential for producing heavy and toxic elements and consequently environmental pollution. Semi-arid climate with seasonal precipitation also increases the erosion and transport of particles and pollutants downstream. These findings could be used as decision-making criteria for the further strategies and the financial assets required for using the mining site. Selection of plants capable of growing in this specific environment is a prerequisite if phytoremediation strategies are to be employed.

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