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Evaluation of heavy metal contamination in soil and water resources around Taknar copper mine (NE Iran)

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Abstract

The study area is located in North Eastern Iran, near Taknar copper deposit where exploration, extraction and processing operations are ongoing. The purpose of this study is to understand the geochemical effects of mining activities in Taknar area and to evaluate the contamination of soil and water resources with heavy metals. The results of pollution indices such as CF, Igeo and EF and multivariate (geo)statistical analysis indicate anthropogenic source for Cu and Se elements, mostly related to mining and mineral processing activities, natural origin of Cr, Ni and Co and both anthropogenic and natural origin for Zn, Pb, Cd, As, Sb and Mo elements. The results also indicate the water and soil of the flotation plant and mining tunnels can be harmful. Fortunately, the water resources used by the staff, downstream aqueduct of the mine and the water of the villages in the south of the mine are free of contaminated elements.

Keywords: *Heavy Metal, Pollution, Water, Soil, Taknar Copper Mine, NE Iran.*

1. Introduction

Industries, agriculture, wastewater, mining and metallurgical processes release pollutants to environments. These pollutants may enter the surface waters or be washed away to lower levels and contaminate groundwater resources. Therefore, areas with contaminated soil often have contaminated water sources (Parvaresh and Saadat 2012). Copper mining is a source of heavy metals. Water and soil contamination with heavy metals, which is better to say potentially toxic elements, during mining activities cause widespread environmental problems in the world (Pinto et al. 2004; Razo et al. 2004; Navarro et al. 2008; Pourret and Hursthouse 2019). Heavy metals resulting from natural or anthropogenic activities cannot be eliminate by chemical or biological processes and therefore accumulate locally or travel far distances. In addition, the acidic waters of the mines from sulfide oxidation during exploration, extraction and even after closing the mine can lead to contamination of water and soil resources (Gray 1997).

Several methods used to analyze the quality of soil and water at places with significant mining activities. Researchers (e.g. Likuku et al. 2013; Gyamfi et al. 2019) used the geo-accumulation (I_{geo}) index, enrichment factor, pollution load index and the degree of contamination to evaluate heavy metal concentration in the soils. The study area is located 30 kilometers northwest of Bardaskan city in NE Iran, (57° 45' 36" E-57° 47 '20" E, 35° 20' 18"-35° 23' 6"; Fig. 1), The small-scale Taknar copper mine is located in the Taknar magmatic zone. Massive sulfide mineralization occurs as layered, massive and stockwork. The major minerals are pyrite ± magnetite ± chalcopyrite ± sphalerite ± and galena. The individual massive sulphide layers range in thickness from millimeters to two cm. Malachite, goethite, and secondary Fe oxides are abundant at the fracture surface (Ghoorchi 2003). Exploration and extraction activities, mineral processing as a flotation plant and heap leaching has also been active in recent years. Due to the increase of mineral tailings and the flotation plant, this mine may cause the contamination of waters and soils by the production of acid and associated heavy and toxic elements.

2. Geological setting

The Taknar zone is located at the northern margin of the Central Iran continental microplate, and it is bordered by Darouneh fault to the south and Taknar fault to the northt, hosting several mines including Taknar copper deposit. This zone consists of the Paleozoic to Cenozoic rock formations (Muller and Walter 1983) composed of slate, chloritic schist, sericitic schist, meta-rhyolite, dacite and meta-diabase. The Taknar copper mine is part of meta volcanic-sedimentary complex (Taknar Formation, Ordovician) and consist of clastic sediments, carbonate, felsic and mafic volcanic and sub-volcanic rocks (Fig. 2). The intrusive rocks are composed of granite, granodiorite, monzonite and diorite. Taknar Formation and most of the intrusive rocks were subjected to low-grade regional metamorphism (Ghoorchi 2003).

3. Methods and Materials

Based on geochemical data, index of enrichment factor (EF), geoaccumulation (I_{geo}), contamination factor (CF) and statistical analysis (cluster and principal component

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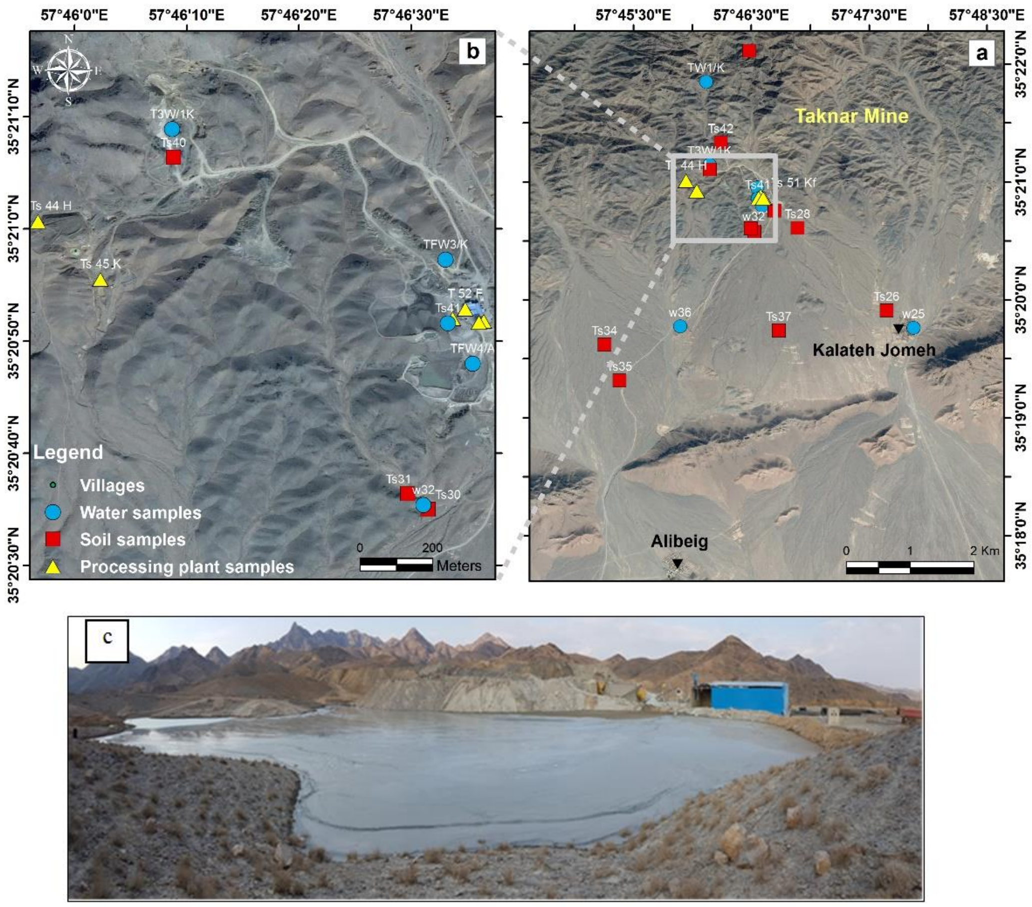

Fig 1. a) The location map of study area. b) The location map of samples in processing plant area. c) Associated mining facilities.

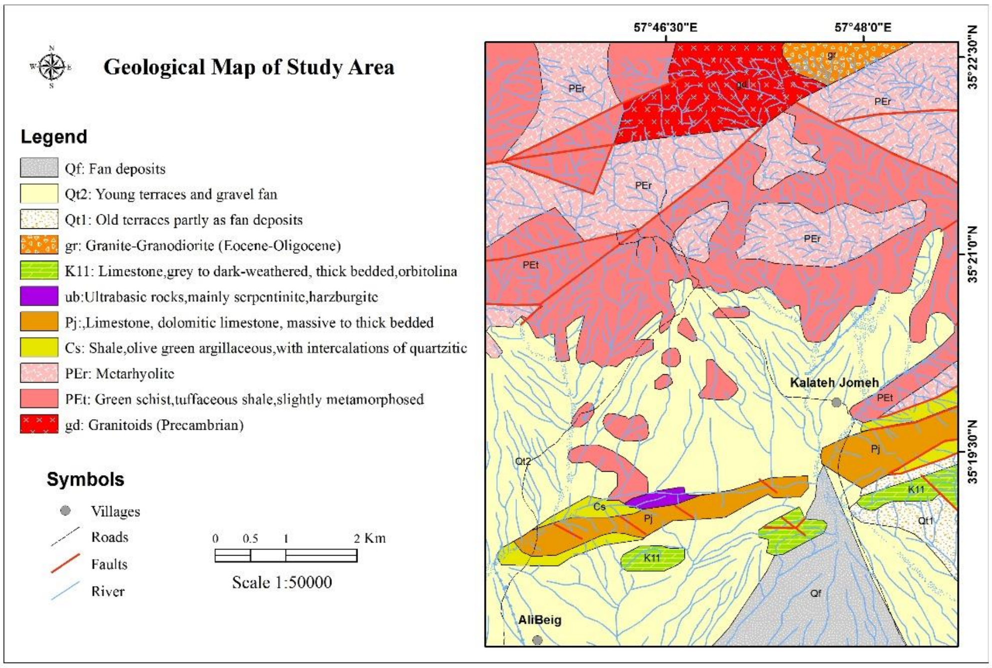

Fig 2. Geological map of Taknar area (after Shahrabi et al. 2006).

analysis) calculated for evaluating contamination in this area. In addition, geological and geochemical sampling used to identify the sources of different samples.

3.1. Sample collection

25 samples were collected from soil, water and mineral processing plant (Fig. 1). Eleven surface soil samples (3-4 Kg each) were taken at depths 0–30 cm from different location. Samples were sieved (0.2 mm sieve) and were collected in polyethylene bags.

The surface and groundwater water samples were taken from the upstream, downstream and close to the active mining and processing area and from an aqueduct in the villages of Kalateh Jomeh and Alibeig. The drainage map used to determine the flow direction. The eight water samples were collected from mine tailing, mining wastewater and drinking water in different polyethylene bottles. At each point, the body of the sampling bottle was soaked several times to minimize the contamination from the sampling instrument. Surface or underground mining and extraction methods of copper can concentrate heavy metals in the tailings and waste rock. To evaluate copper processing effect on soil and waters in Taknar mine, six samples analyzed from heap leaching, waste rock and tailings dam.

3.2. Measurement of physico-chemical properties

A calibrated Extech multimeter used to measure the pH and EC of the soil samples (Table 1). The elemental analysis were performed by ALS Laboratory in England through Inductively coupled plasma mass spectrometry (ICP-MS) method in two packages, for soil and sediment throw ME-MS 61 L (Four Acid Digestion for Near-Total Super Trace Analysis) and for waste and concentrate sample with OG62 (Four Acid Digestion with Inductively coupled plasma atomic emission spectroscopy (ICP-AES) or Atomic absorption spectrometry (AAS) (Ores and High Grade Materials)). Standards, accuracy and precision indicated in https://www.als-testing.co.uk/ website.

A number of parameters such as temperature, pH, TDS, and salinity were also measured at the water-sampling site using the Extech multimeter. Samples of water were acidified with 3% nitric acid and then transferred to Zarazma Laboratory in Tehran within 24 hours to analyze by Inductively coupled plasma - optical emission spectrometry (ICP-OES) method (Table 2 and 3). Standards, accuracy and precision are available on the laboratory's website in http://zarazma.com/. Concentration of metals in processing samples is shown in table 4.

Table1. physicochemical parameters of soil samples in study area

Sample	TS26	TS28	TS29	TS30	TS31	TS34	TS35	TS37	TS39	TS40	TS42
W(Total)(g)	4000	4000	4000	2000	4000	2000	4000	40000	4000	2000	1676.6
W(Sand)	3582.3	3096.9	3361.4	1731.9	3102	1727.2	3641.7	3577.3	2841.2	1057.7	1385.6
W(Clay)	117.4	151.4	191.2	125.6	104.8	60.5	169.7	122.27	80.4	32.3	99.1
% Sand	89.55	77.42	84.03	86.59	77.55	86.36	91.04	89.43	71.03	52.88	82.64
% Clay	2.93	3.78	4.78	6.28	2.62	3.02	4.24	3.06	2.01	1.61	5.91
Texture	Sandy	Sandy	Sandy	Sandy	Sandy	Sandy	Sandy	Sandy	Sandy	Sandy	Sandy
pH	7.63	7.3	7.35	7.44	7.68	7.5	7.53	7.44	7.49	7.21	7.69
EC(µs/cm)	810	2340	2880	1090	2790	680	890	900	530	500	870

Table 2. Physicochemical parameters of water samples in study area

Sample	T(°C)	pH	TDS ($mgKg^{-1}$)	EC(µs/cm)	S ($mgKg^{-1}$)
TFW3/K	20	7.42	2640	6590	710
TFW4/A	87.6 F	7.76	3240	8150	710
T3W/1K	82.4 F	8.30	1420	3570	1.74 ppt
TW1/K	14	8.6	538	1343	653
W25	19	8.40	887	1243	620
W32	9.2	7.8	3.98 ppt	5.68	3.83 ppt
W36	16.3	8.2	4.24 ppt	6.06	3.01 ppt
TS41	12.7	11.54	2.62 ppt	6.26	3.10 ppt

3.3. Quantification of pollution

3.3.1. Enrichment factors (EF)

The EF is a method to find differentiates between anthropogenic or natural sources of potentially toxic elements. This technique depends on the ratio of the concentration of each metal in the soil and the background (Taylor 1964; Barbieri et al. 2014; Liang et al. 2017). Researchers use different reference elements. Iron and Al are more popular. The researchers especially who were working on marine and estuarine sediments used Fe (e.g. Martin and Whitfield 1983, Lee et al. 1998, Bhuiyan et al. 2010; Gue et al. 2014). The geochemistry of Fe element is similar to other traces elements (Emmerson et al. 1997). Its natural concentration tends to be uniform (Daskalakis and O’Connor 1995). Some researchers used the element Al as a reference element, because it is a main component,

Table3. Type of cations and anions in the water samples (mgL^{-1})

Element	Na^+	K^+	Ca^{++}	NO_2^-	NO_3^-	Cl^-	SO_4^-	F^-	PO_4^-	Br^-	HCO_3^-	Th
TFW3/K	1117	7.98	207.2	-	-	-	-	-	-	-	-	-
TFW4/A	1634	58.43	350.7	-	-	-	-	-	-	-	-	-
T3W/1K	620	13.68	58.4	-	-	-	-	-	-	-	-	-
TW1/K	139	4.64	179.3	-	-	-	-	-	-	-	-	-
W25	150	3.26	56.6	<0.1	28	173	307	1.08	<0.1	-	-	-
W32	1580	38.03	214.5	<0.1	52.5	1897	1619	1.4	0.1	-	-	-
W36	738	7.86	607.5	<0.1	48	1755	1669	0.91	0.026	-	-	-
Ts41/A	1271	68.8	334.2	<0.1	38	1988	1559	0.99	<0.1	2.5	300	334.2

Table 4. Concentration of heavy metals in processing samples (values per %)

Sample	Cu	As	Pb	Zn	Cd	Cr	Co	Ni	Mn	Mo	Fe	S
Ts 48 D	0.264	<0.001	<0.001	0.008	<0.001	0.004	0.0012	0.003	0.07	<0.001	3.69	0.27
Ts 44 C	0.847	0.001	0.006	0.018	<0.001	0.006	0.0034	0.004	0.12	<0.001	4.69	0.89
Ts 45 B	36.2	0.002	<0.001	0.019	<0.001	0.01	0.0035	0.006	0.13	0.003	3.79	5.95
Ts 50 E	24.9	0.039	0.025	0.029	<0.001	0.002	0.113	0.008	0.03	0.004	32	28.7
Ts 51 F	27.6	0.004	0.085	0.055	<0.001	0.018	0.0057	0.007	0.06	0.003	9.44	9.24
Ts 52 A	0.248	0.005	<0.001	0.006	<0.001	0.006	0.0064	0.003	0.08	<0.001	6.24	0.78

especially in clay minerals (e.g Loring 1990; Balls et al. 1997; Barbieri et al. 2015). Therefore, in the present study, Al was chosen as the reference element as follow:

$$\mathrm{EF} = \frac{(\frac{C_x}{C_{Al}})Sample}{(\frac{C_x}{C_{Al}})Background} \qquad (1)$$

Where C_x is the measured concentration of the element and C_{Al} is concentration of the Al element. In this equation $(C_x/C_{Al})_{sample}$ show the ratio of element and Al concentrations in the sample and $(C_x/C_{Al})_{background}$ show their ratio in the reference. To calculate the grade of contamination and to comprehend the anthropogenic origin of potentially toxic elements, seven contamination categories were recognized (Table 5).

3.3.2. Geoaccumulation Index (I_{geo})

The (I_{geo}) introduced by Müller (1979) used to evaluate potentially toxic elements pollution in soil samples as follow:

$$I_{geo} = \mathrm{Log}_2[C_n/1.5B_n] \qquad (2)$$

Cn refers to the measured concentration in mgKg^{-1} of the metal n and Bn is the geochemical background value of the metal n in mgKg^{-1}. Factor 1.5 is a constant number for correction lithospheric effects. The I_{geo} was categorized into seven categories of contaminations, ranging from extremely polluted to unpolluted (Guo et al. 2014) (Table 5).

3.3.3. Contamination Factor (CF)

This factor is the ratio of the average concentration of a metal in the soil to that in background:

$$CF = C_{metal}/C_{background} \qquad (3)$$

As shown in table 5, this factor was divided into seven groups based on the severity of contamination from unpolluted (CF=0) to very strong contamination (CF=6) (Muller 1969).

4. Results

4.1. Geochemistry of waters

Acidity or pH is one of the most significant physicochemical properties that have impact on the dissolution of substances in water. Most chemical and biological reactions in aquatic systems have affected by pH (Arun Kumar et al. 2015). The water samples show an alkaline nature (7.42-11.54), which may be due to the existence carbonate minerals in the mining area (Table 2). The acceptable normal range of pH is about 6.5 to 8.5 (WHO 2017). The pH values are close to the limits for drinking water suggested by WHO (2017).

Electrical conductivity (EC) is one of the most important parameters that express the concentration of the elements in water. Electrical conductivity relates to the total soluble salts in water and depends on factors such as ion concentration, ion mobility, ion capacity and temperature (Arun Kumar et al. 2015). In the studied water samples, EC changed from 5.68 to 8150 µs/cm and the variance was quite high. According to the drinking water standard (WHO 2017), the samples with higher electrical conductivity than 1500 µs/cm are not adequate for this purpose (Table 2).

The studied samples show Total dissolved solids (TDS) raging 0.000002 - 3240 mgKg^{-1} (Table 2). The acceptable limit of drinking water is 600 mgKg^{-1} TDS (WHO 2017). The use of high TDS waters can lead to gastrointestinal discomfort and in the long-term lead to kidney stones and heart attack (Sharmila and Rajeswari 2015).

Table 5. Classification of heavy metals potentially toxic elements evaluated with Enrichment Factor (EF) and Index of Geoaccumulation (I_{geo}) based on (Guo et al. 2014). Contamination factor values based on (Muller 1969).

EF range	Description	CF	Description	I_{geo}	Description
$EF \leq 1$	No enrichment	0	No contamination	$I_{geo} \leq 0$	Unpolluted
$1< EF \leq 3$	Minor enrichment	1	None to moderate	$0< I_{geo} \leq 1$	Unpolluted to moderately polluted
$3< EF \leq 5$	Moderate enrichment	2	Moderate	$1 < I_{geo} \leq 2$	Moderately polluted
$5 < EF \leq 10$	Moderately severe enrichment	3	Moderately to strong	$2 < I_{geo} \leq 3$	Moderate to strongly polluted
$10 < EF \leq 25$	Severe enrichment	4	Strongly polluted	$3 < I_{geo} \leq 4$	Strongly polluted
$25 < EF \leq 50$	Very severe enrichment	5	Strong to very strong	$4 < I_{geo} \leq 5$	Strongly to extremely polluted
$EF > 50$	Extremely severe enrichment	6	Very strong	$I_{geo} > 5$	Extremely polluted

4.2. Soil quality

The pH value, electric conductivity (EC), texture and particle size distributions of soil samples are shown in Table 1. The pH values vary from 7.21 to 7.68 (Table 1). The low alkaline nature may be due to the presence of carbonate minerals (Foth 1990). The studied samples show a wide-ranging variation of EC from 500 to 2880 µs/cm. The soil samples were classified as sand (two samples), loamy sand (six samples), sandy loam (two samples), loam (three samples) and silt loam (two samples) based on soil classification (USDA, 1996) (Fig. 3).

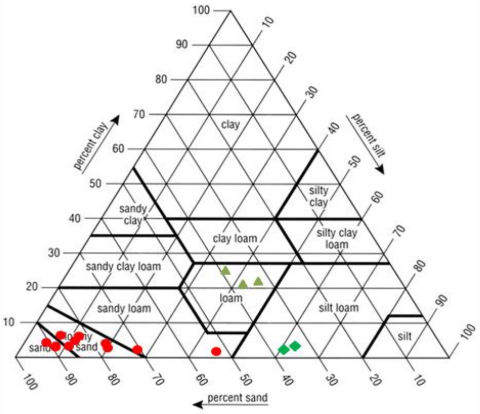

Fig 3. USDA Triangle diagrams of soil classification

4.3. Trace Element Analysis

Concentration of Cu, As, Se, Pb, Zn, Cd, Fe, Mo, Mn, Ni, Co, Cr and Sb element in soil and water samples is shown in Figure 4. As shown, some element as Cu has a wide range and some element like Cr show a narrow range. Concentrations of potentially toxic elements in soil including Cu, Pb, Zn, As, Mo and Cd are relatively high at the mining and processing site and Co, Cr, Ni show the opposite trend and show high values in the southern samples. The results show that the amount of Cu in the soils of the region varies between 29.3 to more than 10000 mgKg^{-1}. The value of Fe varies from 3.3 to 5.8 mgKg^{-1} and the total Pb concentrations are ranging from 4 to 3520 mgKg^{-1}in the studied samples.

The concentration of Zn in the soil samples vary from 72 to 2310 mgKg^{-1}. Selenium content in the soil samples changes from 0.3 to 8.3 mgKg^{-1} (Fig. 4) while its contents in worldwide soils is about 0.33 mgKg^{-1} (Kabata-Pendias and Pendias 2007). The studied soil samples contain Cd element ranging from 0.08 to 4.99 mgKg^{-1} (Fig. 4).

The As Content in studied soil samples range from 7.71 to 50.8 mgKg^{-1} (Fig. 4), which is higher than the global soil (5 mgKg^{-1}) (Kabata-Pendias and Mukherjee 2007).The highest amount of Cu in water sample (0.24 mgKg^{-1}) was measured in one of the mining tunnel and the lowest (0.001 mgKg^{-1}) in the aqueduct in the village of Kalateh Jomeh and Alibeig villages. The maximum Pb concentration in water sample is 0.0103 mgKg^{-1}. The acceptable limit of Pb in drinking water is 15 µg l^{-1} (WHO 2017). The studied water samples contain a significant amount of Se ranging from 7.2 to 20.2 µgKg^{-1} (Fig. 4). Usually content of Se in natural waters is at a level of <1 µg l^{-1} (Kabata-Pendias and Pendias 2007). The threshold value for Se in drinking water has been defined 10 and 45 µg l^{-1} in the USA and 10 µg l^{-1} in other countries (WHO 2017). The studied water samples contain Cd ranging from <0.1 to 14.5 µgKg^{-1}. The threshold value for Cd in drinking water is 5 µg l^{-1} (WHO 2017).

The samples taken from the vicinity of the flotation plant and the heap leaching site (Table 4) have the highest amounts of Cu (270000 to 360000 mgKg^{-1}), As (50 to 390 mgKg^{-1}), Pb (250 to 850 mgKg^{-1}), Zn (250 to 290 mgKg^{-1}) and about 10 mgKg^{-1} Cd. Manganese concentration in these samples range between 1000 and 1300 mgKg^{-1} and Co content has also reported up to 1100 mgKg^{-1}, all above the global average.

5. Discussion

5.1. Pollution of soil

The global average for Cu concentration changes from 8 mgKg^{-1} in sandy soils to 80 mgKg^{-1} in heavy loamy soils (Kabata-Pendias and Mukherjee 2007). Preliminary results show that the concentration of Cu exceed standard soils. Angelone and Bini (1992) refer to less than 100 mgKg^{-1} Pb for unpolluted soil. The Total Pb concentrations in the studied samples are ranging from 4 to 3520 mgKg^{-1}.

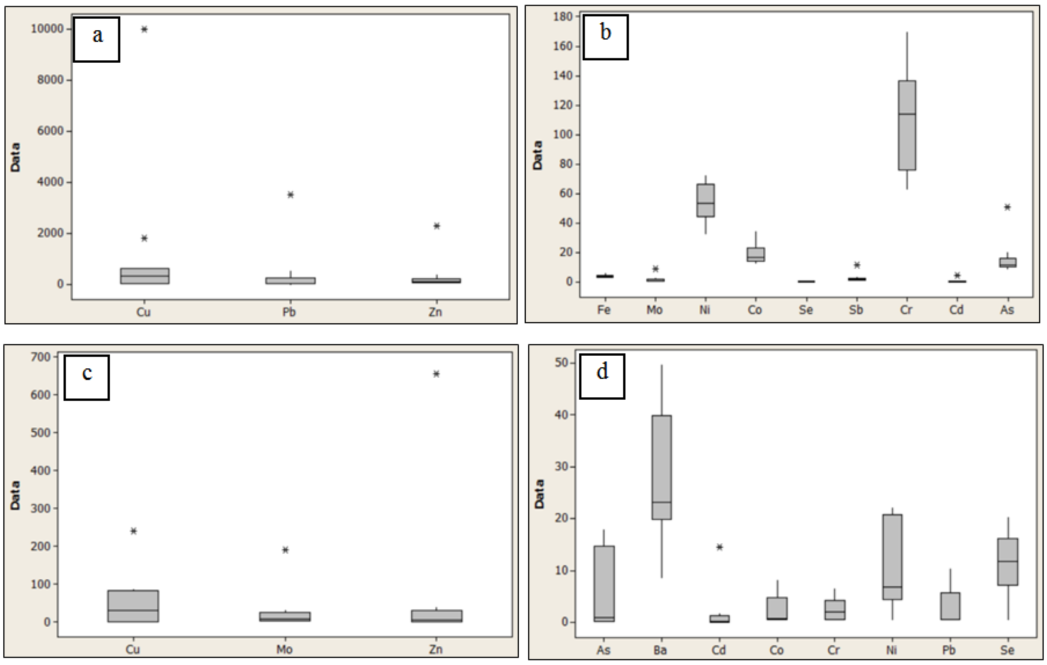

Fig 4. Box-plot of concentration of some potentially toxic elements in (a, b): soil and sediment (mgKg^{-1}) and (c, d): water samples (µgKg^{-1}). Stars (*) shows outliers in the data.

This result shows that Pb has high risk for human. Although Pb usually has slow mobilization, but several factors like acidity and organic component can increase its solubility.

The average Zn for worldwide soils was reported about 64 mgKg^{-1} (Kabata-Pendias and Pendias 2007), therefore the Zn concentration in samples close to Taknar mine are higher than the average worldwide. The lowest content measured from the sample near Kalateh Jomeh village, indicates Zn anomalies are around the mining area. The maximum amount of Se was reported from the mine entrance. Distribution of Se in the geological environment is highly variable depending on different rock types. Selenium is often found in sulfide minerals (e.g. pyrite, chalcopyrite) due to similarities in crystallography. Since the Se content in soils and its distribution is similar to Cu, strongly reflecting mineral deposition and later soil-forming processes.

The Cd value ranging from 0.08 to 4.99 mgKg^{-1} exceeds the average global soil standards (0.5 mgKg^{-1}) (Kabata-Pendias and Pendias 2007). Background elements (Na, K, Ca, Mg, Al, Fe, Ba, Sc, Ti, and Br) are different; depend on soil types (Jiang et al. 1996). Some authors (e.g. Sutherland et al. 2000; Blaser et al. 2000) suggested using element concentrations in a deeper horizon of soils as a local background. In absence of background values from the study area, the background value of the metal and Al concentrations were derived from the Global shale (Turekian and Wedepohl 1961).

5.1.1. Enrichment factor

EF indices has been used to separate anthropogenic source from natural origin of the heavy metals concentration. The calculated EF values vary from 0.4 to 225 (Table 6). The EF values for Cu and Pb are the highest than other metals and it shows extremely high enrichment at specific sites (Fig. 5). The EF values for Zn, Cd and Se are high to extremely high in same samples (Table 6, Fig. 5). The samples were located closer to the Taknar mine show higher EF values. The order of average EF is Cu > Pb> Zn > Cd > Sb > As > Se (Table 6). Differences between the EF values may be influenced by on the amount of metals and the removal rate of them (Ghrefat et al. 2011). The distribution map of the enrichment factor index for Cu, Pb, Zn, Cd, Se and Sb with the anthropogenic origin has shown in Figure 5. EF values greater than 10 indicate that the element comes from anthropogenic origin. The results demonstrate that in the soil of the study area some elements such Co, Cr, Ni, Mn and Mo are not enriched or enriched to a minor degree (Table 6), so these elements are related to lithological origin.

5.1.2. Geoaccumulation index

The calculated geoaccumulation index for the studied samples varies from -0.07 to 2.1, indicating the majority of soil samples are unpolluted, while moderately polluted for Cu, Pb, Se, Zn, Cd, Sb (Table 6). Moreover, the obtained I_{geo} revealed these samples are considered low to moderately contaminated with Cr, Co and Mn. Based on the classification of I_{geo}, the concentrations of Co, Cr, Ni in the soil samples are unpolluted, but Cu, Pb, Zn and Cd show significant variation around the mining area.

Table 6. Summary statistics of EF, EC and I_{geo} for some elements.

Sample	Cu			Pb			Zn			Cd		
	EF	CF	I_{geo}	EF	CF	I_{geo}	EF	CF	I_{geo}	EF	CF	I_{geo}
Ts26	0.9	0.6	-0.3	1.4	1.0	-0.2	1.0	0.7	-0.3	0.8	0.6	-0.4
Ts28	1.8	1.3	-0.04	1.7	1.3	-0.07	1.3	0.9	-0.2	0.8	0.6	-0.4
Ts29	225	222.2	2.1	1.6	1.6	0.03	0.9	0.9	-0.2	1.1	1.1	-0.1
Ts30	12.0	9.4	0.8	16.9	13.2	0.9	2.8	2.2	0.2	2.4	1.8	0.1
Ts31	8.6	7.6	0.7	1.5	1.3	-0.05	1.2	1.1	-0.1	0.6	0.5	-0.4
Ts34	0.8	0.6	-0.4	1.7	1.3	-0.04	1.5	1.2	-0.1	0.8	0.6	-0.3
Ts35	0.8	0.6	-0.3	1.6	1.3	-0.06	1.3	1.0	-0.1	0.8	0.6	-0.3
Ts37	1.2	0.8	-0.2	1.2	0.8	-0.2	1.2	0.8	-0.2	0.8	0.6	-0.4
Ts39	47.6	40.4	1.4	207	176	2.1	28.6	24.3	1.2	19.6	16.6	1.04
Ts40	14.8	14.2	0.9	0.2	0.2	-0.8	0.8	0.7	-0.3	0.3	0.27	-0.7
Ts42	10.9	9.0	0.8	30.5	25	1.2	4.6	3.7	0.4	3.3	2.7	0.3

Sample	As			Sb			Se			Mo		
	EF	CF	I_{geo}	EF	CF	I_{geo}	EF	CF	I_{geo}	EF	CF	I_{geo}
Ts26	1.2	0.9	-0.2	1.12	0.8	-0.25	1.2	0.8	-0.3	0.5	0.4	-0.2
Ts28	1.2	0.8	-0.2	1.17	0.8	-0.2	0.7	0.5	-0.5	0.6	0.4	-0.3
Ts29	0.6	0.6	-0.4	0.6	0.6	-0.4	14	13.8	0.9	0.8	0.8	-0.1
Ts30	1.4	1.1	-0.1	1.8	1.5	-0.01	1.3	1.0	-0.2	0.9	0.7	-0.1
Ts31	1.2	1.0	-0.1	1.5	1.4	-0.04	1.1	1.0	-0.2	0.5	0.5	-0.1
Ts34	1.0	0.8	-0.2	1.4	1.1	-0.1	0.8	0.6	-0.3	0.4	0.3	-0.2
Ts35	1.1	0.8	-0.2	1.02	0.8	-0.3	0.8	0.6	-0.3	0.4	0.3	-0.2
Ts37	0.9	0.7	-0.3	1.05	0.8	-0.3	0.6	0.5	-0.5	0.4	0.3	-0.2
Ts39	4.6	3.9	0.4	9. 5	8	0.7	2.2	1.8	0.1	4.1	3.5	0.1
Ts40	0.7	0.7	-0.3	1.6	1.6	0.02	1.2	1.2	-0.1	0.7	0.7	0.02
Ts42	1.9	1.5	0.02	2.6	2.1	0.1	1.8	1.5	0	1.3	1.1	0.03

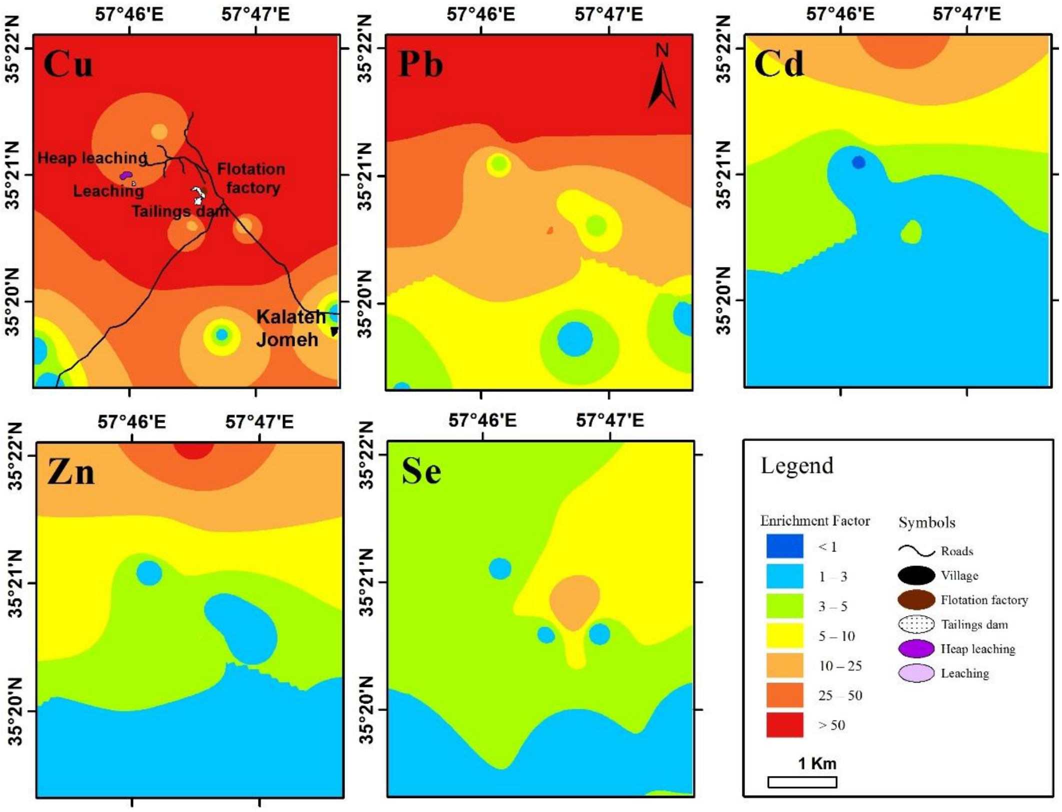

Fig 5. Variation of Cu, Pb, Zn, Cd and Se Enrichment Factor in the soil samples.

For example, Cu is unpolluted near the Kalateh Jomeh village at the south of the study area, whereas moderately to strongly polluted at the mining and processing sites, respectively.

5.1.3. Contamination factor

The calculated contamination factor changed from 0.3 to 222 (Table 6) indicates that the soil samples changes from No contamination to very strong contamination. The samples are extremely polluted with Cu and Pb (CF>6) and high contamination of Zn, Cd and Sb and As for same samples was obtained. The CF values of other elements are low to moderately contaminated (CF< 2).

It needs to note that previous studies (Niloufar 2007) showed high pollution of soil and water samples. Niloufar (2007) has reported high concentration of Cu in soil samples from mining area. The results of the water samples also showed high acid solute conditions. The water samples from aqueduct of the downstream villages showed high concentrations of highly pollutant As and Pb elements (Niloufar 2007). Although previous studies confirmed the poor quality of drinking water, but the results presented here indicate that Cu, Zn, Pb, Cd and Se show pollution around Taknar mine and the soil and water around residential area are without contamination. It may be the result of waste management during this period.

5.2. Water quality

The threshold values for Cu in drinking water is 0.05 µg l^{-1} in most European countries and it has set from 0.04 to 3 µg l^{-1} in other countries (WHO 2017). In this study, the Cu pollution in waters near mining/mineral processing activity shows its pollution was related to Taknar mine. Fortunately, the water resources used by staff did not show contamination and the Pb concentration is within the range of global and domestic drinking water standards. The pervious study (Niloufar 2007) had reported the Pb concentration is dangerous and it should be considerate to its use or potential for mixing with groundwater.

The content of Se (7.2 to 20.2 µgKg^{-1}) is in the normal range in drinking water (10 and 45 µg l^{-1} in the USA standards. The Cadmium varies from <0.1 to 14.5 µgKg^{-1}, some higher than the threshold value for drinking waters (5 µg l^{-1} ,WHO 2017). It was considered as one of the toxic metals, which has special effects on humans, animals, and plants (WHO 2017). The toxicity of Cd in waters depends on water hardness and increase with decreasing the hardness. High values of Cd are associated with high values of Cu concentration, which indicates its source has related to Cu mineralization.

Chemical analysis of samples from the water resources indicates that the samples from the flotation plant tailings and tunnels contain 13 to 18 µgKg^{-1} of As, which would be dangerous if used without proper treatment. One of these samples contains also 0.015 mgKg^{-1} of Cd and over 0.24 mgKg^{-1} of Cu that are above the permitted level. Arsenic has known to be highly toxic to humans and animals. The maximum level of As (MCL) in water is 0.01 mgKg^{-1} (WHO 2017).

5.3. Statistical and cluster analysis

Pollution indices for other elements as Cr, Co, Ni, Mn showed there are no contamination for other elements, so their source are related to the lithology. To ensure, principal component analysis (PCA) was applied to find metal sources in the soil and sediments. The first three principal components (PC1, PC2, and PC3) show 93% of the total variance (Fig. 6). PC1 include 61% of total variability and has high loading on Zn, Cd, Pb, As, Sb, Mo elements. PC2 accounts for 18% of total variance and has positive loading on Cr and negative loading on Cu and Se. PC3 with 14% of total variance has high loading on Cu and Se elements.

PCA indicate origin of Cu and Se in soils is most probably from specific point-source pollution. These results suggest that PC2 and PC3 show completely different geochemical behaviors and sources. PC1 is representative the variability of elements that have controlled by geological process (natural aspects) and anthropogenic sources, PC3 (Cu and Se elements) relates to anthropogenic factors, while PC2 (Cr) corresponds to natural (lithogenic) factors (Fig. 6). Investigation of the Cluster analysis (CA) relationships between potentially toxic elements in the soils showed that the studied elements could divide into two main clusters. The first branch consist Cr-Ni and the second branch can be divided into two sub-branches of (1) Cu-Se and (2) Pb-Zn-Cd-As-Sb-Se based on the branch weight and similarities. The cluster graph shows that Cu and Se and also Cr and Ni were highly correlated with each other, indicating the same origin of the metals in the soils. In addition, the results show that Pb, Zn, Cd, Sb and As have the same origin (Fig. 6). These second branches have significant concentrations in soils and sediments around the mine, so their concentration have related to same geological origin and mining activities.

The Pearson correlation has used to find the association between the studied elements (Table 7). There is a high positive correlation between the Cu-Se (0.995), Cd-As-Zn-Pb-Sb (0.98), Cr-Ni (0.904) and Fe-Co (0.938) Elements. Significant negative correlation found between potentially toxic elements pairs Cr–Fe, which could be related to their different source. The positively correlated ($p<0.01$) Cu-Cd-Pb-Zn-As elements is a characteristic of areas polluted by the copper mining and mineral processing industries (Rybicka 1996; Verner 1996). These results show the geochemical behaviors and sources of Co, Cr, Ni and Fe are different from Cu, Pb, Zn, Cd, As and Se.

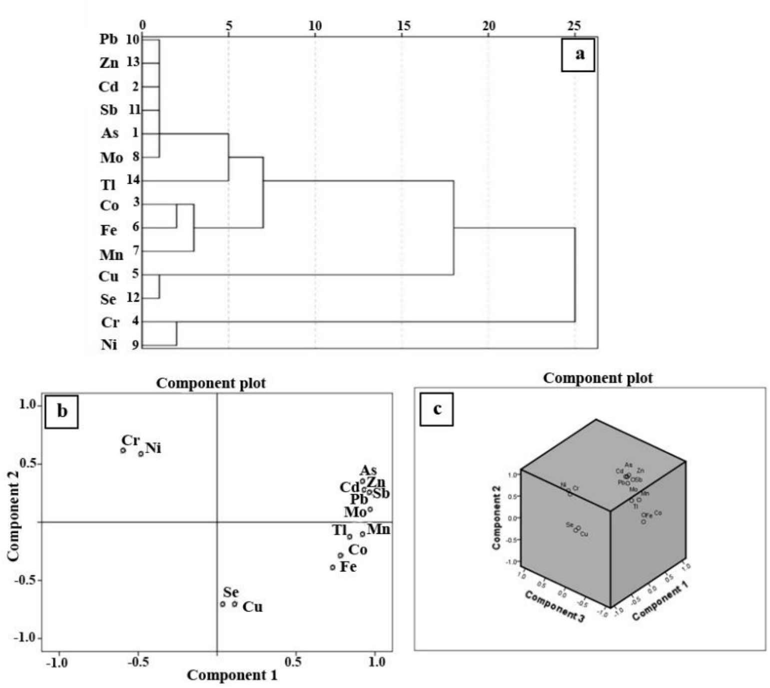

Fig 6. a) Dendrogram using Average Linkage obtained for hierarchical cluster analysis. b and c) 2D and 3D plot of PCA loading for potentially toxic elements

Table 7. Correlation matrix for selected elements from soil samples

	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sb	Se	Zn	Tl	pH	EC
As	1															
Cd	0.984**	1														
Co	0.534	0.560	1													
Cr	-0.321	-0.338	-0.624*	1												
Cu	-0.051	0.075	0.067	-0.251	1											
Fe	0.457	0.448	0.938**	-0.687*	0.099	1										
Mn	0.785**	0.766**	0.864**	-0.564	0.103	0.876**	1									
Mo	0.960**	0.981**	0.659*	-0.460	0.180	0.573	0.854**	1								
Ni	-0.193	-0.221	-0.570	0. 904**	-0.120	-0.579	-0.422	-0.319	1							
Pb	0.987**	0.999**	0.574	-0.347	0.047	0.464	0.776**	0.980**	-0.235	1						
Sb	0.985**	0.986**	0.647*	-0.404	-0.016	0.555	0.830**	0.976**	-0.305	0.990**	1					
Se	-0.129	-0.010	0.002	-0.203	0.995**	0.050	0.043	0.098	-0.078	-0.38	-0.101	1				
Zn	0.985**	0.999**	0.570	-0.345	0.044	0.459	0.769**	0.977**	-0.241	1.00**	0.990**	-0.041	1			
Tl	0.709**	0.721	0.599	-0.515	0.169	0.630*	0.745**	0.749**	-0.544	0.725*	0.773**	0.104	0.735*	1		
pH	0.207	0.081	-0.363	0.449	-0.290	-0.196	0.043	0.021	0.543	0.084	0.082	-0.256	0.081	0.026	1	
EC	-0.319	-0.289	-0.386	-0.268	0.531	-0.180	-0.325	-0.248	-0.100	-0.307	-0.340	0.550	-0.304	-0.088	-0.045	1

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (1-tailed)

The first group can be originated from the mafic and ultramafic rocks in the north of the area and the presence of these elements in the soil can attributed to their lithological origin, where the second group relates to mining activities. Pb, Zn and Cu values exceeded the standard, which require soil remediation around mining area. The coefficient obtained for the EC with Cu and Se elements are positive correlations ($r = 0.5$, $p > 0.05$), confirming the effect of soluble salts in the saline soil and thus a direct impact of anions such as sulfate in determining the electrical conductivity level.

Based on contamination indices and statistical analysis, the distribution of the elements such as Cu, Pb, Zn, Cd and Se were controlled by the anthropogenic sources mainly from mining activity in Taknar mine. On the other hand, distribution of Fe, Mn, Co, Cr, Mo, S has lithological sources. Statistical analysis demonstrates that Cu and Se elements are primarily from anthropogenic sources and Pb, Zn, As, Sb, Cd and Mo may be mixed from natural and anthropogenic inputs. Cr and Ni show completely different sources. Based on statistical analysis, there are three broad element classes: (1) Cu-Se association with anthropogenic origin mostly related to mining and processing industry, (2) Zn, Pb, Cd, As, Sb, Mo with mixed origin mostly related to mine and partly to lithology (3) Cr, Ni and Co with lithogene origin.

6. Conclusion

The metallogenic belt of Taknar is generally rich in copper and associated elements and therefore the soil and water environments are expected to have high concentration of potentially toxic elements. There was concern about soil and water contamination due to mining and processing activities in this area. Results of chemical analysis showed some samples near this mine have higher values than their averages in the global soil standards. As well, drinking water and their pollutant concentration decrease by distances from the mine.

Some indices used for evaluating the degree and extent of contamination. Based on these assessments, samples are in the category moderate to high pollution of Cu, Pb, Zn, Cd and Se. The order of average EF is Cu > Pb> Zn > Cd > Sb > As > Se, indicate pollution of Cu is higher other elements which complies with copper mineralization of Taknar area. The concentration of these elements (especially near the mine entrance) exceeds the set standards, which show the effect of mining activities on soil. The calculated I_{geo}, CF, and EF are in uncontaminated or moderate contaminated for Cr, Co, Ni, Mn and Mo. Relationships between heavy metals concentration in these samples showed Cu and Se are highly correlated with each other, and likewise Cr and Ni are similar which may indicate the same origin of these metals in the soils of the region.

The results from the vicinity of the flotation plant and the heap leaching site indicate it has directly affected by mineral processing activities and by the accumulation of heavy elements in tailings dams or waste dumps of the processing sites. Field observations, chemical analysis and indices calculation indicate that the concentrations of some heavy metals are high in heap-leaching structure, but there is no effect of these elements discharging from the heap-leaching processes to the water and soil resources.

Fortunately, concentrations of potentially toxic elements in the soil and water near villages in the southern part are lower than that in the Taknar mining area. According to the results obtained from contamination indices the most affected area are located in northern part, close to Taknar processing plant and mine. Analysis results show that the Cu and Se have the potential to create environmental hazards in this area. Soil and waters around Taknar mine have high potential for producing heavy and toxic elements and consequently environmental pollution of the area due to the presence of sulfide minerals. This contamination also increases by the extraction of minerals through the flotation and ore processing. Fortunately, the drinking water and soil samples from nearby Kalateh Jomeh and Alibeig villages were unpolluted.

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