Evolution of soil contamination in the abandoned Lakan Lead and Zinc mine by heavy metals, Iran

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Abstract

Soil contamination in the vicinity of the abandoned Lakan Lead and Zinc Mine was studied. The results showed that over the past decades, the environmental pollution was caused by Lead, Zinc tailings dam and acid mine drainage. The average of Lead, Zinc, Cadmium, Copper and Nickel is 1295, 4273, 27, 185 and 92 mg/kg, respectively in the soils of tailings dam. These metals were continuously dispersed downstream from the tailings dam. Geoaccumulation index (Igeo), enrichment factor (EF) and contamination degree (Cd) indicate moderate to high contamination of Lead, Zinc, Cadmium, Copper, Nickel and Cobalt and low contamination of Mercury in soils. Factor and cluster analysis indicate that Cadmium, Lead and Zinc were mainly derived from an anthropogenic source (such as mining and smelting of metal ores), but Cobalt and Mercury were controlled by natural source. Copper and Nickel appeared to be sourced both anthropogenically and naturally.

Keywords: Contamination, Soil, Heavy metals, Lakan, Iran.

1- Introduction

Anthropogenic activities such as mining and smelting of metal ores have increased the occurrence of heavy metal contamination at the Earth's surface. Mining activities have a serious environmental impact on soils and water streams by generating millions of tons of sulfide-rich tailings (Bhattacharya *et al*., 2006). In general, mine soils are physically, chemically and biologically weak (Vega *et al*., 2006), characterized by instability and cohesion, have low contents of nutrients and organic matter and high levels of heavy metals (He *et al*., 2005). Acidic drainage resulting from the oxidation of sulfides from metalliferous mine spoils Leads to the leaching of large quantities of cations, e.g. Fe^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+} (Vega *et al*., 2006; Martínez *et al*., 2013). Waste materials are rich of metal sulfides and have been stored or abandoned around of mining area (Concas *et al*., 2006; Boussen *et al*., 2013; Schindler *et al*., 1980; Vladimir *et al*., 2001).

The Lakan Lead and Zinc processing plant and its tailings dam are close to the rural area and residents of this region are very worry about these contaminants (Fig. 1). The derived heavy metals are transferred to the runoff and surface flow system through the catchment area and adsorbed directly by the soil/sediments and pollute the soils of the study area (Ghadimi *et al*., 2013).

The objectives of this research were; (i) to determine distribution of the metals in study area; (ii) to assess contamination associated with heavy metal in soils and (iii) to determine the source of heavy metals.

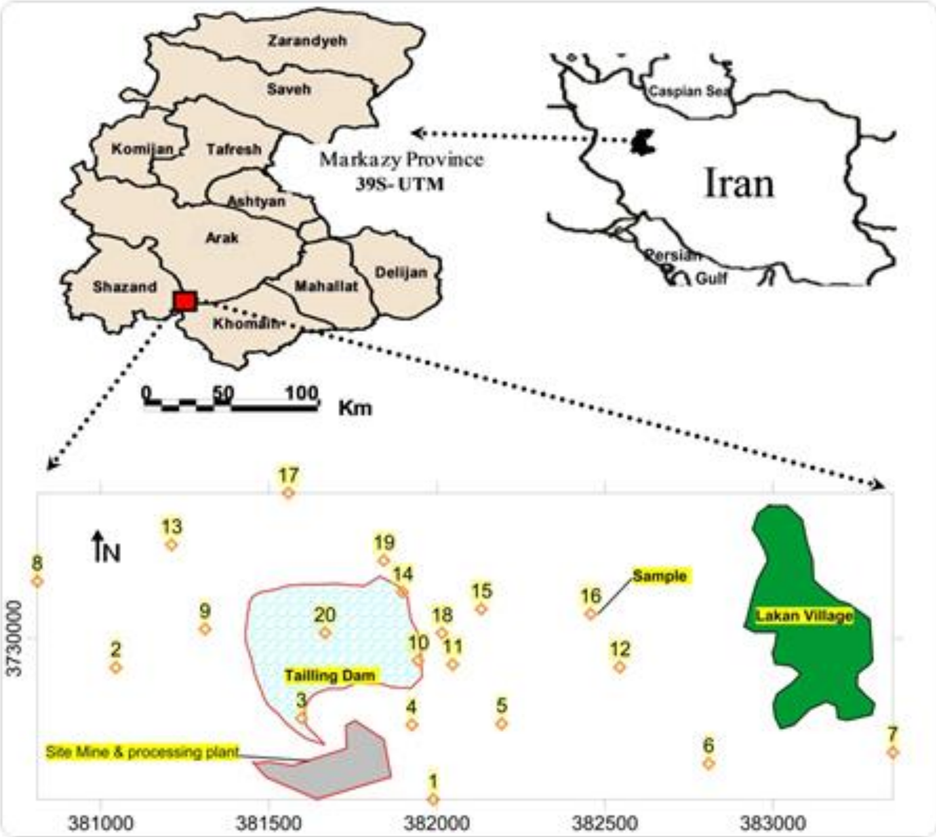

Figure1) Location map of the abandoned Lakan Lead and Zinc mine and tailings dam of the Lakan processing plant. The sample numbers in this map corresponded to those in Table 1.

2- Materials and methods

2.1- The characteristics of study area and sampling

Investigations of metal concentrations in soil/sediments have carried out by the Commission on Environmental Cooperation Progress around the Lakan mine and Lakan processing plant (Khodadadi *et al*., 2007; Hajati *et al*., 2008). The tailings dam, Lakan processing plant and Lakan Lead and Zinc mine were located uppermost of the rural region of Lakan (1.5 km) and 40 km toward the Khomain city. Upstream of the catchment area mainly includes old tunnel mine, while downstream catchment area contains the dam lake.

The soil/sediment samples were collected with an ordinary gravity sediment corer as described by Skogheim (1979). The soil/sediment samples were dried for 6 h at 105°C with water content expressed as a percentage of wet weight. The soil/sediment samples were then ignited for 4 h at 50°C for determining of the loss on ignition as an indirect index of organic matter content (OMC) (Hakanson, 1980). Concentrations of Nickel, Copper, Cobalt, Zinc, Cadmium and Lead in the sediments were analyzed at UCF-Esfahan laboratories by atomic absorption spectrophotometer (Perkins Elmer 460 and 560) using the standard addition technique. For metal analyses ~0.2 g sediment sample (dry wt.) was taken and digested in Teflon 'bomb' for 4 h at 140°C with 2 ml concentrated nitric acid. Mercury was determined utilizing cold vapor atomic absorption at the UCF-Esfahan. The methods of chemical analyses are in Rognerud *et al.* (1993) and Dauvalter (1994). These results are presented in Table 1.

2.2- Geoaccumulation Index (Igeo)

The geoaccumulation index allows estimation of metal contamination (Loska *et al.*, 2004). This method which has been used by Müller (1969) since the late 1960s was applied to several trace metal studies in Europe. The geoaccumulation index is computed from the following Eq. 1:

$$Igeo = \log_2 (C_n / 1.5B_n) \qquad \textbf{Eq. 1}$$

In the present study, geoaccumulation index was calculated using the modified equation given in Loska *et al.* (2004), where Cn is the measured concentration of the element in the soil sample and Bn is the geochemical background value in the Earth's crust (Cariate *et al.*, 2012). Müller (1969) divided the geoaccumulation index into seven classes, they are:

- Igeo ≤ 0: practically uncontaminated
- ۰ < Igeo < 1: uncontaminated to moderately contamination
- ۱ < Igeo< 2: moderately contaminated
- ۲ < Igeo< 3: moderately to heavily contamination
- ۳ < Igeo< 4: heavily contaminated
- ۴ < Igeo< 5: heavily to extremely contaminated
- 5 ≤ Igeo: extremely contaminated

2.3- Enrichment factor (EF)

The equation of Buat-Menard and Cherselet (1979) which was later modified by Loska *et al.* (2004) was used to calculate enrichment factors. This method is based on standardization of an element tested against a reference element. The most common reference elements are manganese, titanium, aluminum, calcium, and iron (Quevauviller *et al.*, 1989; Sutherland, 2000).

If enrichment factor is < 1, the element is depleted in the environment, while in the case of > 1 the element is relatively enriched in the environment (Brumsack, 2006). In this study, aluminum was used as the reference element. Aluminum is one of the most important components in the Earth's crust and its concentration in soil varies with respect to matrix.

Similar to Igeo, the reference environment adopted was the average concentration of elements in the Earth's crust. Enrichment factor was calculated using the modified formula based on Eq. 2 given in Buat-Menard and Chesselet (1979).

$$EF = \frac{\left(\frac{[C_n]}{[C_{ref}]}\right) Sample}{\left(\frac{B_n}{B_{ref}}\right) \text{background}} \qquad \textbf{Eq. 2}$$

Where Cn (sample) is the content of the examined element in the examined environment, Cref (sample) is the content of the reference element in the examined environment, Bn (background) is the content of the examined element in the reference environment; and Bref (background) is the content of the reference element in the reference environment. Enrichment factor (EF) is divided into five groups (Sutherland, 2000):

Table 1) Concentration of heavy metals (mg/ kg) in the soil samples around of the tailings dam.

	Concentration (mg/kg)						
No.	Ni	Cu	Co	Zn	Cd	Pb	Hg
1	163	195	126	6946	35	2105	0.004
2	95	195	69	1996	18	605	0.002
3	69	186	260	41068	85	12445	0.014
4	118	181	270	43180	137	13085	0.03
5	65	190	130	13695	53	4150	0.009
6	40	205	91	11467	45	3475	0.011
7	104	230	102	3069	27	930	0.012
8	92	145	92	2607	13	790	0.002
9	174	172	138	4372	28	1325	0.006
10	10	181	163	17556	63	5320	0.014
11	68	185	108	10758	40	3260	0.009
12	104	152	92	2805	12	850	0.004
13	152	141	125	2904	8	880	0.002
14	129	210	105	4174	28	1265	0.005
15	50	195	71	5164	21	1565	0.004
16	39	167	61	1419	7	430	0.002
17	90	135	95	1452	5	440	0.001
18	91	208	93	1170	15	365	0.005
19	92	159	89	2310	13	700	0.004
20	167	787	365	33181	67	10055	0.055
N Valid	20	20	20	20	20	20	20
Mean	95	210	132	10564	36	3202	0.01
Median	92	185	103	4273	27	1295	0.005
Minimum	10	135	61	1170	5	365	0.001
Maximum	174	787	365	43180	137	13085	0.06
*PEGS2	18	13	17	47	23	0.1	0.08

*Predicted Empirical Global Soil (Cariate *et al*., 2012)

- (EF< 2) Deficiency to minimal enrichment
- (EF= 2– 5) Moderate enrichment
- (EF= 5– 20) Significant enrichment
- (EF= 20– 40) Very high enrichment

(EF 40) Extremely high enrichment

2.4- Assessment of contamination degree

A significant number of indicators have been designed to approximate the quality of soils (Caeiro *et al*., 2005). In our case, assessment of soil contamination level is performed by the quantification of the Pollution Index (Chen *et al*., 2005) with the Contamination Factor (C_f) calculated and by the Contamination Degree (Cd) (Hakånson, 1980). Eq. 3:

$$C_f = C_{heavy\ metal} / C_{background} \qquad \textbf{Eq. 3}$$

$$C_d = \sum C_f$$

The C_f is the ratio between the concentrations of each metal in the soils and the reference background value (Table 1); and C_d is the contamination degree calculated as the sum of the C_f of each of considered metals. According to the variables, the variation in C_d can be defined as:

- $C_d < n$: low degree of contamination
- $n < C_d < 2n$: moderate degree of contamination
- $2n < C_d < 3n$: high degree of contamination
- $C_d > 3n$: very high degree of contamination

Where *n* is the number of contaminants involved in the C_d determination.

The following terminology is suggested for describing the contamination factor (C_f) (Hakanson, 1980):

- $C_f < 1$: Low contamination factor
- $1 \leq C_f < 3$: Moderate contamination factor
- $3 \leq C_f < 6$: Considerable contamination factor
- $C_f \geq 6$: Very high contamination factor

The following terminology is adopted to describe the degree of contamination (Cd values) for seven substances indicating serious anthropogenic pollution (Hakanson, 1980):

- Cd < 7: low degree of contamination
- 7 ≤ Cd < 14: moderate degree of contamination
- 14 ≤ Cd < 21: high degree of contamination
- Cd ≥ 21: very high degree of contamination

2.5- Statistical analysis

Univariate and bivariate statistical analysis was applied to the compositional data to estimate basic statistical parameters and to find the correlation coefficients between the different metals. Additionally, a multivariate statistical analysis of the factor analysis (FA) and cluster analysis (CA) were performed to identify the factors that could explain the correlation model between the data variables (Idris, 2008; Sielaff and Einax, 2007). The factor analysis was performed using a Spearman correlation matrix (significance level 0.05) to identify the possible sources of metal contamination in the study area and to evaluate the degree of association between the variables (metal). The factor analysis technique allows simplification of data complexity by reducing the number of variables to the orthogonal factors, thus facilitating the visualization of meaningful correlations (Kaiser, 1958; Jollife, 2002). The values of the factor matrix can be improved by using the varimax rotation method, which maximizes factor variance (Kaiser, 1958). It is an orthogonal rotation that minimizes the number of variables that have high loadings on each factor.

Cluster Analysis (CA) was also used to find homogeneous groups of samples based on their geochemical compositions. The single linkage was used for the regrouping of samples and to identify distribution model of the metal content in the soils. The variables with reduced distance are more similar than those with longer distances and therefore, could be grouped within the same cluster (Césari, 2007). The results obtained can be represented in a dendrogram, which shows the levels of similarity between the different variables. This method is very efficient and produces high stable groups structures (Zupan *et al*., 2000). Factor analysis and cluster analysis are complementary techniques; both compress a large amount of data into more manageable groups and increase significance. However, cluster analysis is considered more efficient in producing structures and groups clearly, and is relatively more stable. The statistica software package has been used for the data processing.

3- Results and discussion

3.1- Distribution of heavy metals in soils

The atmospheric emissions of Nickel, Copper, Cobalt, Cadmium, Zinc, Lead and Mercury from the concentrators and waste waters from tailings dam and mines are likely to be the main sources of elements in soils and sediments around the Lakan Lead and Zinc mine. Water is well buffered with slightly neutral pH and this favors accumulation of mobile elements like Nickel in the sediments (Hakanson and Jansson, 1983; Hajati, *et al*, 2008; Rognerud and Fjeld, 1990, 1993; Rekolainen *et al*., 1986; Johanson, 1989; Verta *et al*., 1989; Dauvalter, 1994). The prevailing north-western winds distribute the pollution plume mainly in a south-eastern direction downstream of the tailings dam. Atmospheric deposition of these elements is low in other locations the tailings dam. The highest Nickel, Copper, Cobalt, Cadmium, Zinc and Lead concentrations, exceeding the background values were measured in samples 1, 5, 9, 13, 14 and 18. Considerable accumulation of heavy metals attributed to the tailings dam. Concentration of Nickel, Copper, Cobalt, Cadmium, Zinc, Lead and Mercury in the soils and sediments has shown influence of atmospheric emissions from Lead and Zinc concentrator between mine site and tailings dam (Table 1 and Fig. 2).

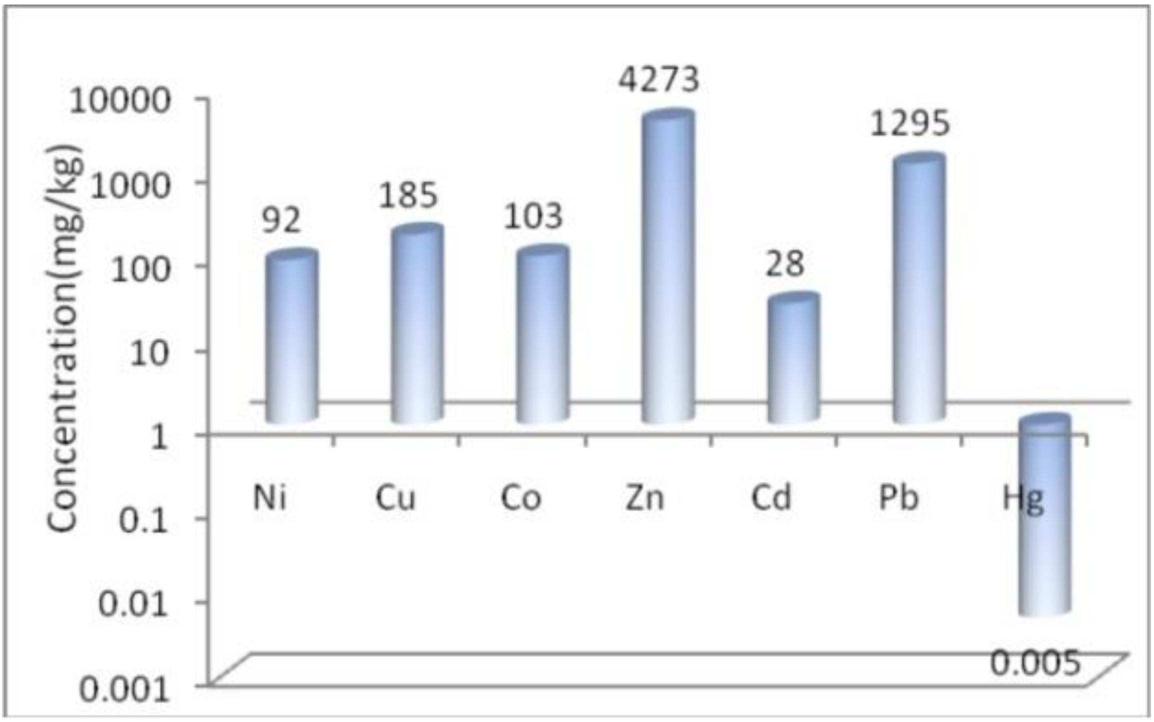

Figure 2) Concentration of metals (mg/kg) in soils of Lakan

Nickel concentration in Lakan soils is between 10 and 174 mg/kg with an average of 92 mg/kg. (Table1). Igeo values for Nickel vary from -0.60 to 0.70 with an average of 0.50.

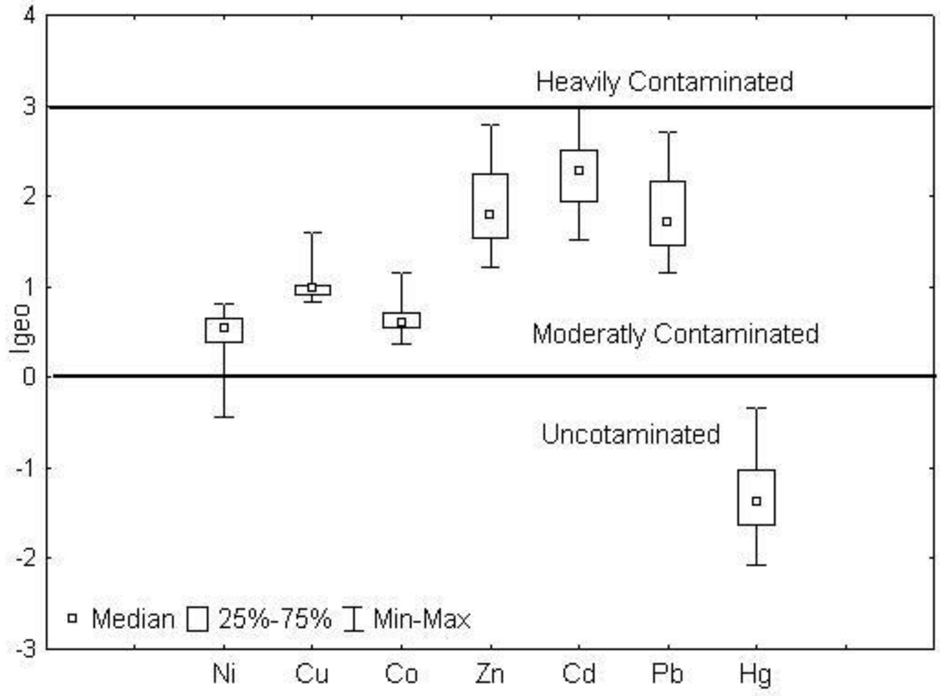

Figure 3) Geoaccumulation index for metals in soils of Lakan.

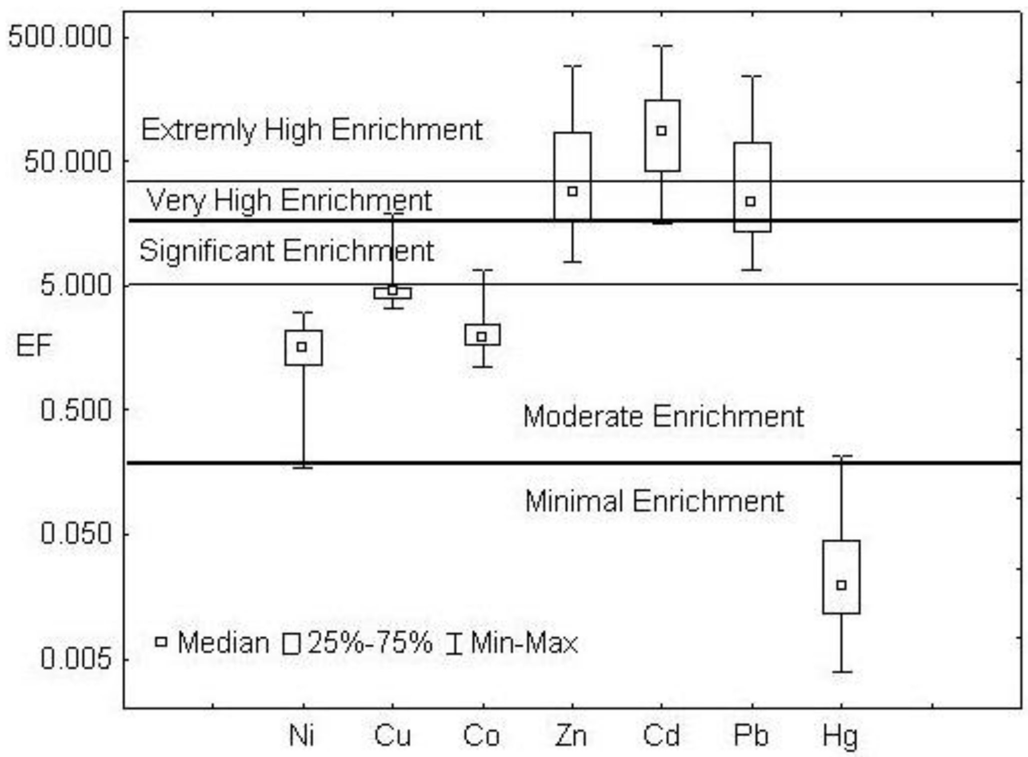

Figure 4) Enrichment factors for metals in soils of Lakan.

Based on the average values of Igeo, Lakan soils are uncontaminated to moderately contaminated. The average EF value is 3.80, indicating that soils collected from the study area are moderately enriched. Copper content of soils in the Lakan region is between 135 and 787 mg/kg with an average of 187 mg/kg which is noticeably greater than that in uncontaminated soils (Table1). The Igeo values range from 0.90 to 1.60 with an average of 0.50 for Copper (Fig. 3). The minimum Igeo denotes uncontaminated to moderately contaminated while maximum values express the soil as moderately contaminated (Müller, 1969). The EF values range from 4.50 to 40.00 for Cobalt (Fig. 4) with an average value of 5.20 which falls in class of significant enrichment.

Cobalt content of soils in the Lakan region is between 61 and 365 mg/kg with an average of 103 mg/kg which is applicably higher than that in uncontaminated soils (Table1). The Igeo values range from 0.30 to1.20 for Cobalt with an average of 0.7 (Fig. 3). The values of Igeo indicated uncontaminated to moderately contaminated (Müller, 1969). The EF values range from 1.10 to 5.40 for Cobalt (Fig. 4) with an average value of 3.20 implying minimal enrichment to significant enrichment. Zinc is a mobile element (Roa, 2001). The minimum Zinc concentration in Lakan soils is 1170 mg/kg and the maximum value is 43,180 mg/kg (Table1 and Fig. 2). The average Zinc concentration is 4273 mg/kg (Table 1). Igeo values vary from 1.10 to 2.80. The lowest value indicates that soils are moderately contaminated and the highest value is indicative of moderate to heavily contamination. The average value shows moderate contamination. The average EF value is 3.00, which indicates moderately enrichment.

The Cadmium values obtained in Lakan soils range from 5 to 137 mg/kg (Fig. 1) with an average of 27 mg/kg as shown in Table 1. The Igeo reveals that all the samples examined fall into class of uncontaminated to moderately contaminated and moderately to heavily contaminated (ranging from 1.80 to 2.90) (Fig. 3). The EF for Cadmium ranges from 42 to 400 (Fig. 4). The minimum and maximum values imply extremely high enrichment. Lead showed a different pattern from the other heavy metals. High Lead concentrations were observed in soils and sediments of the uppermost tailings dam reaches and processing plant (Table 1). The main source of Lead is from flotation processes in Lakan processing plant. These concentrators also emit Lead outside the processing plant. Thus, fine particles containing Lead are moved far from the dam. Therefore, increase in Lead was observed close to tailings dam and near to the processing plant. Among the heavy metals, Lead is the most immobile element and Lead content in soil is closely associated with clay minerals, Mn-oxides, Al and Fe hydroxyls, and organic material (Norrish, 1975). In general, the highest Lead concentrations are recorded in organic-material-rich soils where Lead behaves as an adsorbent (Kabata-Pendias, 2000). Lead concentrations in Lakan soils are between 365 and 13,085 mg/kg with an average of 1,295 mg/kg (Table 1). Kaljonen (1992) found that the upper limit of concentration for Lead is 17 mg/kg in soils. In another study by Shacklette *et al.* (1971), the upper limit for Lead in uncontaminated soils was given as 50 mg/kg. Igeo values for Lead vary from 1.20 to 2.60 with an average of 1.60 (Fig. 3). Based on the average value, Lakan soils are moderately contaminated while the maximum values implied that soils are moderately to heavily contaminated. The average EF value is 45 indicating that soils collected from the study area corresponded to extremely high enrichment (Fig. 4). The minimum Mercury concentration in Lakan soils is 0.001 mg/kg and the maximum value is 0.06 mg/kg (Table 1 and Fig. 2). The average Mercury concentration is 0.005 mg/kg (Table1). The Igeo calculated for Mercury changes from -2.20 to 0.80 (Fig. 3). The average Igeo classifies soils as uncontaminated (Müller, 1969). The EF for Mercury ranges from 0.10 to 1.80 (Fig. 4). The minimum and maximum EF values imply deficient to minimal enrichment.

Based on the calculated Igeo values, Lakan soils are moderately contaminated by Nickel, Copper, Cobalt, Cadmium and Zinc but not by Lead and Mercury (Fig. 3). The average EF value indicated that soils collected from the study area corresponded to extremely high enrichment of Zinc, Cadmium and Lead, and for Nickel, Copper, Cobalt, moderately enrichment and for Mercury minimal enrichment (Fig. 4).

3.2- Assessment of Contamination Degree

Maximum values of contamination factor (C_f) for heavy metals, with the exception of Nickel and Copper, were noticed for soil/sediments of sample 4 at distances ~20 m from tailings dam and ~200 m from processing plant (Fig. 5 and Table 2).

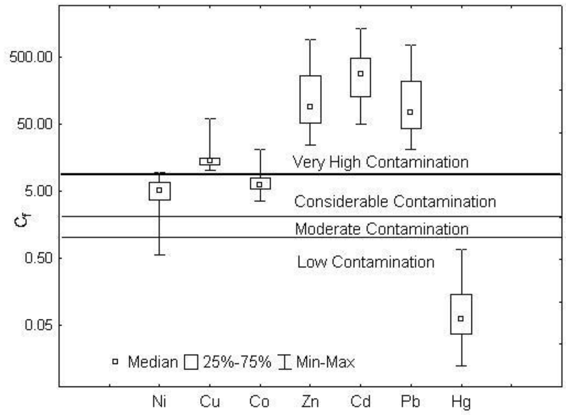

Figure 5) Contamination factors (C_f) metals in soils of Lakan.

This area has very high C_f values for Nickel, Copper, Cobalt, Zinc, Cadmium and Lead, according to the Hakanson (1980) classification.

Sample 3 has very high C_f value for Lead, Cadmium and Zinc, considerable values for Copper and Cobalt, a moderate value for Nickel and a low value for Mercury.

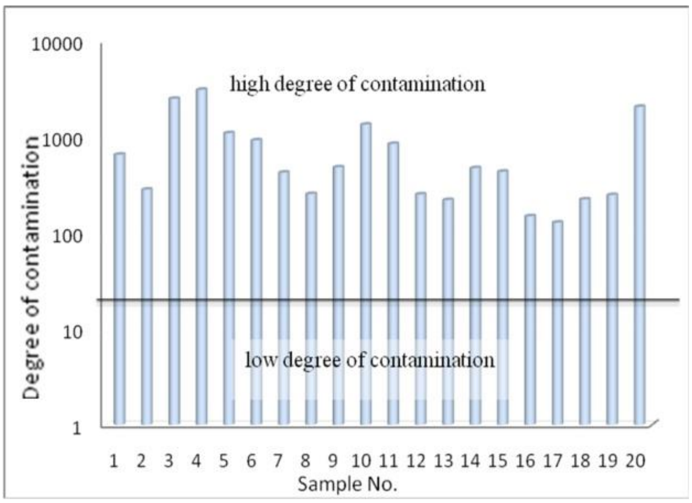

Figure 6) Contamination degree of metals in soils of Lakan.

Based on Cd values calculated for seven elements (Nickel, Copper, Cobalt, Zinc, Cadmium, Lead and Mercury) (Table 2), Lakan region generally presents very high degree of contamination (Fig. 6).

4- Heavy metal pollution source analysis

Because heavy metals in soils have now been shown to threaten the health of humans, it is important to identify and control sources of pollution. Numerous factors control heavy metals abundance; e.g., the original heavy metal contents of rocks and parent materials, processes of soil formation, contamination by human activities, and other anthropogenic factors (Li *et al*., 2001). Statistical analysis was implemented to determine the relationship between heavy metals and factor analysis was performed to determine the most common pollution sources.

4.1- Correlation between heavy metals

Table 3 depicts the correlation coefficient matrix, listing the Pearson product moment correlation coefficients. Very significant correlations were found between Mercury and Copper (r = 0.86), Mercury and Cobalt (r = 0.90), Mercury and Zinc (r = 0.76), Mercury and Lead (r = 0.76), Lead and Cobalt (r = 0.89), Lead and Zinc (r = 1), Lead and Cadmium (r= 0.94), Cadmium and Cobalt (r = 0.98), Cadmium and Zinc (r = 0.94), Zinc and Cobalt (r = 0.98) and Cobalt and Copper (r = 0.70) at the $p < 0.01$ level. High correlations between specific heavy metals in the soils may reflect similar levels of contamination and/or release from the same sources of pollution (Håkanson and Jansson, 1983; Li *et al*., 2001). There were strong positive correlations between Mercury, Cobalt, Zinc, Lead, Cadmium and Copper, but Nickel did not show significant correlation with these metals (see Table 3). The elements Mercury, Cobalt, Zinc, Lead, Cadmium and Copper are grouped together, indicating anthropogenic sources.

4.2- Factor analysis

Factor analysis has been applied to determine the degree of pollution by heavy metals of lithogenic origin and anthropogenic sources (Sun *et al*., 2010; Chen *et al*., 2005; Zhou *et al*., 2007; Rodríguez *et al*., 2009; Facchinelli *et al*., 2001; Khali *et al*., 2013).

The results of factor analysis for heavy metal contents are listed in Table 4. According to these results, Nickel, Copper, Cobalt, Zinc, Cadmium, Lead and Mercury concentrations could be grouped into a two-factor model, which accounted for 88.68% of all of the data variation. The initial factor matrix indicated that Cobalt, Zinc, Cadmium, Lead and Mercury are associated, displaying high values in the first factor (F1, a contribution rate of 69.01%), and that the correlation between these five heavy metals was significant (Table 4 and Fig. 7).

Table 4) Statistical results from factor analysis (Marked loadings are >0.70).

Element	Factor 1	Factor 2
Ni	-0.12	0.81*
Cu	0.38	0.80*
Co	0.84*	0.5
Zn	0.98*	0.1
Cd	0.95*	-0.01
Pb	0.98*	0.1
Hg	0.74*	0.59
Eigenvalue	4.83	1.37
Total variance (%)	69.01	19.66
Cumulative (%)	69.01	88.68

Table 2. Contamination factors (C_f) and contamination degree (C_d) for soils around the tailings dam.

No.	C_f							contamination degree
	Ni	Cu	Co	Zn	Cd	Pb	Hg	C_d
1	9.1	15	7.4	148	350	124	0.05	653
2	5.3	15	4.1	43	180	36	0.025	282
3	3.8	14.3	15.3	874	855	732	0.175	2494
4	6.6	13.9	16	919	1375	770	0.375	3100
5	3.6	14.6	7.7	291	530	244	0.113	1092
6	2.2	15.8	5.4	244	450	204	0.138	922
7	5.8	17.7	6	65	275	55	0.15	425
8	5.1	11.2	5.4	55	130	46	0.025	254
9	9.7	13.2	8.1	93	280	78	0.075	482
10	0.6	13.9	9.6	373	630	313	0.175	1341
11	3.8	14.2	6.4	229	400	192	0.113	845
12	5.8	11.7	5.4	60	120	50	0.05	253
13	8.5	10.9	7.4	612	80	52	0.025	220
14	7.2	16.2	6.2	89	280	74	0.063	473
15	2.8	15	4.2	110	210	92	0.05	434
16	2.2	12.8	3.6	30	75	25	0.025	149
17	5.1	10.4	5.6	31	50	26	0.013	128
18	5.1	16	5.5	25	150	21	0.063	223
19	5.1	12.2	5.2	49	135	41	0.05	248
20	9.3	60.5	21.5	706	670	591	0.688	2059

These results imply that Cobalt, Zinc, Cadmium, Lead and Mercury can be defined as anthropogenic and may originate from similar pollution sources.

This result coincides with the conclusion of the correlation analysis. Analysis of the regional characteristics shows that the highest concentration of these five heavy metals appeared in the vicinity of the tailings dam, and downstream of dam including samples 3, 4, tailings dam, 5, 6, 10 and 11 (Fig. 8).

The source of heavy metals in this area comes mainly from metal processing such as flotation and grinding in Lakan Lead and Zinc processing plant. The correlation analysis also indicated that Nickel and Copper had no significant correlation with the other five heavy metals (Table 4). According to the results, heavy metal concentrations in soils of 20 samples could be grouped into a two factor model, which accounted for 88.68% of all the data variation. Analysis of the regional characteristics show that the highest concentration of these two heavy metals appeared the vicinity of the processing plant including samples 1, 9, 13 and 14 (Fig. 8). The source of these heavy metals is likely from metal replacement processing by CuSO4 in Lakan Lead and Zinc processing plant.

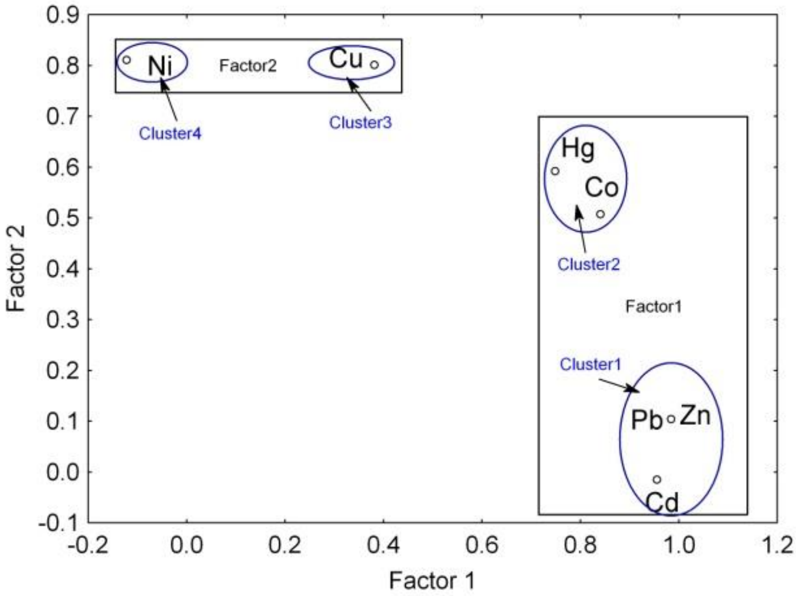

Figure 7) Factor analysis results in the two-dimensional space, plot of loading of the first and second factor.

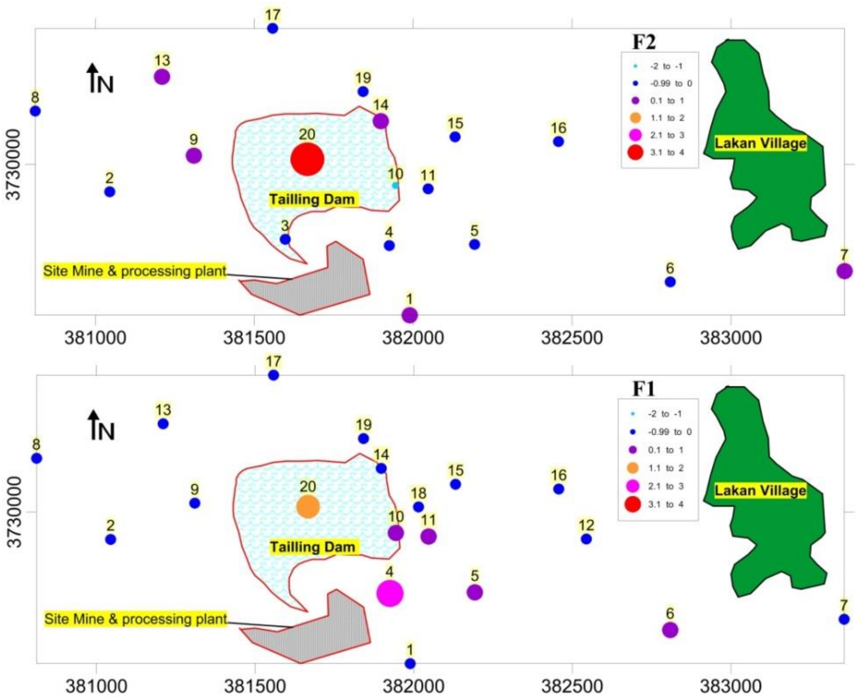

Figure 8) Geographical distribution of the factor scores (F1 and F2) in the studied area.

4.3. Cluster analysis

The results imply that some different anthropogenic activities occurred in the soils as illustrated in Fig. 9. The samples were hierarchically clustered on the basis of normalized metal concentrations in the soils. Four groups defined by this procedure were identified as cluster 1, cluster 2, cluster 3 and cluster 4. Cluster 1 is composed of Cadmium, Lead and Zinc and was mainly derived from anthropogenic inputs. Metal sulfides, especially pyrites, can be oxidized easily under natural weathering conditions and has resulted large quantities of acidic drainage and transferred into the surrounding environment through atmospheric dispersion and through the flow of water. Metals were released from the tailings dam due to the low acidity and high salinity of percolating solutions. This was one of the most important sources of heavy metals as Zinc, Lead and Cadmium in the environment surrounding the mine (Khodadadi *et al*., 2007; Hajati *et al*, 2008).

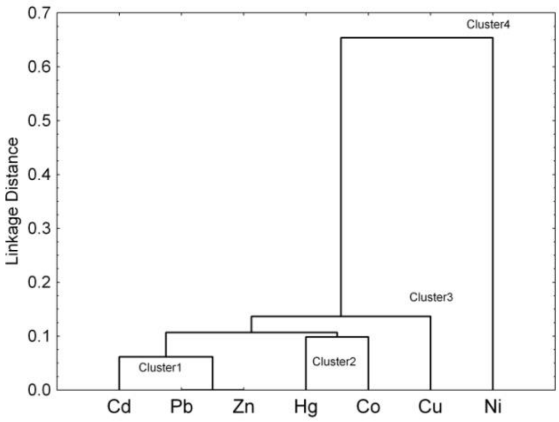

Figure 9) Hierarchical clustering analysis shows the relevant association among the elements

Cluster 2 includes Cobalt and Mercury and was controlled by natural source and because of mining activity in the Lakan area, background of these elements especially Cobalt are high. Cluster 3 and cluster 4 include Copper and Nickel, respectively (Fig. 9). Copper and Nickel appeared to be sourced both anthropogenically and naturally (Solgi *et al*., 2012). Zinc is prepared by addition of solid Zinc to a Copper sulfate solution. Copper will get replaced by Zinc (Zn + CuSO4 → ZnSO4 + Cu) in the Lakan processing plant (Khodadadi *et al*., 2007).

Soils around Lakan processing plant have natural Nickel and Nickel has become the Ni2+ into the soils of Lakan area. Therefore, it has been oxidized according to the equation: $Ni + CuSO_4 \rightarrow Cu + NiSO_4$. Here Nickel has been oxidized during the reaction and Copper is acting as an oxidant which gets replaced by Nickel (Khodadadi *et al*., 2007). In this case, Nickel has anthropogenic input (Solgi *et al*., 2012; Jordanova *et al*., 2013). Soil samples of the cluster 1, cluster 3 and cluster 4, in this case, represent the samples affected by contamination and cluster 2 represents uncontaminated sites. The similarity of the factor analysis and cluster analysis confirms the interpretations (Fig. 7 and Fig. 9).

5- Conclusions

This paper aimed to investigate the impact of a Lead and Zinc mine on the soils in the Lakan area. High level contaminations of metal was detected in the entire mine area. Almost, all samples reportes maximum tolerable concentrations of Lead, Zinc, Cadmium, Copper and Nickel. High concentrations of Lead, Cadmium and Zinc were detected in many of the samples, showing the extent of contaminate dispersion from the mine. The high significant correlation obtained between all the metals suggests their common origin in mining activities (i.e., flotation and grinding operation).

Analyses of heavy metals (Nickel, Copper, Cobalt, Zinc, Cadmium, Lead and Mercury) from 20 stations spread throughout the Lakan area indicate that metal concentrations show significant spatial variation. This study also suggests that the metal contamination cannot be simply evaluated by examining metal concentrations alone. The metal enrichment factor (EF) and geoaccumulation index (Igeo) of Cadmium, Lead, Zinc, Nickel, Copper and Cobalt suggest that their concentrations are above background levels, while concentration of Mercury is generally lower than background concentration. However, concentrations above background were observed for individual metals in localized areas. These localized elevated concentrations could be related to point source discharges related to mining activities.

Contamination degree showed values of total Lead, Zinc, Cadmium, Nickel and Copper in soils that were above the Predicted Empirical Global Soil values. Most of the samples in the study area were observed high contaminated. Therefore, we conclude that it would be necessary to remove or stabilize the mine spoils from the Lakan mine, since it is a source of soil pollution. The results of statistical analyses suggest that source of Cadmium, Lead and Zinc is anthropogenic activities (such as tailings dam, flotation and milling in the processing plant). Cobalt and Mercury are naturally, Copper and Nickel appeared to be sourced both anthropogenically and naturally.

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