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Statistical evaluation of topsoil heavy metal pollution around a lead and zinc production plant in Zanzan province, Iran

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ABSTRACT

Heavy metal contamination was evaluated around the National Iranian Lead and Zinc Company (NILZ) in Zanzan province. Collected data were used to appraise the degree of soil contamination and also the source of pollution in the study area based on geoaccumulation index (I_{geo}), and enrichment factor (EF). The levels of Fe, Zn, Cd and Pb in the samples exceed those reported in literature. The analyzed soils can be considered unpolluted to moderately polluted by Cd and Pb, and moderately polluted by Zn. Evaluated EF also showed moderate to severe enrichment of the soil samples by Zn and Pb, and very strong enrichment by Cd. These results indicated an anthropogenic contribution mainly for Zn, Cd and Pb elements. Bivariate correlation among the investigated metals showed the contamination of soil around the study area resulted from the NILZ Company activity. Based on the Mann-Whitney assessment, it was found that the presence of Co, Cu, Zn, Cd and Pb was also attributed to the plant. Parametric and non-parametric tests revealed the leaching of metals to deeper soil layers. Hierarchical Clustering Analysis (HCA) allowed categorizing the investigated metals in three groups. These groups were cluster I (Zn, Cd, Co and Ni), cluster II (Pb and Cu) and Fe in an independent cluster III. Principal Component Analysis (PCA) and Factor Analysis (FA) elucidated the anthropogenic source of the pollutants.

Key words: Heavy metals; Geoaccumulation index; Enrichment factor; Statistical analysis.

INTRODUCTION

Heavy metals, because of their high toxicity, abundance and ease of accumulation are well known for having detrimental effects on various plant and animal organisms. On the other hand some heavy metal ions, in acceptable concentrations are needed for growth, development and health of living organisms.

Natural emission of most of heavy metals into the atmosphere is low due to their negligible volatility. Though, their emission rates are increasing due to anthropogenic sources. The anthropogenic sources (such as industrial, agricultural, municipal and mining activities) increase heavy metals concentrations that affect nearby ecosystems (Imanpour Namin *et al.*,

2011). Most of these emissions are released into the lower atmosphere where mammals live and breathe, increasing the occurrence of the related health problems such as lead poisoning, cadmium Itai-itai disease, cobalt, and nickel carcinogenesis (Viamonte Ros, 2008).

The toxic properties of some heavy metals encourage the monitoring and evaluation of heavy metal contents in sources directly affecting the life and health of creatures (Surindra, 2009; Momodu & Anyakora, 2010). Determining the heavy metals concentration in soil, dust, plants and sediments are very important in monitoring environmental pollution which has been the subject of several studies (Chen *et al.*, 2010; Sampson Atiemo *et al.*, 2011; Khosropour, *et al.*, 2013). A precise

evaluation of heavy metal pollution caused from human activities and their comparison with Maximum Contaminated Levels (MCLs) standards allow administrators and planners to make suitable decisions to prevent and control the negative impacts of such pollutants on people who are exposed to such contaminants. Soil pollution is a principal environmental activity because soil is a finite, non-renewable natural resource. Contamination of soil by heavy metals due to rapid anthropogenic activities has been investigated in recent years (Bermudez *et al.*, 2010; Chen *et al.*, 2010; Stafilov *et al.*, 2010; Rafiei *et al.*, 2010; Mohammadi *et al.*, 2012).

The Angoran area in Zanjan province, located in Northwest of Iran, has a large metalliferous site and has been considered a traditional mining region having large reserves of lead and zinc in this area.

Mining, transportation of concentrated ore by trucks and smelting units within the province presents a risk of contamination of soils, plants, surface and ground water resources through the dissemination of metals by wind action and/or by run-off from tailings (Chehregani *et al.*, 2009). Many related industries developed in Zanjan province, notably, the National Iranian Lead and Zinc (NILZ) Company which is one of the largest of its kind in the Middle East a large market capitalization.

The lack of a systematic investigation of the probable heavy metal contaminations around the location of this company, encouraged an assessment of the heavy metal pollutions of soils in this industrial zone. In this study, the presence and concentrations of seven heavy metals (Fe, Co, Ni, Cu, Zn, Cd and Pb) in soil samples collected from the NILZ Company and its surrounding environment neighborhoods were determined using atomic absorption spectroscopy.

The multivariate statistical analysis was conducted to categorize the heavy metals and to distinguish the source of the contaminants. This permitted ascertaining the influence of the pollution sources around the NILZ Company. This study was carried out in the summer of

2011 in the Phase Equilibria Research and Environmental Science Research Laboratories, University of Zanjan, Zanjan, Iran.

MATERIALS AND METHODS

The study area

Bonab Industrial Estate (BIE) and its surrounding environment, located in Zanjan province (Northwest Iran), was selected for this study. The study area has a cold, dry climate characterized by cool-dry summers and cold company (36° 66' N, 48° 48' E) located within BIE, approximately 12 km east of Zanjan city. The company has an important role in the local economy. It was established in 1994 with a current consumption of about 300,000 tons of raw ore and an annual production of 55000 tons of lead and zinc. The tailings from BIE, estimated to be about 2.5 million tons, contain a variety of toxic elements, notably Pb, Zn, and Cd dumped in the vicinity of the Estate and exposed to wind and rain, contributing to soil and water contamination (Mohammadi & Eslami, 2007).

Sample collection and storage

One hundred twenty six composite samples were collected based on a network in the study area divided into two sections. Section I was limited to the boundaries of the NILZ Company. In this Section 38 samples were collected at two different soil depths of 0-15 and 15-30 cm. Section II, with a total number of 88 samples, was a circle with a radius of 5 km around this plant. In this Section the samples were collected only at a depth of 0-15 cm (Fig. 1).

Each sampling station represents a square block grid (2 m dimensions) where five topsoil samples (from the center and the corners) were collected, mixed and were used as one composite sample.

Preparation and analysis of samples

All samples were collected with a stainless steel spatula, air dried for two weeks and kept in plastic bags. In the laboratory the soil samples were ground by mortar and pestle, sieved

through a 2 mm mesh sieve, and then oven-dried at 50°C for about 48 h. The samples were then stored in polyethylene bags and re-homogenized before being used. The pH and electrical conductivity (EC) of the soil samples (1:1 w/w solid to distilled water ratio) were measured using a pH- and an EC-meter Hach (model HQ 40d). The soil samples were digested using aqua regia digestion method (ISO 11466, 1995); 3 g of soil samples was placed in a 100 ml round bottom flask with 21 ml of concentrated hydrochloric acid (35%) and 7 ml concentrated nitric acid (65%). The solution was kept at room temperature overnight before a water condenser was attached and the solution heated to boiling for 2 h. Twenty-five ml distilled water was then added to the condenser before filtering the mixture through a Whatman (No. 42) filter paper. The filtered

residue was rinsed twice with 5 ml of water and the solution was made up to 100 ml.

The metal contents were extracted into aqueous phase by the method reported by Lindsay & Norvell (1978). The procedure was as follows; a sample of 10 g soil was added in 20 ml mixture of 0.005 mol.L⁻¹ diethylene triaminepentaacetic acid (DTPA), 0.01 mol.L⁻¹ CaCl₂ and 0.01 mol.L⁻¹ triethylamine (pH 7.3).

This mixture was shaken for 2 h and then filtered through a Whatman (No. 42) filter paper and the extracts were analyzed by a Varian 220AA flame atomic absorption spectrometer (air/acetylene flame) for the heavy metal concentrations and three replicate measurements were performed on each sample. All the standard solutions were prepared from analytical grade chemicals (Merck and Fluka).

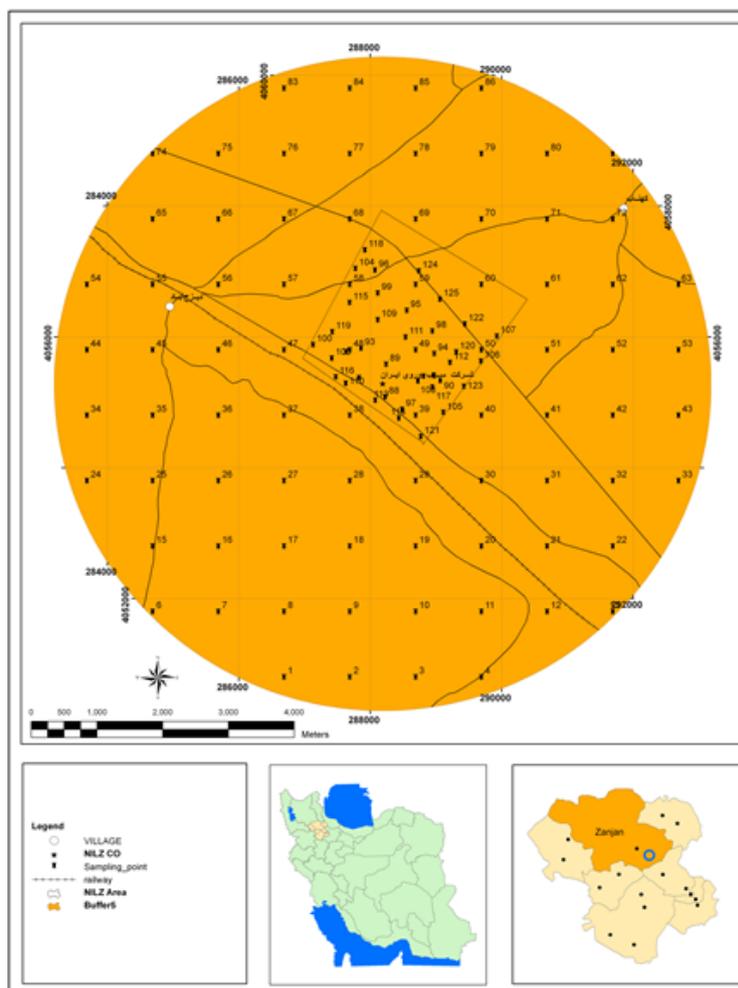


Fig. 1. Location map of the studied area indicating sampling points.

Statistical data analysis

Statistical analyses (Zamani *et al.*, 2012) were performed by using SPSS (PASW Statistics 18) and the STATISTICA 8 software.

Analysis of the experimental sampled data was carried out using Pearson correlation matrix, Cluster Analysis (CA), Principal Component Analysis (PCA) and Factor Analysis (FA) and Hierarchical Cluster Analysis (HCA) methods.

RESULTS AND DISCUSSION

pH and Electrical conductivity of the samples

Soil's pH is a predictor of various chemical activities. Furthermore, electrical conductivity is a measure of the presence of salts in the samples, regardless of the type of salt. Electrical conductivity and pH of investigated soil samples are given in Table 1. The pH values are in a narrow interval between 7.39 and 8.39. This range suggests neutral to sub-alkaline conditions for the soil samples. The electrical conductivity measurements present a medium to high electrical conductivity (213-2183 s.cm⁻¹) of the samples. Statistical investigations show that at significance level of $p < 0.01$, there is no correlation between pH and EC for the sampled data.

Investigation of heavy metal contents in the samples

Descriptive statistics including minimums, maximums, means, medians, standard deviations of the studied heavy metal concentrations in the samples collected from both sections I and II at a depth 0 - 15 cm are summarized in Table 2. The amounts of metals (in mg kg⁻¹) were found in the range 1646.00-106667.00 for Fe; ND - 4.16 for Co; ND - 69.87 for Ni; 4.83 - 85.97 for Cu; 50.88 - 30167.00 for Zn; ND - 234.67 for Cd; and ND - 2990.00 for Pb. The order of metal contents in the topsoil based on their mean values varies as: Fe > Zn > Pb > Ni > Cu > Cd > Co.

According to the Canadian Soil Quality Guidelines (CSQG), it can be considered that the mean concentrations of Co, Ni, Cu, Zn and Pb in the study area placed within the limits for agricultural and industrial land use.

However, the maximum concentration of Zn and Pb were above the values reported by CSQG. A comparison of the investigated metal contents with those reported in typical literature ranges (TR) shows Fe, Zn, Cd and Pb are outside the limits of TR.

Bioavailability of heavy metal contents

Although total soil heavy metal concentrations is commonly used to indicate the extent of contamination, a more reliable quantity of contamination could be demonstrated by DTPA - extractable concentration (namely bioavailable) which provides the amount of metals available for plant uptake (Andrea *et al.*, 2010), and the mobility of these metals in soils (Fuentes *et al.*, 2004). The statistical parameters of DTPA-extractable Fe, Co, Ni, Cu, Zn, Cd and Pb contents in the samples are presented in Table 3. The samples were gathered from sections 1 and 2 (depth 0 - 15). As expected, the results show that bioavailable heavy metal contents in soils are less than the total metal contents. However, a direct relationship was observed between the two parameters. The bioavailable contents of metals increased with those of total heavy metal contents. The mean bioavailable order of heavy metals in the topsoil varies as: Fe > Zn > Pb > Cu > Ni > Cd > Co, which is similar to that observed for total heavy metals in topsoils, except for Ni and Cu. A relative quantity which results from the division of bioavailable metal quantity to its total content, in percent, is called the extractable metal percentage. This parameter is a measure of the corresponding metal mobility in the soil samples.

The values shown in column 7 of Table 3 are the evaluated extractable metal percentages which are the percentage of bioavailable to that of total amount of heavy metals in the samples of each station.

The results reveal high values for cadmium and lead contents (49.70 and 30.60, respectively), indicating an anthropogenic source of pollution. Bioaccumulation of such metals in food chains are inevitable and pose a potential risk to public health.

Bivariate correlations between bioavailable and total heavy metal contents

Bivariate correlation is useful for determining the extent of association between bioavailable and total heavy metal contents. For normally distributed variables, the Pearson method can be used to calculate the correlation coefficients. As the data in the present study do not fit a normal distribution, the Spearman method was applied. This method is not dependent on the modality of data distribution.

Significant correlations between total and DTPA- extractable metals were found for Cu, Cd and Pb.

This can be attributed to the ionic form of these metals in the soil samples (Table 4). The determination of cobalt by DTPA extractable metal method did not show detectable values.

Bivariate correlations between total heavy metal contents

Bivariate correlations evaluate the probability of a common source of metals in soil samples. Based on the results shown in Table 5, a strong negative correlation between Fe and Co was observed. In addition, there was a weak positive correlation between Fe with Ni and Cu. Another observation in Table 5 concerns the presence of significant binary correlations between Co/Zn, Co/Cd, Co/Pb, Ni/Cu, Cu/Pb, Zn/Cd and Cd/Pb. The main metals of concern at the NILZ Company are zinc and lead. As significant correlations were found between two metals and other metals investigated in this study, it could be concluded that the pollution of soil samples originated from this plant.

Table 1. Electrical conductivity (EC) and pH of the investigated samples.

	Min.	Max.	Mean	Standard deviation
pH	7.39	8.39	7.98	0.21
EC* (s cm ⁻¹)	238.00	2183.00	445.73	272.54

* Measured at 25°C.

Table 2. Descriptive statistics of heavy metal contents (mg kg⁻¹) in topsoil samples.^a

Element	Min.	Max.	Mean	Median	Stdev ^b	CSQG ^c	TR ^d
Fe	1646.00	106667.00	24756.00	23783.00	10976.00	-	7000-10000
Co	ND ^e	20.33	4.16	3.53	3.91	40 ^f -300 ^g	-
Ni	ND	69.87	26.38	24.90	13.81	150 ^f -500 ^g	2-750
Cu	4.83	85.97	18.31	17.18	8.18	150 ^f -500 ^g	2-250
Zn	50.88	30167.00	684.11	111.14	3489.00	600 ^f -1500 ^g	1-900
Cd	ND	234.67	5.79	0.53	26.43	-	0.01-2
Pb	ND	2990.00	119.59	23.83	345.42	375 ^f -1000 ^g	2-300

^a Samples were from sections 1 and 2 (depth 0-15 cm) and for 126 samples; ^b Standard deviation; ^c Canadian soil quality guidelines (Bermudez *et al.*, 2010); ^d Typical literature ranges (Abbollino *et al.*, 2002); ^e Not detectable; ^f/^g Agricultural and industrial land uses respectively.

Table 3. Descriptive statistics for bioavailable heavy metal contents (mg kg⁻¹).^a

Element	Min.	Max.	Mean	Median	Stdev	Metal extractable (%)
Fe	9.97	70.04	40.13	41.03	10.50	0.20
Co	ND	ND	ND	ND	ND	ND
Ni	0.01	1.61	0.46	0.34	0.35	4.35
Cu	0.10	5.52	1.21	1.15	0.80	7.65
Zn	0.87	46.04	5.02	4.09	5.00	4.82
Cd	ND	1.43	0.25	0.21	0.18	49.70
Pb	ND	22.10	4.83	3.91	3.70	30.60

^a Samples were from sections 1 and 2 (depth 0-15 cm) and for 88 samples.

Table 4. Spearman correlation coefficients (r_s) between DTPA extractable contents and total contents of metals.

Total contents	r_s	DTPA extractable						
		Fe	Co	Ni	Cu	Zn	Cd	Pb
	r_s	-0.058	-	0.095	0.235	0.092	0.442	0.551
	p^a	0.594	-	0.386	0.028	0.394	0.000	0.000
	n^b	88	-	85	88	88	77	82

^a probability; ^b number of samples.

Table 5. Spearman correlation matrix of soil's total heavy metals.

Metal	Fe	Co	Ni	Cu	Zn	Cd
Co	-0.535 ^b					
Ni	0.200 ^a	-0.040				
Cu	0.232 ^a	0.034	0.570 ^b			
Zn	0.023	0.528 ^b	0.236 ^b	0.398 ^b		
Cd	-0.098	0.575 ^b	0.167	0.331 ^b	0.671 ^b	
Pb	-0.121	0.522 ^b	0.282 ^b	0.555 ^b	0.714 ^b	0.760 ^b

Comparison of heavy metal contents between the stations within and outside NILZ Company (section I & II)

Descriptive statistics of heavy metal contents in the two studied sections (inside and outside the NILZ Company) are given in Table 6. The results reveal that the metal contents in the samples selected from within the plant's borders (section I) are significantly higher than those from the outside area (section II).

An independent sample T-test was used for testing the difference between the two sample means (Zamani *et al.*, 2012). However, instead of an independent sample T-test, one can use the Mann-Whitney U test. This latter is a non-parametric test, which differentiates it from the T-test (Einax *et al.*, 1997; Miller and Miller, 2005). These methods are used for comparing the mean values of metal contents in samples obtained from the two sections. This investigation shows that, except for nickel, the mean values of the metal ions in the samples selected from Section I (inside the plant's border) differed significantly from those found in the samples obtained from Section II (outside the NILZ Company's border). However, the comparison of means for metals in both Sections, investigated using both parametric and non-parametric methods, showed a significant difference between them. This

difference indicates that the presence of Co, Cu, Zn, Cd and Pb metals in Section I (in the vicinity of the NILZ Company) can be attributed to the plant's activities.

Bivariate correlations between total heavy metal contents in different soil profiles

In order to assess the diffusion and probable leaching of the studied metals in the soils in Section I (inside the plant's boundaries), the soil metal contents and their distribution at two different depths i.e. 0 - 15 and 15 - 30 cm were studied (Table 7). The results reveal that the average abundance order of the heavy metal contents in the two soil profile samples is similar. This order was Fe > Zn > Pb > Ni > Cu > Co. Statistical evaluation given subsequently describes the variation in absolute value of these metals in the investigated depths.

The calculated Spearman coefficients for total mean heavy metals in soil profiles 0-15 and 15-30 cm (Table 8) states that, except for Fe, there is a significant and positive correlation between all studied metals (regardless of the soil profiles). Therefore, it can be concluded that leaching of Co, Ni, Cu, Zn, Cd and Pb ions from surface soil to deeper soil profiles has been occurred in the studied area.

Both parametric and non-parametric tests show that there is not a significant difference between

the means of the two soil depths (0-15 and 15-30 cm). This outcome reconfirms the occurrence

of leaching of metals to deeper soil profiles in the studied area.

Table 6. Statistical descriptions of heavy metal contents (mg kg⁻¹) in topsoil samples. ^a

Sample's site	Element	Min	Max	Mean	Median	Stdev ^b
Section I (Inside NILZ Company)	Fe	13866.67	50000.00	22315.55	21633.33	6899.69
	Co	ND ^c	18.33	4.75	3.83	3.12
	Ni	1.77	69.87	28.80	27.27	11.53
	Cu	12.97	85.97	21.60	18.33	11.58
	Zn	50.88	30166.67	1577.20	216.08	5736.57
	Cd	0.20	234.67	13.46	2.20	41.75
Section II (Outside NILZ Company)	Pb	10.00	2990.00	277.84	95.67	529.58
	Fe	1646.67	106666.67	26111.85	24433.33	12524.71
	Co	ND	20.33	2.86	1.57	5.17
	Ni	ND	62.70	24.99	23.15	14.87
	Cu	4.83	24.20	16.48	16.53	4.62
	Zn	56.33	4191.67	187.95	93.33	469.64
	Cd	ND	26.33	1.06	0.47	3.34
	Pb	ND	173.00	24.65	17.33	27.55

^aSamples were from sections 1 and 2 (depth 0-15 cm) and for 126 samples; ^bStandard deviation; ^cnot detected.

Table 7. Statistical description of metal distribution within NILZ Company by soil depths (mg kg⁻¹).^a

Element	Depth (cm)	Min.	Max.	Mean	Median	Stdev. ^b
Fe	0-15	13866.67	50000.00	21644.74	21050.00	6728.74
	15-30	466.67	66666.67	23696.49	21983.33	10254.39
Co	0-15	ND ^b	18.33	4.80	3.87	3.16
	15-30	1.30	15.27	4.06	3.90	2.48
Ni	0-15	1.77	69.87	28.82	27.07	12.24
	15-30	13.73	57.93	28.49	28.01	8.41
Cu	0-15	12.97	85.97	21.85	17.85	12.47
	15-30	2.53	52.37	18.74	16.33	9.17
Zn	0-15	50.88	30167.00	1764.80	229.35	6225.61
	15-30	48.83	44666.67	2232.28	132.33	8111.67
Cd	0-15	0.2	234.67	14.61	2.20	45.08
	15-30	0.07	94.33	6.53	0.96	16.14
Pb	0-15	10.00	1806.67	234.12	116.83	354.94
	15-30	4.67	4323.33	260.07	71.00	715.47

^aNumber of samples 38; ^bStandard deviation; ^cNot detected.

Table 8. Spearman correlation coefficients (r_s) between total mean heavy metals in two different profiles.

		0-15 cm						
		Fe	Co	Ni	Cu	Zn	Cd	Pb
15-30 cm	r_s	0.278	0.438	0.541	0.365	0.707	0.809	0.809
	p	0.091	0.015	0.000	0.024	0.000	0.000	0.000
	n	38	30	38	38	38	38	38

Contamination levels of the samples

The evaluation of the soil's contamination levels was made by the assessment of Enrichment Factors (EF) and Geoaccumulation Indexes (Igeo) (Vega *et al.*, 2008; Rafiei *et al.*, 2010). These factors and indexes depend on the

background metal levels of the samples. The average metal contents in the world shale (World Average Shale, W.A.S.) and in the world soils are often used to provide background metal levels (Vega *et al.*, 2008; Rafiei *et al.*, 2010). As noted before, the iron

content of the soil samples is not related to anthropogenic activities, thus the mean Earth's crust's Fe concentration ratio was chosen as reference for determining EF and Igeo indexes. EF was calculated using equations 1.

$$EF = \frac{\left(\frac{[M]}{[Fe]}\right)_{\text{soil}}}{\left(\frac{[M]}{[Fe]}\right)_{\text{W.A.S.}}} \quad (1)$$

Igeo was obtained with equation 2:

$$Igeo = \log_2 \left(\frac{[M]_{\text{soil}}}{1.5 [M]_{\text{W.A.S.}}} \right) \quad (2)$$

Where M is the investigated element, and the subscripts "soil" and "W.A.S" indicate which medium the concentration refers.

Due to the lack of the regional background data the values of EF and Igeo were calculated by using the values of concentrations of metals in Shale, reported elsewhere (Mason and Moore, 1982). These values were: 47200 mg.kg⁻¹ for Fe, 19 mg.kg⁻¹ for Co, 68 mg.kg⁻¹ for Ni, 45 mg.kg⁻¹ for Cu, 95 mg.kg⁻¹ for Zn, 0.3 mg.kg⁻¹ for Cd and 20 mg.kg⁻¹ for Pb.

The calculated EF factors and Igeo indexes are given in Table 9. Classification introduced by Huu *et al.* (2010) considers the levels of soil pollution in six categories. This classification is presented using EF factors of the examined samples. Based on this classification it was concluded that, for the soil samples, there is no enrichment for Co and Ni elements, moderate to severe enrichment by Zn and Pb and very severe enrichment of the samples by Cd. According to the classification established for Igeo (Müller, 1979) the analyzed soils could be considered unpolluted by the elements Fe, Co, Ni, and Cu; unpolluted to moderately polluted by Cd and Pb; and moderately polluted by Zn. It is worthwhile to note that many of the polluted soils were sampled from stations located within the boundaries of the NILZ Company (i.e., Section I). In addition, these results indicate an anthropogenic contribution mainly for Zn, Cd and Pb elements. Nonparametric tests show the mean values of

EF factors and Igeo indexes significantly differ at the 0.05 probability levels between the two sampling areas i.e. section I and section II.

Cluster analysis classification of the investigated heavy metals

In Cluster Analysis, variables of a sample are considered as objects in an n-dimensional hyperspace (n=number of variables). These variables are described by n-components vectors. The agglomerative Hierarchical Clustering Analysis (HCA) procedure is used to evaluate similarities among the samples. In this way, a dendrogram is achieved, in which correlations among the samples can be deduced (Miller and Miller, 2005; Abollino *et al.*, 2002; Einax *et al.*, 1997).

The raw data were standardized before using cluster analysis. This standardization was done by using the corresponding Z scores. By using the Z scores of samples, the squared Euclidean distance can be calculated.

Thereafter, the classification was done using Ward's method (Einax *et al.*, 1997). The corresponding hierarchical dendrogram was drawn in which the distance axis represents the degree of association between the groups (Fig. 2). The lower distances reveal more significant associations.

Based on the results of HCA, the heavy metals were classified into three clusters using a criteria value of rescaled distance between 10 and 15 (Fig. 2). There are four heavy metals (Zn, Cd, Co and Ni) in cluster I, two metals (Pb and Cu) in cluster II and only one metal (Fe) in cluster III. By clustering the studied metals using a lower distance criterion (less than 5), a close relationship was observed for the subgroups Zn/Cd and Cu/Pb. The HCA was used by applying EF factors and Igeo indexes. This analysis shows the attribution of the metals in three categories.

The first one contained the element already interpreted as lithologic (i.e. Fe); the second category includes the anthropogenic elements (Pb/Cu, Zn/Cd) and the third is a group of mixed anthropogenic and lithologic sources (Ni/Co).

Table 9. Classification of metal levels of contamination in the soil samples.

	Element	n ^a		Min	Max	Mean	Median	Stdev ^b	Classification ^c
		Valid	Missing						
Enrichment factors	Co	45	81	ND ^d	2.84	0.50	0.40	0.53	0
	Ni	123	3	ND	12.20	0.97	0.75	1.16	0
	Cu	126	0	0.09	11.15	0.97	0.76	1.10	0
	Zn	126	0	1.01	1776.13	35.13	4.55	191.53	3
	Cd	118	8	ND	1909.73	48.30	3.65	228.02	4
	Pb	120	6	ND	287.23	13.95	2.40	37.03	3
Geoaccumulation indices	Fe	126	0	-5.43	0.59	-1.64	-1.57	0.65	0
	Co	45	81	ND	-0.49	-3.31	-3.00	1.44	0
	Ni	123	3	ND	-0.46	-2.20	-1.95	1.31	0
	Cu	126	0	-3.80	0.35	-1.98	-1.97	0.51	0
	Zn	126	0	-0.56	8.65	1.08	0.57	1.51	2
	Cd	118	8	ND	9.03	0.88	0.24	2.13	1
	Pb	120	6	ND	6.64	0.06	-0.33	2.24	1

Table 10. Factor loadings for varimax rotated PCA of metal data in soil samples. ^a

	Factor 1	Factor 2	Factor 3
Fe	-0.04	-0.03	-0.90
Co	0.56	0.26	0.47
Ni	0.71	0.12	-0.38
Cu	0.10	0.96	-0.07
Zn	0.94	-0.06	0.17
Cd	0.92	0.11	0.13
Pb	0.05	0.95	0.17
Eigen value	2.87	1.71	1.16
% variance	40.94	24.53	16.63
% Cumulative	40.94	65.46	82.10

Principal component analysis and factor Analysis

Principal components analysis (PCA) is a multivariate technique in which new variables are calculated as linear combinations of the old ones (metal concentrations in the present case). The principal components (PC, new variables) are uncorrelated between themselves and the first PCs keep the main part of the variance of the original data set. Before using this analysis, the raw data are normalized to reduce the influence of high value data (Moller *et al.*, 2005; Miller & Miller, 2005).

The major objective of factor analysis (FA) is to reduce the contribution of less significant

variables to simplify even more the data structure given by PCA. This can be achieved by rotating the axis defined by PCA. This procedure allows constructing new variables (called factors). Factor loadings obtained by PCA with varimax for various metals are presented in (Table 10). Loadings greater than 0.70 are marked as bold in Table 10.

The heavy metal grouping is shown in the plot (Fig. 3) of the first two principal components generated from the main factors, Factors 1 and 2 (Table 10). Factor 1 accounts for 40.94% of the total variance, High loadings on the elements Co, Ni, Zn and Cd indicates the influence of local anthropogenic activities and lithology on

soil samples. On the other hand, Factor 2 explains that about 24.53% of the variance was composed by Cu and Pb. This factor had high loadings of anthropogenic sources. Factor 3 accounts for 16.63% of the total variance, was composed by only Fe, and represents the lithologic source. Factor 1 represents the contribution of metals from lithologic sources

and anthropogenic activities, while Factor 2 represents the contribution of metals from local anthropogenic sources.

The results of the statistical analysis and distribution of the pollutants suggest that the NILZ Company represents the most important anthropogenic source of pollution in the investigated area.

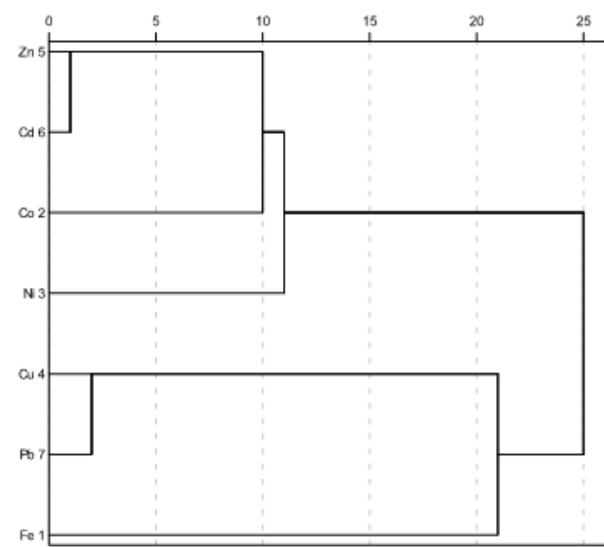


Fig. 2. Dendrogram of heavy metal concentrations in soil samples.

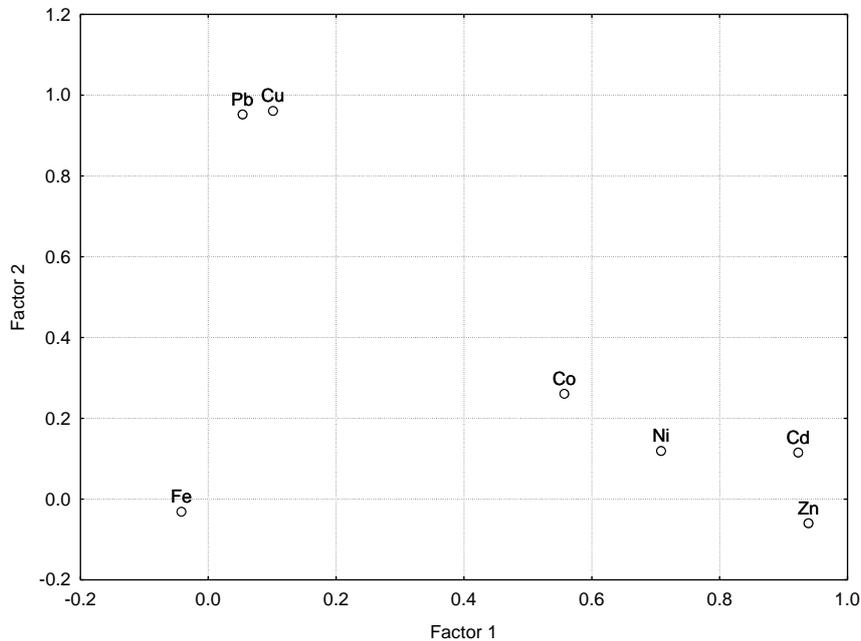


Fig. 3. Factor loading for studied heavy metals (Rotation: Varimax normalized; Extraction: Principal components).

CONCLUSION

An assessment was done on heavy metal contamination in 126 soil samples collected

from an area with a radius of 5 km, centering around the National Iranian Lead and Zinc Company (NILZ) in Bonab Industrial Estate

(Zanjan province-Iran). Results indicated that the study area is contaminated by the metals Fe, Co, Ni, Cu, Zn, Cd and Pb. The amounts of metals (in mg kg⁻¹) were found in the range 1646.00-106667.00 for Fe; ND - 4.16 for Co; ND - 69.87 for Ni; 4.83 - 85.97 for Cu; 50.88 - 30167.00 for Zn; ND - 234.67 for Cd; and ND - 2990.00 for Pb. The order of metal contents in the topsoil based on their mean values varies as: Fe > Zn > Pb > Ni > Cu > Cd > Co. The high percentage of DTPA-extractable metals, enrichment factors and the geoaccumulation indexes suggest an anthropogenic source of pollution. Correlation analysis, cluster analysis and factor analysis were used to determine the potential source of contamination. The results show that there are three main pollutant sources namely, lithologic (for Fe), anthropogenic (for Pb and Cu) and both lithologic-anthropogenic (for Co, Ni, Zn and Cd) in the studied area. The comparison of heavy metal soil content inside and outside the NILZ Company's boundaries demonstrates increasing soil contaminations in soil samples close to this industry. This means that the presence of Pb and Zn indicates main anthropogenic sources of heavy metals in this area. This can be considered detrimental for people who consume the corresponding waters, vegetables and food crops grown in these soils. Further research and more intensive sampling and examination are required to monitor any change or increase of soil metal content in the investigated area and its cumulative negative impacts on the health and safety of the residents.

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ارزیابی آماری آلودگی فلزات سنگین در خاک سطحی اطراف یک کارخانه تولید سرب و روی در استان زنجان، ایران

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چکیده

در این مقاله آلودگی فلزات سنگین در اطراف شرکت ملی سرب و روی ایران مورد بررسی قرار گرفته است. برای ارزیابی آلودگی خاک و همچنین منبع آلودگی در محدوده مورد مطالعه، داده‌های جمع‌آوری شده از شاخص زمین‌انباشتگی (Igeo) و ضریب تغلیظ (EF) استفاده شد. سطح میزان فلزات آهن، روی، کادمیم و سرب در نمونه‌ها بیش از مقادیر گزارش شده در منابع بود. نمونه‌های خاک بررسی شده نسبت به کادمیم و سرب در محدوده غیرآلوده تا آلودگی متوسط، و نسبت به روی دارای آلودگی متوسط بودند. مقادیر ضریب تغلیظ برآورده شده همچنین نشان داد نمونه‌ها نسبت به روی و سرب از تغلیظ متوسط تا بالا و نسبت به کادمیم از تغلیظ بسیار بالا برخوردارند. این نتایج نشان داد که یک عامل انسان‌زاد، به ویژه در آلودگی نمونه‌ها نسبت به روی، کادمیم و سرب وجود دارد. آنالیز همبستگی دو متغیره در بین فلزات مورد بررسی نشان داد آلودگی در محدوده مورد بررسی ناشی از فعالیت شرکت سرب و روی است. بر اساس برآورد روش مان-ویتنی حضور کبالت، مس، روی، کادمیم و سرب به فعالیت کارخانه نسبت داده شد. آزمون‌های پارامتری و ناپارامتری روشویی فلزات لایه‌های پایین‌تر خاک را بیان می‌کرد. تحلیل خوشه‌ای سلسله‌مراتبی (HCA) اجازه داد تا فلزات مورد بررسی در سه گروه قرار گیرند. این گروه‌ها شامل خوشه ۱ (روی، کادمیم، کبالت و نیکل)، خوشه ۲ (سرب و مس) و آهن در یک خوشه مستقل ۳ بودند. تحلیل اجزاء اصلی (PCA) و تحلیل پارامتری (FA) بیان‌کننده منشأ انسان‌زاد در آلودگی‌ها بود.

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