

Multivariate and geostatistical analyses of selected heavy metals in surface soils of Semnan industrial complex and surrounding areas

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ABSTRACT

Thirty years activities in Semnan industrial complex (SIC) have arisen concerns on accumulation of heavy metals in surface soil. The objectives of this study were to determine the concentration and spatial distribution of Pb, Zn, Cu, Ni, Cd and Cr in surface soils of SIC and surrounding areas and to identify origin of these heavy metals. Study area was divided into seven geomorphic units according to landforms and parent materials diversity. Ninety-three composite surface (0-10 cm) soil samples were collected in an area of 117 km². Concentrations of heavy metals were measured in aqua-regia extracts, using atomic absorption spectrometry. Average concentrations of Pb, Zn, Cd, Cu, Ni and Cr were 49.2, 84.4, 1.6, 22, 20.1 and 9.7 mg kg⁻¹ with ranges of 11.6-511.2, 34.1-247.9, 0.7-2.8, 16.9-42.0, 9.2-27.9 and 3.5-22.3 mg kg⁻¹, respectively. The maximum concentrations of Pb, Zn, Cd and Cu were found in the SIC. The spatial distribution of these heavy metals indicated gradual increase in concentrations along the prevailing wind direction. Concentrations of Ni and Cr did not show any specific spatial distribution pattern in relation to activities in SIC and other geomorphic units. According to the principal components analysis results, PC1 with the highest loadings for Pb, Zn, Cd and Cu was recognized as anthropogenic components, whereas the PC2 including Ni and Cr was lithogenic components. The cluster analysis also showed similar grouping. The results indicated considerable increasing in the Pb, Zn and Cd concentrations in the soil, during nearly short period of industrialization. It should be consider to make necessary decision to prevent more pollution.

Key words: Industrial complex; Soil pollution; Anthropogenic pollution; Principal components analysis.

INTRODUCTION

Soil contamination is an emergent environmental concern which significantly reduces the environment quality and threats human health (Canbay *et al.* 2010). Toxicity, cumulative effects, long-term storage time in the environment, carcinogenic properties and non-degradability make the heavy metals one of the most hazardous soil pollutants (Mico *et al.* 2006; Qing *et al.* 2015). The concentration of heavy metals in the soils is an important indicator of soil quality evaluation (Ling-yu *et al.* 2010).

Anthropogenic and lithogenic sources are the two main origins of heavy metals in the soil. Mining, metallurgy, electronic industries, sewage sludge, waste disposal sites, emissions from urban transportation and agricultural fertilizers are the main anthropogenic sources of heavy metals (Wei & Yang 2010; Alloway 2013; Zamani *et al.* 2015). Lithogenic source reflects elemental composition of geologic formations or soil parent materials. Weathering of parent materials and pedogenic processes release and distribute the elements through the soil profile (Palumbo *et al.* 2000; Mohammadpour *et al.* 2016; Ayoubi *et al.* 2018).

It is necessary to identify heavy metal sources and delineate high risk areas before any pollution control planning (Chen *et al.* 2009). Geostatistical analyses is a common and powerful technique to highlight the spatial distribution of heavy metal concentrations in relation to potential pollutant sources (Lu *et al.* 2012; Dankoub *et al.* 2012; Hu *et al.* 2013; Li *et al.* 2013). Principle component analysis and cluster analysis are the two multivariate statistics

methods to group the heavy metals according to their similarity variations (Rodriguez *et al.* 2008; Taghipour *et al.* 2011; Li *et al.* 2012; Lu *et al.* 2012; Sajn & Gosar 2014).

In recent decades, urbanization and industrialization have been increased and consequently the soils have been contaminated with heavy metals. Therefore, many researches have been conducted to identify the intensity of soil pollution in urban and industrial areas (Wei & Yang 2010; Argyraki & Kelepertzis 2014; Sajn & Gosar 2014). Such investigations have been revealed the pollution of the soil in large cities, urban and industrial areas by heavy metals (Dayyani & Mohammadi 2010; Dankoub *et al.* 2012; Esmaeili *et al.* 2014; Ayoubi *et al.* 2018; Karimi *et al.* 2018). Development of the industrial complex areas has become common from second half of twentieth century. In Iran, industrialization started from the middle of the last century, markedly developed during recent decades (Monavari 2001) and many industrial complexes have been established at the margins of cities. Semnan is a major city in central Iran, 200 km away from Tehran. Semnan industrial complex (SIC) was founded in 1985 located in the southern slopes of Alborz Mountains (Fig. 1). After 30 years of industrial activities, there is no information on the heavy metal contents in its soil. The objectives of this study were to 1) determine the effect of industrial activities on increasing the concentration of Pb, Zn, Cu, Ni, Cd and Cr in the surface soil of SIC and surrounding areas and 2) identify origin of these heavy metals in the soil using multivariate and geostatistical analyses.

MATERIALS AND METHODS

Area description and sampling

The study area is located between $53^{\circ} 26' E$ to $53^{\circ} 36' E$ longitudes and $35^{\circ} 34' N$ to $35^{\circ} 41' N$ latitudes (Fig. 1). Semnan industrial complex (SIC) unit is located at ~8 km in east of Semnan. Mean annual temperature and precipitation are $16^{\circ} C$ and 181.9 mm, respectively (Semnan Province Meteorological Administration 2010). Prevailing winds are from northwest and north direction (Fig. 1).

Mean altitude of the area is 1132 m above mean sea level. Sediments of the area come from highlands upstream consisting of andesite, rhyolite, limestone, shale, sandstone and marly materials (Aghanabati & Hamed 1995).

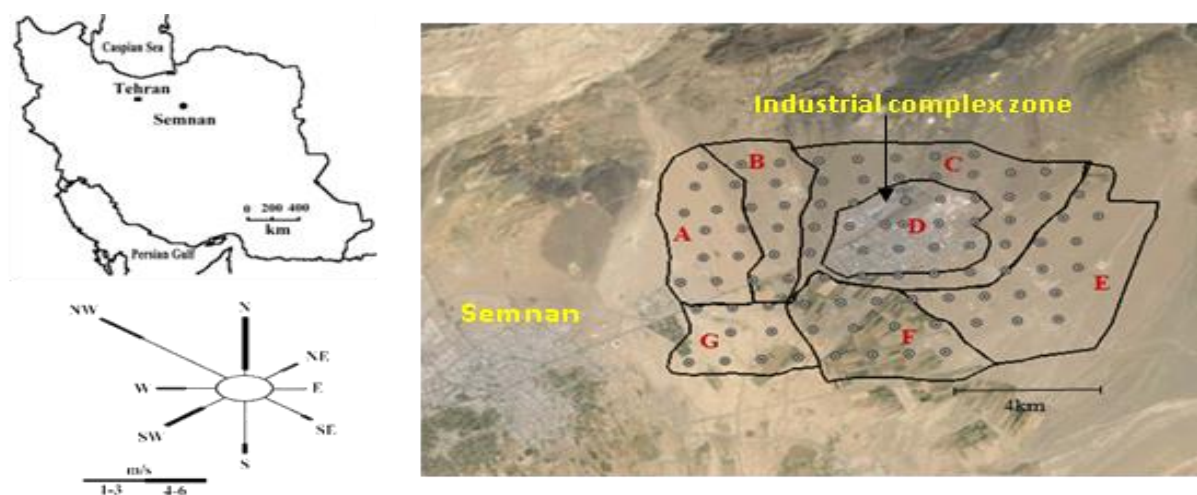


Fig. 1. Location of the study area, distribution of sampling points and wind rose of the study area; The A to G units are described in the text.

Study area located on the piedmont and clay flat landscapes. To understand the effect of natural factor on heavy metal concentrations, seven geomorphic units (A to G) were identified considering landform types and sediment origins (Fig. 1). The piedmont consists of four alluvial fans that are delineated in units A, B, C and E. The sediments of these alluvial fans originated from large watershed with different geologic materials. SIC is located inside the C unit which the boundary of this zone delineated in unit D. Units F and G are parts of the piedmont plain and clay flat, respectively.

Ninety three composite soil samples (0-10 cm) were collected at distance intervals about 1 km, in an area of 117 km² (Fig. 1). Each composite sample was made of five subsamples, taken at the center and at vertices of a 50 m-sided square. The sampling locations were determined using a GPS (Global Positioning System) device.

Laboratory analyses

The soil samples were air-dried and passed through a 2-mm sieve, to remove stones and plant material, before analysis and used for laboratory analyses. Soil pH was measured in 2:1 water to soil suspension. Calcium carbonate equivalent (CCE) was measured using acid neutralization method (Allison 1960). Particle size distribution (clay, silt & sand) was determined using pipet method (Gee & Bauder 1986). Soil organic carbon content was measured using wet oxidation method (Walkley & Black 1934).

The heavy metals were extracted using aqua-regia procedure (ISO/CDT 1995) and the concentrations of Pb, Zn, Cu, Ni, Cd and Cr were measured in aqua-regia extracts by atomic absorption spectroscopy. The reference standard was used to validate the measurement and the recoveries were 95 to 104%. The measurement for some samples were repeated to determine the analytical precision. Difference between the concentrations of the replicates was lower than 5%.

Statistical and geostatistical analyses

Descriptive statistics include mean, median, minimum, maximum, standard deviation, coefficient of variation (CV), skewness and kurtosis were calculated. The Kolmogorov-Smirnov test was used to test the normality of the data distribution. Logarithmic transformation was applied to normalize abnormal data. Linear correlation, principal component and cluster analyses were calculated using the SPSS software (19.0 version) (IBM Corp 2010) to describe and interpret the relationship among the heavy metal concentrations and soil properties. PCA is a method to transform a large data set into a set of principle components. These components can be used to elucidate the relationships of the variable (Rencher 2002). Geostatistical studies are consisted of two stages of variography (identification and modeling of spatial structure variables through semivariogram analysis) and estimation (kriging). In this study, semivariogram functions were used to indicate variations in a variable with distance using the equation 1 as follows (Goovaerts 1997):

$$\gamma_h = \frac{1}{2N_h} \sum_{i=1}^{N_h} (Z_{(xi)} - Z_{(xi+h)})^2 \quad (1)$$

where, $\gamma(h)$ is semivariogram, $N(h)$ is the number of sample pairs that are separated by a distance h , $Z(x_i)$ is the value of variable Z at location x_i and $Z(x_i+h)$ is the value of variable Z at location x_i+h .

All variographic analyses were performed in the variowin software (2.2 version). After the variography, estimation operations (interpolation) and ordinary kriging mapping were performed for each variable in the ArcGIS software (10.2 version). Kriging estimator which has high potential for determining spatial distribution of heavy metals in soil (Webster & Burges, 1980; Karimi *et al.* 2017) is used as an appropriate method for interpolating and mapping spatial distribution of heavy metals examined.

MAE (mean absolute error), MBE (mean bias error) and RMSE (root mean square error) were used to evaluate the accuracy of geostatistical modeling using equations 2 - 4 as follows:

$$MAE = \frac{1}{N} \sum_{i=1}^N \{|\hat{Z}(X_i) - Z(X_i)|\} \quad (2)$$

$$MBE = \frac{1}{N} \sum_{i=1}^N \{\hat{Z}(X_i) - Z(X_i)\} \quad (3)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N \{Z(X_i) - \hat{Z}(X_i)\}^2} \quad (4)$$

N is the number of observations, $Z(X_i)$ is the measured values of each variable, and $\hat{Z}(X_i)$ is the estimated values of each variable.

The closer value of MAE to zero indicates more accuracy and if MBE is equal to zero, indicating a model with no diversion.

The positive and negative values of MBE represent overestimating and underestimating, respectively. Lower RMSE shows the best fit. These indices were used to evaluate and select the best models for spatial distribution modeling (Webster & Oliver 2007).

RESULTS AND DISCUSSION

Soil properties and Heavy metal concentrations

Sand fraction in the piedmont units (A, B, C, D and E) was the dominant fraction and exceeded to ~90%. In F and G units, clay and silt with highest amounts of ~24 and ~42% were the dominant fractions. The average calcium carbonate equivalent was 25.9% which ranged from 13 to 39%. The average pH values was 7.4. EC increased from 0.1 dS m⁻¹ in the piedmont to 17 dS m⁻¹ in the clay flat. The soil organic carbon content was < 0.5% which was > 1% in the agricultural lands in F and G units. Descriptive statistics of heavy metal concentrations are presented in Table 1. The concentration ranges of Pb, Zn, Cu, Cd, Ni and Cr were 11.6-511.2, 34.1-247.9, 16.9-42, 0.7-2.8, 9.2-27.9 and 3.5-22.3 mg kg⁻¹ with mean values of 49.2, 84.4, 22, 1.6, 20.1 and 9.7 mg kg⁻¹, respectively.

Table 1. Statistical parameters of heavy metal concentrations (mg kg⁻¹) in the study area

Heavy metal	Mean	Median	Min	Max	Skewness	Kurtosis	SD	CV (%)	K-S
Pb	49.2	38.8	11.6	511.2	6.4	49.0	56.8	115.4	0.02*
Zn	84.4	71.1	34.1	247.9	1.9	5.2	37.6	44.5	0.01*
Cu	22.0	21.4	16.9	42.0	3.1	14.2	3.7	16.8	0.01*
Cd	1.6	1.7	0.7	2.8	-0.4	2.4	0.3	19.0	0.12
Ni	20.1	19.6	9.2	27.9	0.1	0.4	3.4	17.1	0.70
Cr	9.7	9.1	3.5	22.3	1.12	1.9	3.6	37.2	0.30

SD - Standard deviation, CV - Coefficient of variation, *Asymptotic significance > 0.05 (2-tailed).

Fig. 2 shows the boxplot of heavy metals in the geomorphic units. Mean Pb concentration in unit D (93.9 mg kg⁻¹) was significantly higher than in the other units. The highest Pb concentration (511.2 mg kg⁻¹) occurred in unit D within the steel plant and has shown as outlier point on the boxplot. The lowest mean of Pb concentration (26.9 mg kg⁻¹) was found in unit G. Although C and D units were located in an alluvial fan with the same parent materials and unit D (SIC) was surrounded by unit C, the average Pb concentrations in these units (93.9 and 43.2 mg kg⁻¹ respectively) were significantly different (Fig. 2).

The pattern of variations in Zn concentrations in the study area were nearly similar to Pb (Fig. 2). The highest mean value of Zn level in units D and E were 126.9 and 99 mg kg⁻¹, respectively, with the maximum of 247.9 mg kg⁻¹ in unit D. Also, the mean and maximum Cd concentrations (1.9 and 2.8 mg kg⁻¹ respectively) was found to occur in unit D. Noteworthy, according to the southern and southeastern prevailing winds (Fig. 1) and considering the location of E unit along the wind direction, the wind is probably responsible for accumulation of this element in the unit E. Unlike the Pb and Zn, the highest mean Cu concentration was found in unit E, although the maximum concentration of this element was in the unit D and appeared as outlier on boxplot (Fig. 2). The mean concentrations of Ni and Cr did not show any relation to unit D. Even the least mean concentrations of Ni and Cr (18.2 and 8.6 mg kg⁻¹ respectively) occurred in unit D. The geochemical background concentrations of Pb, Zn, Cu, Cd, Ni and Cr were 24, 61.3, 20.8, 1.6, 19 and 8.7 mg kg⁻¹, respectively. The dashed lines in boxplots in Fig. 2 exhibited geochemical background, indicating that the concentrations of the Pb, Zn, Cu and Cd in the majority of the samples from units D, E and F were higher than background concentration.

Spatial distribution

Results of Kolmogorov-Smirnov test (Table 1) showed the abnormal distribution with positive skewness for Pb, Zn and Cu in contrast to normal distribution for Cd, Ni and Cr concentrations (p<0.05). Logarithmic transformation was used to achieve normal distribution for Pb, Zn and Cu concentrations. Usually, an element with lithogenic origin has normal distribution and anthropogenic factors such as industrial activities, change the concentration of heavy metals and cause abnormal distribution (Zhao *et al.* 2010). Semivariograms and their parameters for heavy metal concentrations are shown in Fig. 3 and Table 2.

As shown in Table 2 the best models for Zn and other heavy metals were gaussian and spherical ones, respectively. Zn and Pb exhibited the highest range (R), while Cr and Ni displayed the lowest one (3130 and 2676 m, respectively). According to McGrath *et al.* (2004) the close-range values can be attributed to the similar source of the elements. The nugget to sill ratio, with values less than 0.25, between 0.25 and 0.75, and greater than 0.75 was classified to strong, moderate, and weak spatial dependence classes respectively (Cambardella *et al.* 1994; Xie *et al.* 2007).

According to Cambardella *et al.* (1994) and Kravchenko (2003), when the nugget/sill (N/S) ratio, as a characteristics of strength in the spatial structure of data, was equal or greater than 0.75, this corresponded to a weak spatial structure; i.e., at least 75% of the data variability consisted of unexplainable, short distance and random variation. In this study, spatial dependency classes of Zn and Cd were strong, while those of other elements were moderate (Table 2).

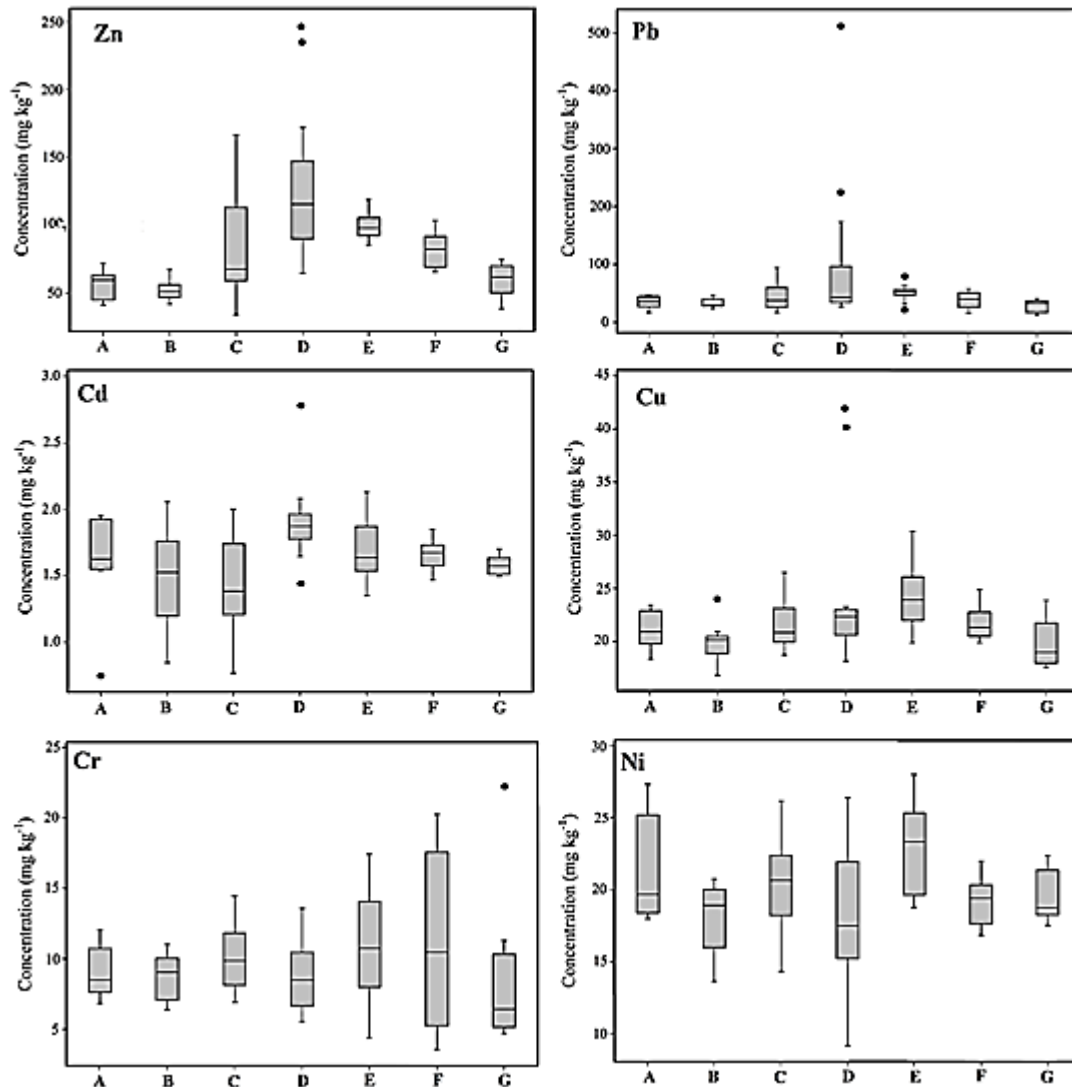


Fig. 2. Box plots showing the concentrations of Pb, Zn, Cu, Cd, Ni & Cr in different studied units; Dashed lines indicated the background concentration.

In fact, high values of spatial dependency class could be an indicative of overcoming of structural variance on random variance of the variables. This represents the appropriate pattern of sampling with relatively suitable accuracy of laboratory analysis (Dayyani & Mohammadi 2010).

Higher spatial correlation length compared to the sampling intervals, shows the appropriate spatial correlation of the data (Dragović *et al.* 2014). Therefore, it seems that the efficiency of the geostatistical method is weak at such times, hence we should use other statistical methods.

Due to high dependency of kriging estimations to semivariogram models, the MAE, MBE and RMSE were used to choose the best fitting model. As mentioned above, lower values of MAE and RMSE as well as closer value of MBE to zero, imply more accurate semivariogram model (Webster & Oliver 2007).

According to the results presented in Table 2, the selected models exhibit relatively high accuracy. Among the examined elements, Cu displayed the lowest MAE and RMSE (0.095 and 0.138) and also MBE (0.002) representing high accuracy of the model chosen.

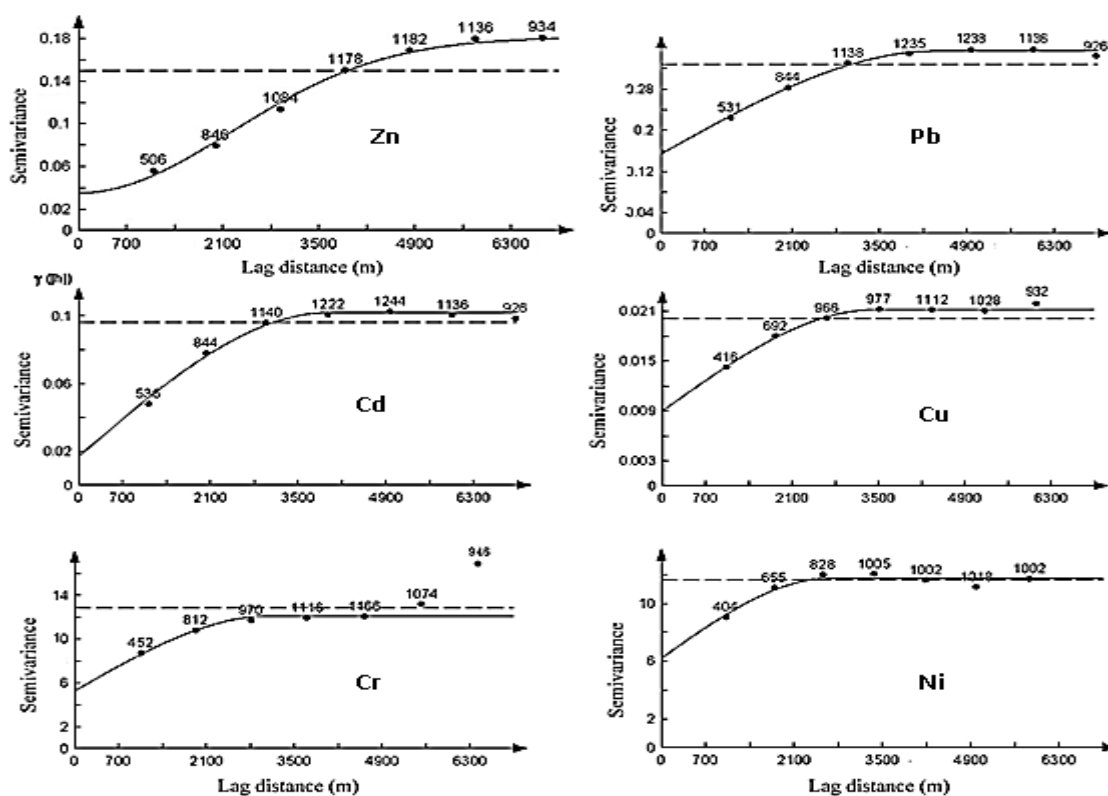


Fig. 3. Semivariograms of studied heavy metals.

Table 2. Variogram models, interpolation parameters and cross-validation statistics of heavy metals in the study area (n=93).

Heavy metal	Model	Range (m)	Nugget	Sill	Nugget/Sill	Spatial dependency	MBE	MAE	RMSE
Pb	Spherical	4410	0.154	0.353	0.43	Moderate	0.003	0.343	0.495
Zn	Gaussian	5451	0.035	0.181	0.19	Strong	0.004	0.188	0.265
Cu	Spherical	3439	0.009	0.021	0.42	Moderate	0.002	0.095	0.138
Cd	Spherical	3990	0.017	0.102	0.16	Strong	0.010	0.200	0.279
Ni	Spherical	2676	6.199	11.758	0.52	Moderate	-0.097	0.442	3.218
Cr	Spherical	3130	5.259	12.128	0.43	Moderate	-0.058	0.442	3.362

MBE: mean bias error, MAE: mean absolute error, RMSE: Root mean square.

In previous section, heavy metals were analyzed from viewpoint of classical statistics and the role of industrial activities in the increased Pb, Zn, Cu and Cd levels was determined. Continuous spatial distribution maps were known to provide more precise information on heavy metal level variations and also are useful to determine their controlling factors (Li *et al.* 2013; Lu *et al.* 2012). Spatial distribution maps revealed similar spatial patterns for Pb, Zn, Cu and Cd (Figs. 4a-d). The highest Pb, Zn and Cd levels occurred in unit D. Interestingly, the amount of these elements increased continuously from west to east, which is nearly along the direction of prevailing wind. The pattern of Pb, Zn, Cu and Cd level distributions indicated the importance of industrial activities in unit D as the pollution source and wind influence on the distribution of heavy metals. Geostatistical analyses revealed the close relation between heavy metal spatial distributions and prevailing winds in soils around the steel production facility in Smederevo, Serbia (Dragović *et al.* 2014). Based on spatial distribution maps of Ni and Cr (Fig. 4), no relationship was observed between the concentration of these elements and industrial activities (unit D) as well as prevailing wind. Furthermore, unlike other elements, the Ni and Cr levels in unit D were lower than in the other units. Many studies have reported that in urban and industrial areas, the Pb, Zn, Cu and Cd contents are enhanced by anthropogenic activities, while Ni and Cr levels are less affected by industrial activities and mainly are of lithogenic origin (Rodriguez *et al.* 2013; Lee *et al.* 2013; Dragović *et al.* 2014).

Barati *et al.* (2012) found the highest Ni and Cr levels in the soils on igneous and metamorphic parent materials. The Ni and Cr levels are strongly influenced by geologic formation and the most amounts of these elements were reported in basic and ultrabasic rocks (Barati *et al.* 2012; Karimi *et al.* 2017). The parent materials in the present were a mixture of sedimentary and felsic rocks (Aghanabati & Hamedei 1995), hence Ni and Cr levels were not too high (Table 1).

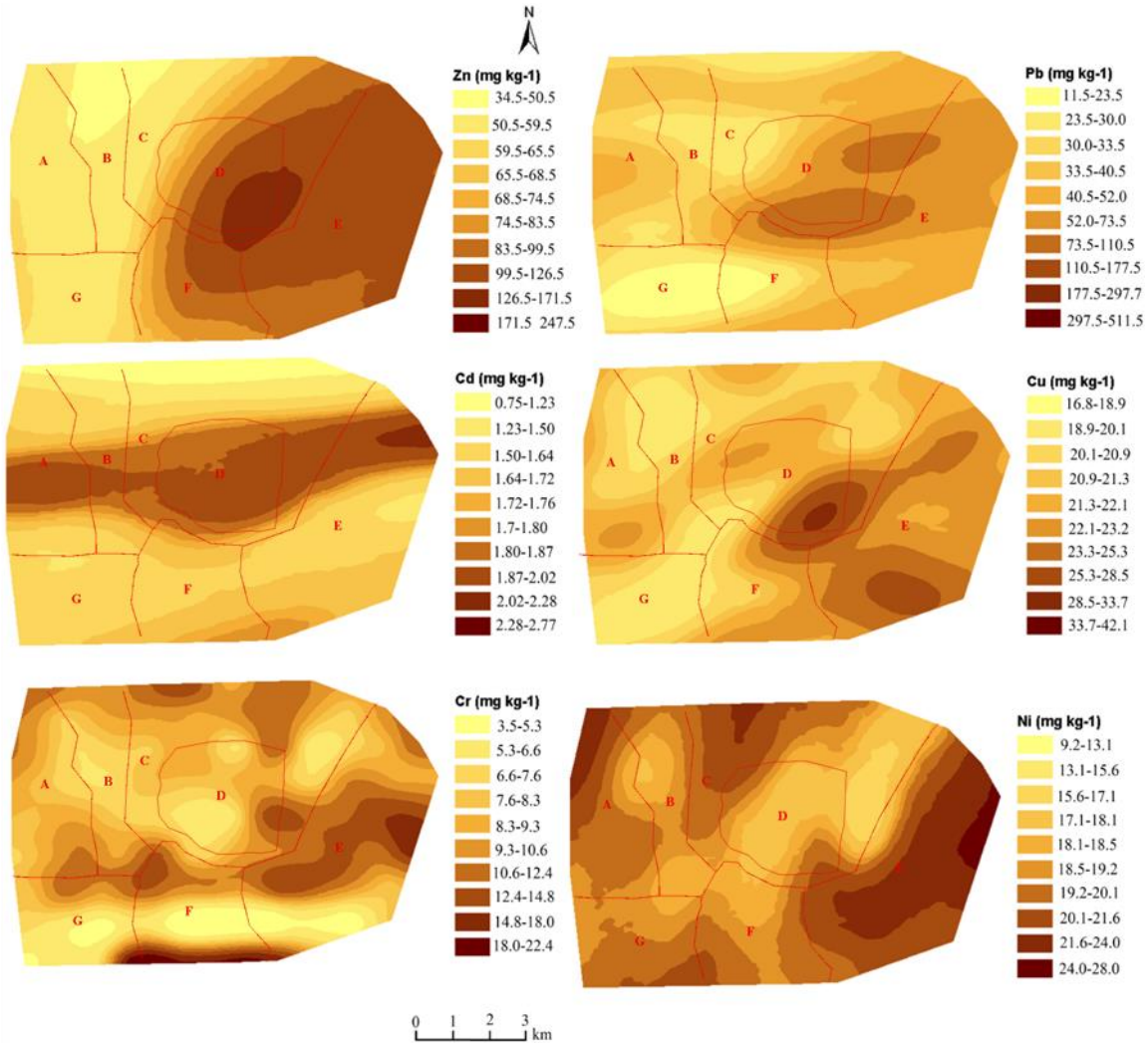


Fig. 4. Spatial distribution of Pb, Zn, Cu, Cd, Ni & Cr in surface soils of the study area.

Correlation between heavy metals

Table 3 shows the Pearson correlation coefficient between heavy metals. There was not significant relationship between soil properties and heavy metals. Positive significant correlation coefficient was observed between Pb and Zn ($p < 0.05$, $r = 0.51$), Cu and Zn ($p < 0.05$, $r = 0.61$) and also Cr and Ni ($p < 0.05$, $r = 0.37$) (Table 3).

Table 3. Correlation matrix of heavy metals in surface soil of the study area (n= 93).

Heavy metal	Pb	Zn	Cu	Ni	Cd	Cr
Pb	1					
Zn	0.51*	1				
Cu	0.20*	0.61*	1			
Ni	-0.12 ^{ns}	0.07 ^{ns}	0.25*	1		
Cd	0.02 ^{ns}	-0.01 ^{ns}	-0.11 ^{ns}	-0.22*	1	
Cr	0.01 ^{ns}	0.04 ^{ns}	0.16 ^{ns}	0.37*	-0.05 ^{ns}	1

*Correlation is significant at the 0.05 level (2-tailed), ns = Correlation is not significant.

Usually, high values of correlation coefficients between heavy metals imply the similar source of the elements (Li *et al.* 2013; Esmaeili *et al.* 2014). Usually the Pb and Zn levels in urban and industrial areas increased due to anthropogenic factors, resulting in significant correlation between these two elements (Sun *et al.* 2010). The high correlation between Cr and Ni levels can be attributed to concordant variation of these elements in parent materials (Barati *et al.* 2012; Rodriguez Martín *et al.* 2013).

Principle component analyses (PCA) and cluster analyses (CA)

PCA and CA are two common methods for grouping and extracting relationships between data and are useful statistical multivariate techniques to elucidate the factors controlling heavy metal levels in soils (Li & Feng 2012; Lu *et al.* 2012; Li *et al.* 2013; Alizadeh Ketek Lahijani *et al.* 2018). According to the results of PCA (Table 4), the initial eigenvalues of the two first components were higher than 1 and both explained 62.56 % of the total variance. PC1 and PC2 accounted for about 36 and 26 % of the total variance, respectively.

PC1 exhibited strong and positive relation to Zn (0.90) while partly to Pb, Cd and Cu (0.64-0.69). High loading values of heavy metal concentrations in extracted PCs can be attributed to same origin (Rodriguez *et al.* 2008; Taghipour *et al.* 2011; Li *et al.* 2012; Lu *et al.* 2012). A number of studies revealed that Pb, Zn, Cd and to some extent Cu are released to soil by industrial activities. Accordingly, the PC1 was identified as anthropogenic component. Ni and Cr with the highest loading values (0.80 and 0.75, respectively) were grouped in PC2.

As mentioned previously, Ni and Cr did not affected by industrial activities in the area, hence PC2 can be described as lithogenic component. Rodríguez *et al.* (2008), Li *et al.* (2013) and Li Yuan *et al.* (2004), reported similar PCA results for Ni and Cr that imply lithogenic origin of Cr and Ni in the soil. Esmaeili *et al.* (2014) reported that the existence of Cd, Pb and Zn in one component was linked to agricultural soils influenced by human activities, whereas Cr, Ni, Co, Al and Fe in another component, controlling by parent rocks.

Spatial distributions of the PC1 and PC2 are presented in Fig. 5. Highest values of PC1 (Pb, Zn, Cu and Cd) were observed mainly in unit D (industrial complex zone), while no obvious trend was observed by PC2 with the highest loading factors of Cr and Ni in the study area. Rodriguez *et al.* (2008) and Esmaili *et al.* (2014) provided the same results for Cr and Ni based on the principal components analysis.

Cluster analysis is a statistical method for grouping data according to the degree of their similarity or proximity. Through cluster analysis, data or observations are divided into clusters with different level of similarity (Bai *et al.* 2011). The cluster analysis result has shown in Fig. 6 indicating that the first cluster (C1) contains Pb, Zn, Cu and Cd.

Table 4. Total variance explained and component matrixes (two selected principal components) for heavy metals in soil.

Component	Initial eigenvalues			Extraction sums of squared loadings ^a			Rotation sums of squared loadings ^b		
	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
1	2.16	36.04	36.04	2.16	36.04	36.04	35.83	35.83	
2	1.59	26.52	62.56	1.59	26.52	62.56	26.73	62.56	
3	0.79	13.29	75.85						
4	0.66	11.06	86.91						
5	0.54	9.05	95.96						
6	0.24	4.03	100						
Heavy metal	Component matrix			Rotated component matrix					
		1	2		1	2			
Zn		0.92	0.01		0.9	0.15			
Pb		0.70	0.38		0.69	-0.11			
Cd		0.66	-0.21		0.65	-0.34			
Cu		0.59	-0.43		0.64	0.48			
Ni		0.08	0.80		-0.03	0.85			
Cr		0.07	0.75		-0.03	0.75			

^aExtraction method: principal component analysis, ^b Rotation method: varimax.

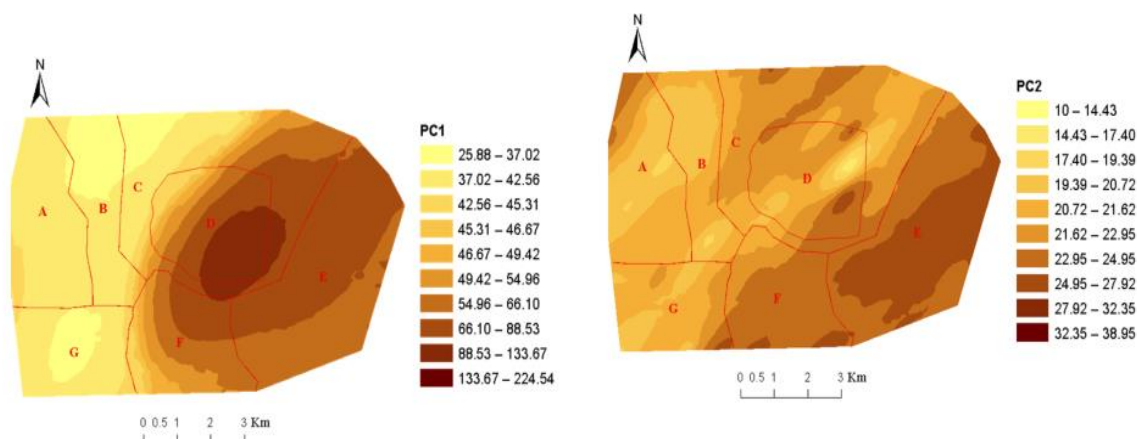


Fig. 5. Spatial distribution maps of PCA1 (anthropogenic components) and PC2 (lithogenic components).

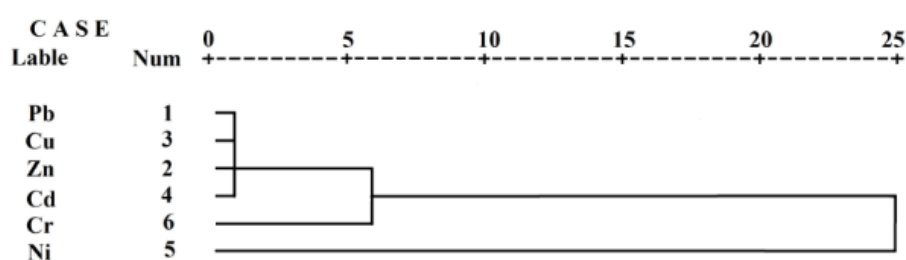


Fig. 6. Dendrogram of hierarchical cluster analysis of the heavy metals.

CONCLUSION

During four recent decades, the industrial complex areas have been developed near the great cities of Iran and could be the source of potential soil pollution by heavy metals. The results of this study revealed that the Pb, Zn, Cd and Cu concentrations were elevated in surface soils of industrial complex and distributed alongside the wind direction. The Cr and Ni levels were not affected by industrial activities. Using a set of statistical techniques including geostatistical, cluster and principle component analyses the heavy metals examined have been classified into lithogenic (Cr and Ni) an anthropogenic (Zn, Pb, Cd and Cu) groups. Kriged maps provide comprehensive information from spatial variation of heavy metals in the study area. These maps revealed the gradual increases in Pb, Zn, Cd and Cu levels from the west to the east of study which was concordant with prevailing wind direction. However, the Cr and Ni distribution maps did not show any specific pattern of variation. Even, the amounts of these two elements in the industrial complex were lower than in the other units. The findings of this study highlighted the emergent pollution of the soils in industrial complex area and surrounding lands. Therefore, it is necessary to designed strategies to prevent or decrease the input of heavy metals by industrial activities.

REFERENCES

- Alizadeh Ketek Lahijani, H, Naderi Beni, A & Tavakoli V 2018, Heavy metals in coastal sediments of South Caspian Sea: natural or anthropogenic source? *Caspian Journal of Environmental Sciences*, 16: 47-63.
- Aghanabati, A & Hamed, AR 1995, 1:250,000 geological quadrangle map of Semnan. Geological Survey of Iran, Tehran Naghsheh, Iran.
- Allison, LE 1960, Wet combustion apparatus and procedure for organic and inorganic carbon in soil. *Soil Science Society America Proceeding*, 24: 36-40.
- Alloway, BJ 2013, Sources of heavy metals and metalloids in soils. In: Alloway, BJ (Ed.). *Heavy Metals in Soils*, Springer Netherlands, pp. 11-50.
- Argyaki, A & Kelepertzis, E 2014, Urban soil geochemistry in Athens, Greece: the importance of local geology in controlling the distribution of potentially harmful trace elements. *Science of the Total Environment*, 482-483: 366-377.

- Ayoubi, S, Soltani, Z & Khademi, H 2018, Particle size distribution of heavy metals and magnetic susceptibility in an industrial site. *Bulletin of Environmental Contamination and Toxicology*, 100: 708-714.
- Bai, J, Xiao, R, Cui, B, Zhang, K, Wang, Q, Liu, X, Gao, H & Huang, L 2011, Assessment of heavy metal pollution in wetland soils from the young and old reclaimed regions in the Pearl River Estuary, South China. *Environmental Pollution*, 159: 817-824.
- Barati, S, Mirghaffari, N, Sefianian, A & Khodakarami, L 2012, Spatial distribution of Cr, Co and Ni in surface soils of Hamedan province. *Journal of Natural Environment*, 65: 283-295.
- Cambardella, CA, Moorman, TB, Parkin, TB, Karlen, DL, Turco, RF & Konopka, AE 1994, Field scale variability of soil properties in Central Iowa soils. *Soil Science Society of America Journal*, 58: 1501-1511.
- Canbay, M, Aydin, A Kurtulus, C 2010, Magnetic susceptibility and heavy-metal contamination in topsoils along the Izmit Gulf coastal area and IZAYTAS (Turkey). *Journal of Applied Geophysics*, 70: 46-57.
- Chen, T, Liu, XM, Li, X, Zhao, KL, Zhang, JB & Xu, JM 2009, Heavy metal sources identification and sampling uncertainty analysis in a field-scale vegetable soil of Hangzhou, China. *Environment Pollution*, 157: 1003-10.
- Dankoub, Z, Ayoubi, S, Khademi, H & Sheng-Gao, L 2012, Spatial distribution of magnetic properties and selected heavy metals in calcareous soils as affected by land use in the Isfahan region, central Iran. *Pedosphere*, 22: 33-47.
- Dayani, M & Mohammadi, J 2010, Geostatistical assessment of Pb, Zn and Cd contamination in near-surface soils of the urban-mining transitional region of Isfahan, Iran. *Pedosphere*, 20: 568-577.
- Dragović, R, Gajić, B, Dragović, S, Dordević, M, Dordević, M, Mihailović, N & Onjia, A 2014, Assessment of the impact of geographical factors on the spatial distribution of heavy metals in soils around the steel production facility in Smederevo (Serbia). *Journal of Cleaner Production*, 84: 1-13.
- Esmaeili, A, Moore, F, Keshavarzi, B, Jaafarzadeh, N & Kermani, M 2014, A geochemical survey of heavy metals in agricultural & background soils of the Isfahan industrial zone, Iran. *Catena*, 121: 88-98.
- Gee, GW & Bauder, JM 1986, Particle-size analysis. In: Klute, A (Ed.), *Methods of soil analysis. Part 1. Physical and mineralogical methods. Agronomy monograph, No. 9. 2nd (Ed.)*. American Society of Agronomy and Soil Science Society of America, Madison, WI. pp. 383-411.
- Goovaerts, P 1997, *Geostatistics for natural resources evaluation*. Oxford University Press, New York, USA, p. 83.
- Hu, Y, Liu, X, Bai, J, Shih, K, Zeng, EY & Cheng, H 2013, Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. *Environmental Science and Pollution Research*, 20: 6150-6159.
- IBM Corp 2010, *IBM SPSS statistics for Windows, version 19.0*. Armonk, NY: IBM Corporation.
- ISO/CD 11466 1995, *Soil quality-extraction of trace elements soluble in Aqua-Regia*, Switzerland. The International Organization for Standardization, p. 12.
- Karimi, A, Haghnia, GH, Safari, T & Hadadian, H 2027, Lithogenic and anthropogenic pollution assessment of Ni, Zn and Pb in surface soils of Mashhad plain, northeastern Iran. *Catena*, 157: 151-162.
- Kravchenko, AN 2003, Influence of spatial structure on accuracy of interpolation methods. *Soil Science Society of America Journal*, 67: 1564-1571.
- Li, X, Liu, L, Wang, Y, Luo, G, Chen, X, Yang, X, Guo, R, Wang, H, Cui, J & Xingyuan, H 2013, Heavy metal contamination of urban soil in an old industrial city (Shenyang) in Northeast China. *Geoderma*, 192: 50-58.
- Li, Feng, LN 2012, Multivariate and geostatistical analyses of metals in urban soil of Weinan industrial areas, Northwest of China. *Atmospheric Environment*, 47: 58-65.
- Ling-yu, B, Xi-bai, Z, Lian-fang, L, Chang, P & Shu-hui, L 2010, Effects of land use on heavy metal accumulation in soils and sources analysis. *Scientia Agricultural Sinica*, 9: 1650-1658.
- Lu, A, Wang, J, Qin, X, Wang, K, Han, P & Zhang, S 2012, Multivariate and geostatistical analyses of the spatial distribution and origin of heavy metals in the agricultural soils in Shunyi, Beijing, China. *Science of the Total Environment*, 425: 66-74.
- McGrath, D, Chaosheng, B & Carton, O 2004, Geostatistical analysis and hazard assessment on soil Pb in Silver mines area, Ireland. *Environmental Pollution*, 127: 239-248.
- Mico, C, Recatala, L, Peris, M & Sánchez, J 2006, Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere*, 65: 863-872.

- Mohammadpour, Gh, Karbassi, A & Baghvand A 2016, Pollution intensity of nickel in agricultural soil of Hamedan region. *Caspian Journal of Environmental Science*, 14: 15-24.
- Monavari, M 2001, Directory of environmental impact assessment of industrial zones. 1st Ed., EPA, p. 152 (In Persian).
- Palumbo, B, Angelone, M, Bellanca, A, Dazzi, C, Hauser, S, Neri, R & Wilson, J 2000, Influence of inheritance and pedogenesis on heavy metal distribution in soils of Sicily, Italy. *Geoderma*, 95: 247-266.
- Qing, X, Yutong, Z & Shenggao, L 2015, Assessment of heavy metal pollution and human health risk in urban soils of steel industrial city (Anshan), Liaoning, Northeast China. *Ecotoxicology and Environmental Safety*, 120: 377-385.
- Rencher, AC 2002, Methods of multivariate analysis. Second Edition, John Wiley & Sons, Inc., New York, p. 738.
- Rodriguez Martín, JA, Carbonell, G, Nanos, N & Gutiérrez, C 2013, Source identification of soil mercury in the Spanish islands. *Archives of Environmental Contamination and Toxicology*, 64: 171-179.
- Rodriguez, JA, Nanos, N, Grav, JM & Gil, L 2008, Multiscale analysis of heavy metal contents in Spanish agricultural topsoils. *Chemosphere*, 70: 1085-1096.
- Saby, NPA, Thioulouse, J, Jolivet, CC, Ratie, C, Boulonne, L & Bispo, A 2009, Multivariate analysis of the spatial patterns of 8 trace elements using the French soil monitoring network data. *Science of the Total Environment*, 407: 5644-5652.
- Sajn, R & Gosar, M 2014, Multivariate statistical approach to identify metal sources in Litija area (Slovenia). *Journal of Geochemical Exploration*, 138: 8-21.
- Semnan Province Meteorological Administration 2010, Bulletin of Semnan Province Meteorological Administration, p. 68 (In Persian).
- Sun, YB, Zhou, QX, Xie, XK & Liu, R 2010, Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. *Journal of Hazardous Materials*, 174: 455-462.
- Taghipour M, Ayoubi S & Khademi H 2011, Contribution of lithologic and anthropogenic factors to surface soil heavy metals in western Iran using multivariate geostatistical analyses. *Soil and Sediment Contamination: An International Journal*, 20: 921-937.
- Walkley, A & Black, IA 1934, An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science*, 37: 29-38
- Webster, R & Oliver, MA 2007, Geostatistics for environmental scientists, Second Edition, Wiley Press, p. 330.
- Webster, R & Burges, TM 2002, Optimal interpolation and isarithmic mapping of soil properties III-changing drift & universal kriging. *Journal of Soil Science*, 31: 505-524.
- Wei, BG & Yang, LS 2010, A review of heavy metal contaminations in urban soils, urban road dusts & agricultural soils from China. *Microchemical Journal*, 94: 99-107.
- Xie, Z, Li, J & Wu, W 2007, Application of GIS & geostatistics to characterize spatial Variation of soil fluoride on Hang-Jia-Hu Plain, CCTA, China. *Computer & Computing Technologies in Agriculture*, 1: 253-266.
- Zamani, A, Yaftian, MR & Parizanganeh A 2015, Statistical evaluation of topsoil heavy metal pollution around a lead and zinc production plant in Zanjan Province, Iran. *Caspian Journal of Environmental Sciences*, 13: 349-361.
- Zhao, YC, Wang, ZG, Sun, WX, Huang, B, Shi, XZ & Ji, JF 2010, Spatial interrelations and multi-scale sources of soil heavy metal variability in a typical urban-rural transition area in Yangtze River Delta region of China. *Geoderma*, 156: 216-227.

تجزیه تحلیل‌های چند متغیره و زمین‌آماری برخی از عناصر سنگین در خاک‌های سطحی شهرک صنعتی سمنان و اراضی اطراف آن

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چکیده

سی سال فعالیت‌های صنعتی در شهرک صنعتی سمنان، باعث ایجاد نگرانی درباره تجمع عناصر سنگین در خاک سطحی شده است. اهداف این مطالعه، تعیین غلظت و پراکنش مکانی عناصر سرب، روی، مس، نیکل، کادمیم و کروم در خاک سطحی شهرک صنعتی سمنان و اراضی اطراف آن و شناسایی منشا این عناصر بود. منطقه مورد مطالعه بر اساس نوع لندفرم و مواد مادری، به هفت واحد ژئومورفیک تقسیم شد. نود و سه نمونه مرکب سطحی (صفر تا ۱۰ سانتی‌متر) از محدوده‌ای به وسعت ۱۱۷ کیلومتر مربع جمع‌آوری شد. غلظت عناصر سنگین در عصاره تیزاب سلطانی توسط دستگاه جذب اتمی اندازه‌گیری شد. غلظت میانگین سرب، روی، کادمیم، مس، نیکل و کروم به ترتیب ۴۹/۲، ۸۴/۴، ۱/۶، ۲۲، ۲۰/۱ و ۹/۷ میلی‌گرم بر کیلوگرم با دامنه ۵۱۱/۲-۱۱/۶، ۱۶/۹-۲۴۷/۹، ۳۴/۱-۲۴۷/۹، ۰/۷-۲/۸، ۱۶/۹-۴۲ و ۹/۲-۲۷/۹ و ۳/۵-۲۲/۳ بود. بیشترین غلظت عناصر سرب، روی، کادمیم و مس در محدوده شهرک صنعتی مشاهده شد. نقشه پراکنش مکتبی این عناصر سنگین، نشان‌دهنده کاهش تدریجی غلظت این عناصر در جهت باد بود. غلظت نیکل و کروم، هیچ‌گونه الگوی تغییرات مکانی در محدوده شهرک صنعتی و سایر واحدها نداشت. بر اساس نتایج تجزیه به مولفه‌های اصلی، مولفه اول با بیشترین بار برای سرب، روی، کادمیم و مس به عنوان مولفه انسان‌زاد و مولفه دوم با بیشترین مقدار برای نیکل و کروم، به عنوان مولفه زمین‌زاد معرفی شدند. آنالیز خوشه‌ای هم نتایج مشابهی نشان داد. نتایج این مطالعه نشان داد که غلظت عناصر سرب، روی و کادمیم در خاک به مقدار قابل توجهی در طول زمان نسبتاً کوتاه صنعتی شدن افزایش یافته بود. این نکته باید مورد توجه تصمیم‌سازان برای جلوگیری بیشتر از آلودگی خاک، مورد توجه قرار گیرد.

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