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Original Article

Assessment of Heavy Metal Contamination in Surface Soils of Ahvaz IV Industrial Estate, Khuzestan Province, Iran

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Abstract

Background and Purpose: In the environment, heavy metals in high concentration are toxic to most organisms. Human activities have continuously increased the concentration of these metals in the environment such as soils. In the present study, soil samples collected from Ahvaz IV industrial estate in Khuzestan Province.

Materials and Methods: The soil samples were taken from 9 stations in 4 cardinal directions at two distances (300 and 600 m) with three replicates in 2013. Samples subjected to bulk digestion and chemical partitioning. The concentrations of Fe, Mn, Ni, and Sn in soil were determined by inductively coupled plasma atomic emission spectroscopy. We used geo-accumulation index (I-geo) and pollution index (Ipoll) to assessment the soil contamination in the soil samples. Furthermore, all statistical analyses were performed using the SPSS statistical package.

Results: I-geo and Ipoll results indicated that the soil samples are unpolluted to moderately polluted for all metals. The anthropogenic portion of metals are as follows: Fe (93%) > Ni (84.2%) > Mn (79.5%) > Sn (64%). Furthermore, the percent of anthropogenic pollution was more than percent of the natural portion.

Conclusion: Metals concentration had the highest rate at a distance of 300 m from the contaminant of the source. The result of cluster analysis showed that there is strong relationship among all metals.

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Key words: Soil Contamination, I-geo, Heavy Metal, Anthropogenic Pollution, Ahvaz IV Industrial Estate

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1. Introduction

Soil constitutes a crucial component of rural and urban environments, and soil contamination by heavy metals is a significant environmental problem worldwide (1,2). Metals are considered to be one of the main sources of the environmental pollution since they have significant effects on its ecological quality (3). Metals in urban soil have been shown to be very useful tracers of environmental pollution. Sources and accumulate of heavy metals in soils mainly include natural occurrence derived from parent materials and anthropogenic origin such as mining, industrial and energy production, agricultural, construction, vehicle exhaust, waste disposal, as well as coal fossil fuel combustion (3-10). Due to rapid industrialization, excessive application of metals and synthetic chemicals in the terrestrial environment coupled with deficient environmental management has led to a large-scale pollution in the environment. Soils contaminated by heavy metals from human activities have raised serious concern in recent decades regarding potential risk to human health through the direct intake, bioaccumulation through food chain, and their impacts on ecological system (11,12). Furthermore, exposure to the high amount of heavy metals can arises serious problems to human (13).

Apart from the source of heavy metals, the physicochemical properties of soil also affect the concentration of heavy metals in soils (14). The knowledge of the heavy metal accumulation in soil, the origin of these metals and their possible interactions with soil properties are priority objectives in the environmental monitoring (15). Heavy metals and trace elements are also a matter of concern due to their no biodegradable nature and long biological half-life's (16,17). Organic matter and pH are the most important parameters controlling the accumulation and the availability of heavy metals in soil environment (14).

Elements are distributed throughout soil and sediment components and associated with them in various ways such as ion exchange, adsorption, precipitation, and complexion (18). Sequential extraction can provide information about the identification of the main binding sites, the strength of element binding to the particulates and the phase associations of trace elements in soil (19). Following this basic scheme, some modified procedures with different sequences of reagents or operational conditions have been developed (20-24).

Essential heavy metals (Cu, Zn, and Mn) as well as non-essential heavy metals Cd, Cr and Pb are considered highly toxic for human life (25). In the Earth crust, Fe is the most abundant metal and is essential to all organisms, except for few bacteria. Its excess in the body causes liver and kidney damage (2). Nickel is a known hematotoxic, immunotoxic, neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic, hepatotoxic and carcinogenic agent. Nickel exposure causes the formation of free radicals in various tissues in both human and animals which lead to various modifications to DNA bases, enhanced lipid peroxidation, and altered calcium and sulfhydryl homeostasis (26). Iron and Mn oxides and organic matter either as bulk phases or as coatings of mineral particles are the main binders in sediments (27).

Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on different parts of the vegetables exposed to the air from polluted environments (28). Heavy metals may enter the human body through inhalation of dust, direct ingestion of soil and consumption of food plants grown in metal contaminated soils (29). In addition, people may come in contact with heavy metals in industrial work, pharmaceutical and agriculture. Children may be poisoned as a result of playing in contaminated soil. Symptoms vary, depending on the nature and

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the quantity of the heavy metal ingested. Patients may complain of nausea, vomiting, diarrhea, stomach pain, headache, sweating, and a metallic taste in the mouth. Depending on the metal, there may be blue-black lines in the gums (2). Several researches have indicated the need of a better understanding of soils contamination arising from the industrial activities (30-32). Hence, considering the importance of this approach, the aim of this study was assessment the vertical distribution of some heavy metals (Fe, Mn, Ni, and Sn) in soil samples collected from different stations of Ahvaz IV industrial estate using geochemical indicators such as geo-accumulation index (I-geo) and pollution index (Ipoll).

2. Materials and Methods

2.1. Description of the study area

Ahvaz IV industrial complex is located in 18th km Southeast of Ahvaz City. The study area is located in 48° 52' 18" longitude and 31° 16' 31" Latitude with an approximate altitude of 17 m above sea level. Active units in the industrial complex include the exploitation, desalination, and gas compression.

2.2. Soil sampling

Soil samples were collected in 9 stations including 4 cardinal directions at two distances (300 and 600 m) with three replicates. Furthermore, a sample was considered in the northwestern and the distance of 1800 m from the source of contamination as a control sample. Figure 1 shows sampling stations.

The soil samples were obtained with a hand auger from topsoil between depths of 15 and 30 cm. The first 15 cm of top layer was not sampled for avoiding the surface contaminants. The blank sample was obtained from topsoil at 1800 m distance from source pollution. Soil samples were collected with a polyethylene scoop and stored in plastic bags. The soil samples were air-dried and passed through a 2 mm plastic sieve to move gravel and rocks, put in plastic bags.

2.3. Samples preparation and data analysis

Briefly, 0.1 g of each homogenized sample was digested by triacid attack (HF-$HClO_4$-HNO_3) in a Teflon vessel and heated in a microwave oven at 180° C for 10 minutes. The digested solution was diluted to a known volume with double distilled water, and then it was analyzed for metals by inductively coupled plasma atomic emission spectroscopy. Statistical grouping of the concentrations of each element between different sampling stations and correlation analysis was performed using the SPSS 19.0 (SPSS Inc., Chicago, IL, USA) statistical package.

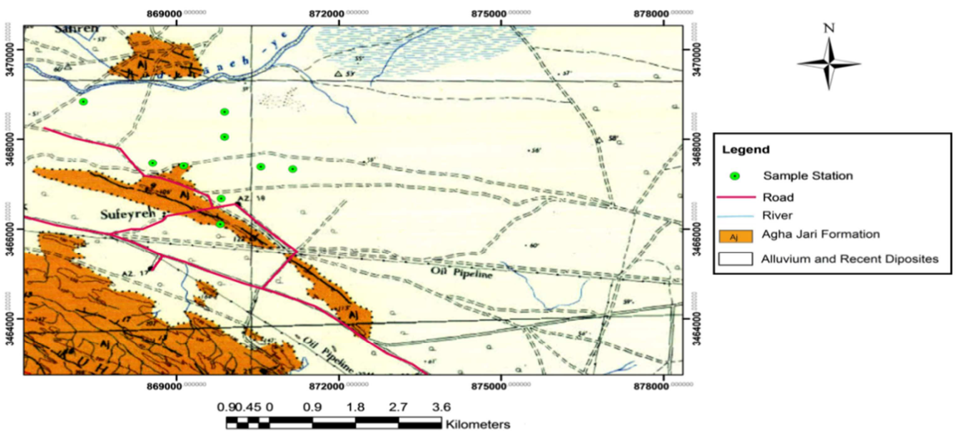

Figure 1. Sampling stations of Ahvaz IV industrial estate, Khuzestan Province, Iran

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2.4. Assessment of geo-accumulation and pollution index

To evaluate the magnitude of contaminants in the soil profile and intensity of heavy metal pollution at the different depths of soil, I-geo was computed according to the abundance of species in source material to that found in the Earth's crust and the following equation was used to calculate the I-geo (33):

$$\text{I-geo} = \text{Log2}\,[\text{Cn}/(1.5\text{Bn})] \qquad (1)$$

Where, Cn is the concentration of element "n," Bn is the geochemical background value and 1.5 is the background matrix correction factor due to lithogenic effects.

In the present study, a newly developed formula which is a modification of the I-geo is introduced as follows (34):

$$\text{Ipoll} = \text{Log2}\,[\text{Bc}/\text{Lp}] \qquad (2)$$

Where, Ipoll, Bc, and Lp are indicative of pollution intensity, bulk concentration, and lithogenous portion, respectively. Muller as well as other researchers have used the concentration of metals in shale as a substitute for Bn, and applied a factor of 1.5 for normalization to background metals concentrations. In the present study, Bn was computed by subtraction of the anthropogenic portion of metals from bulk concentration. Since there was not any need in these evaluations to use the shale metal concentrations, the constant factor (1.5) was eliminated.

The geo-accumulation index (I-geo) and pollution index (Ipoll) scale consists of seven grades or classes (0 to 6) ranging from unpolluted to highly polluted (Table 1).

2.5. Calculation of the enrichment factor (EF)

A common approach to estimate how much the soil and sediment is impacted (naturally and anthropogenically) with heavy metal is to calculate the EF for metal concentrations above uncontaminated background levels. The EF of a heavy metal in sediment can be calculated with the equation (3) (36,37):

$$\text{EF} = [C_{metal}/C_{normalizer}]_{soil}/[C_{metal}/C_{normalizer}]_{control} \qquad (3)$$

Where, C_{metal} and $C_{normalizer}$ are the concentrations of heavy metal and normalizer in soil and in unpolluted control, respectively.

3. Results

The mean concentrations of heavy metal in the soil samples of Ahvaz IV industrial estate ranged from 18013 ± 323 to 21125 ± 388 mg/kg for Fe; 215 ± 3.04 to 320 ± 3.23 mg/kg for Mn; 93.73 ± 1.99 to 150.44 ± 1.21 mg/kg for Ni; and 8.05 ± 1.67 to 13.02 ± 1.31 mg/kg for Sn (Table 2). Statistical grouping of the concentrations of each element in the different samples of soil by analysis of variance and Duncan multiple range test indicated that there were significant differences within and between most of the evaluated samples ($P < 0.05$) (Table 2). Heavy metal concentrations were the highest at south station in distance 300 m from source pollution. Natural and anthropogenic pollution in soil of Ahvaz IV industrial estate are given in table 3.

Table 1. Definition of pollution index based on I-geo and Ipoll (35)

Value	Class	Pollution intensity
< 0	0	unpolluted
0-1	1	unpolluted to moderately polluted
1-2	2	moderately polluted
2-3	3	moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly to very strongly polluted
> 5	6	Very strongly polluted

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Table 2. Mean values of heavy metal contents in the soil samples of Ahvaz IV industrial estate (mg/kg)

Stations sample No.	SD ± Metals level heavy			
	Fe	Mn	Ni	Sn
E1 3	21088 ± 276[d]*	320 ± 3.23[e]	150.44 ± 1.21[de]	13.02 ± 1.31[de]
E2 3	19001 ± 254[a]	231 ± 3.22[a]	104.03 ± 2.10[a]	9.05 ± 1.11[a]
N1 3	21001 ± 329[e]	312 ± 3.51[e]	146.17 ± 3.01[de]	12.56 ± 2.03[de]
N2 3	18987 ± 332[bc]	269 ± 3.05[cd]	120.91 ± 1.77[bc]	8.05 ± 1.67[bc]
W1 3	21125 ± 388[c]	302 ± 2.99[d]	140.17 ± 2.11[cd]	11.5 ± 1.21[cd]
W2 3	18179 ± 279[b]	215 ± 3.04[bc]	100.27 ± 3.04[ab]	9.10 ± 1.14[ab]
S1 3	19678 ± 404[f]	287 ± 4.57[f]	130.04 ± 1.95[e]	10.14 ± 1.82[e]
S2 3	18013 ± 323[a]	221 ± 3.16[ab]	99.87 ± 2.03[ab]	9.03 ± 1.13[ab]
Blank 3	18985 ± 387[c]	226 ± 3.15[a]	93.73 ± 1.99[a]	9.40 ± 0.98[a]
Mean concentration	19561.89	264.78	120.62	10.20
**Average shale	47,200	850	50	6

*[a, b, c…] the letters represent the statistical differences between mean values of heavy metal contents among the different sampling stations according to Duncan multiple range test (P = 0.05). **World geochemical background value in average shale (38). SD=Standard deviation

Table 3. Natural and anthropogenic pollution in soil of Ahvaz IV industrial estate

Stations	Fe	Mn	Ni	Sn
Natural pollution (%)				
E1	3.68	28.13	19.45	42.79
E2	12.36	13.86	11.71	32.49
N1	4.78	27.57	22.89	42.01
N2	4.73	24.17	12.06	21.74
W1	3.22	26.83	14.99	38.61
W2	12.7	13.46	21.71	35.74
S1	3.11	24.74	10.21	35.31
S2	10.16	13.64	15.47	33.89
Blank	9.97	12.39	13.59	41.49
Anthropogenic pollution (%)				
E1	96.32	71.87	80.55	57.21
E2	87.64	86.14	88.29	67.51
N1	95.22	72.43	77.11	57.99
N2	95.27	75.83	87.94	78.26
W1	96.78	73.17	85.01	61.39
W2	87.3	86.51	78.29	64.26
S1	96.89	75.26	89.79	64.69
S2	89.84	86.36	84.53	66.11
Blank	90.03	87.61	86.41	58.51

Calculated I-geo and Ipoll values based on the average shale are presented in table 4. Furthermore, statistical analysis between mean concentration of heavy metals in soil samples and background levels and correlation coefficient of heavy metals in soil samples are shown in tables 5 and 6, respectively.

The cluster analysis of heavy metals for soil samples of Ahvaz IV industrial estate is shown in figure 2.

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Table 4. I-geo and Ipoll of heavy metals in soil samples of Ahvaz IV industrial estate

Sampling station	Element			
	Fe	Mn	Ni	Sn
I-geo				
E1	0.089	0.075	0.60	0.47
E2	0.080	0.054	0.42	0.30
N1	0.089	0.073	0.58	0.42
N2	0.080	0.063	0.48	0.27
W1	0.085	0.071	0.56	0.38
W2	0.077	0.050	0.40	0.30
S1	0.083	0.067	0.52	0.34
S2	0.076	0.052	0.40	0.30
Blank	0.080	0.053	0.38	0.31
Ipoll				
E1	0.13	0.11	0.90	0.70
E2	0.12	0.08	0.62	0.45
N1	0.13	0.11	0.88	0.63
N2	0.12	0.09	0.72	0.40
W1	0.12	0.10	0.84	0.57
W2	0.11	0.07	0.60	0.45
S1	0.12	0.10	0.78	0.50
S2	0.11	0.07	0.59	0.45
Blank	0.12	0.08	0.59	0.47

Table 5. Statistical analysis between mean concentration of heavy metals in soil samples and background levels

Element	t	df	P	Mean difference	95% confidence interval of the difference	
					Lower	Upper
Fe	-134.839	26	< 0.001	27,749.1111	-28,172.1276	-27,326.0946
Mn	-74.80	26	< 0.001	-586.3300	-569.2499	-601.4167
Ni	17.396	26	< 0.001	70.6277	62.2822	78.9733
Sn	12.934	26	< 0.001	4.1966	3.5297	4.8636

Table 6. Pearson correlation coefficient matrix for heavy metals

Element	Fe	Mn	Ni	Sn
Fe	1			
Mn	0.93*	1		
Ni	0.91*	0.98*	1	
Sn	0.91*	0.82*	0.83*	1

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

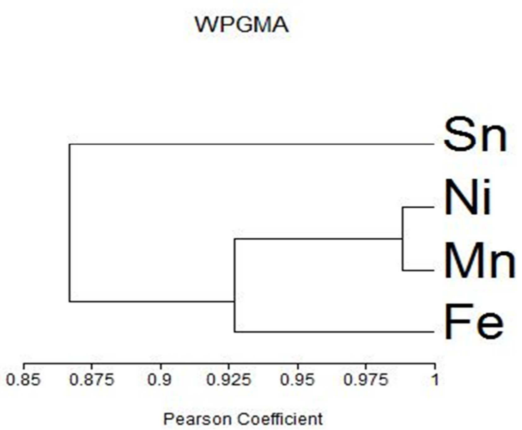

Figure 2. Cluster analysis of heavy metals in Ahvaz IV industrial estate

4. Discussion

Based on the results of this study, the portions of all metals bounded to anthropogenic phase were higher than that of them bounded to natural phase in soil. This indicates that the accumulation of heavy metals is due to anthropogenic sources, i.e., the heavy industry in the soil. The concentration of metals at distance of 300 m from pollutant source was most level. Based on the I-geo and Ipoll values, the soil in the Ahvaz IV industrial estate was uncontaminated to moderately contaminated

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for Fe, Mn, Ni, and Sn. Cluster analysis was one of the multivariate analyses used in this study to originate statistics of elements by Cluster software. Correlation analysis, which is one of the approaches of Explore software, was used to achieve the similarity coefficients and dendrograms. Then, it assigns the similarity of the samples. Finally, Using Ipoll index compared with the intensity of the contamination the elements were analyzed. The result of cluster analysis showing that there is strong relationship among all metals (Pearson coefficient > 0.7), especially between Ni and Mn and both of them with FE. Because Fe originates of terrestrial sources, it can be resulted that Ni and Mn originates of terrestrial sources, too. Industrial activities, mining and exploitation of oil reservoirs are the main cause of pollution in the area. Ghiyasi et al., 2010 (39) determined the origin and concentrations of heavy metals in agricultural land around aluminum industrial complex. In their research lithogenous origin of Zn, Sn and Cr is emphasized, while this relation is not seen for Ni and Cd. Asaah et al., 2006 (40) were examined pollution in surface soils of the Bassa industrial zone using I-geo and results showed that soils in this area were moderately to very highly polluted. Sekabira et al., 2010 (41) determined heavy metal pollution in the urban stream sediments and its tributaries. factor analysis results reveal three sources of pollutants as explained by three factors (75.0%); (i) mixed origin or retention phenomena of industrial and vehicular emissions; (ii) terrigenous; and (iii) dual origin of zinc (vehicular and industrial). The results of Pearson correlation coefficient analysis showed that elemental pairs Fe/Mn, ($r = 0.93$, $P < 0.05$); Fe/Ni , ($r = 0.91$, $P < 0.05$); Fe/Sn ($r = 0.91$, $P < 0.05$); Mn/Ni, ($r = 0.98$, $P < 0.05$); Mn/Sn , ($r = 0.82$, $P < 0.05$); and Ni/Sn, ($r = 0.83$, $P < 0.05$) are significantly correlated with each other.

Conflict of Interests

The Authors have no conflict of interest.

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