

Heavy Metals (Mg, Mn, Ni and Sn) Contamination in Soil Samples of Ahvaz II Industrial Estate of Iran in 2013

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Background & Aims of the Study: Due to the rapid industrial development in Khuzestan province of Iran during recent years, this study was performed to analyze the variation of metals concentrations (Mg, Mn, Ni, and Sn) in soil samples of Ahvaz II Industrial estate during the spring season of 2013.

Materials & Methods: In this experimental study, 27 topsoil samples were collected from nine stations. The intensity of the soil contamination was evaluated, using a contamination factor (Cf) and geo-accumulation index (I-geo).

Results: The mean soil concentrations (in mg kg⁻¹ (dry weight)) were in ranged within 870-1144 (Mg), 188-300 (Mn), 93-199 (Ni) and 9-15 (Sn). The data indicated that the I-geo value for all metals falls in class '1'. Also the Cf value for Mg and Mn falls in class '0', the Cf value for Sn falls in class '1' and the Cf value for Ni falls in the classes of '1' and '2'. The result of the Pearson correlation showed that there were significant positive associations between all metals.

Conclusions: According to the results which were achieved by a cluster analysis, there were significant positive associations among all metals based on Pearson correlation coefficient, especially between Ni and Sn; also both of them with Mn. Because the Ni originates from oil sources it can be resulted that Mn and Sn originate from oil sources, too. Therefore, industrial activities and exploitation of oil reservoirs are the main cause of pollution in that area. Also, it can be concluded that, with increasing the distance from the source of pollution, the accumulation of contaminants in the soil samples decreased.

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Background

Disposal of heavy metals and soil pollution by toxic metals are significant environmental problems of the worldwide (1,2). In particular, heavy metal pollution of surface soils due to the increase of industrialization and urbanization has become a serious concern in many developing countries (3-5). The accumulation of heavy metals in surface soils is affected by

many environmental variables such as parent material and soil properties, as well as by human activities, including rapidly expanding industrial areas, traffic, farming, wastewater irrigation, mine tailings, disposal of high toxic metal wastes, leaded paints and gasoline, land application of fertilizers, animal manures, sewage sludge, pesticides, coal combustion residues, petrochemicals leakage and atmospheric deposition (1,6,7)

Even though some heavy metals are essential elements for a wide range of organisms and play structural roles in many proteins, excess in environment has caused detrimental effects damaging plants, animal and human health through enter the food chain (8). Heavy metals, such as Cd, Cr, Hg, Pb, etc., have been classified as carcinogenic to humans and wildlife by International Agency for Research on Cancer (IARC) (9,10).

The assessment of the potential ecological risk of heavy metal contamination was proposed as a diagnostic tool for controlling purposes of the environmental pollution as a result of the increasing content of heavy metals in soils and sediments (11). Therefore, the knowledge of distribution and concentrations of heavy metals in the soils could help to detect the source of pollution in the terrestrial ecosystems (12-15). For assessment of heavy metals contamination in soil and sediment, several indices such as enrichment factor, geo-accumulation index, the potential ecological risk index, pollution load index and anthropogenic pollution index have been introduced extensively (16-18).

Ahvaz II industrial estate is located in 6th km southeast of Ahvaz City, Iran, with 48° 46' 31" longitude and 31° 18' 56" latitude and an approximate altitude of 17 meters above the sea level. The area of this region is 2820000 m². Also the main industrial activities in the area of the study were the exploitation, desalination and gas compression units. Previous studies have observed very strongly pollution of Cd in the surface soils of the Ahvaz II industrial estate of Iran (19). Sobhanardakani and Ahmadi (2015) assessment the Cr and Ni concentrations in topsoil samples around the Arak III Industrial estate of Iran and reported that the mean concentrations of metals in all samples are significantly lower than the WHO permissible limits for soil contamination (20).

Aims of the study:

Due to the heavy metal pollution monitoring is needed in order to provide the baseline data which can be used by local authorities for environmental management, this study was conducted to analyze the heavy metals (Mg, Mn, Ni and Sn) contamination in soil samples of Ahvaz II industrial estate of Iran, using geo-accumulation index (I-geo) and Contamination factor (Cf) in 2013.

Materials & Methods

Soil sampling

A total of 24 surface soil samples were collected at least 300 and 600 m away from the cardinal directions of Ahvaz II industrial estate. All soils were sampled at the surface (15 to 20 cm in depth), using hand driven stainless steel augers. Also 3 samples were considered in the north western and the distance of 1800 m from the source of contamination as control sample. Figure 1 shows sampling stations. The collected soil samples were dried at 60 °C, sieved through a 2.0-mm nylon sieve to remove sand, gravel, plant debris and stored in glass bottles at room temperature (1)

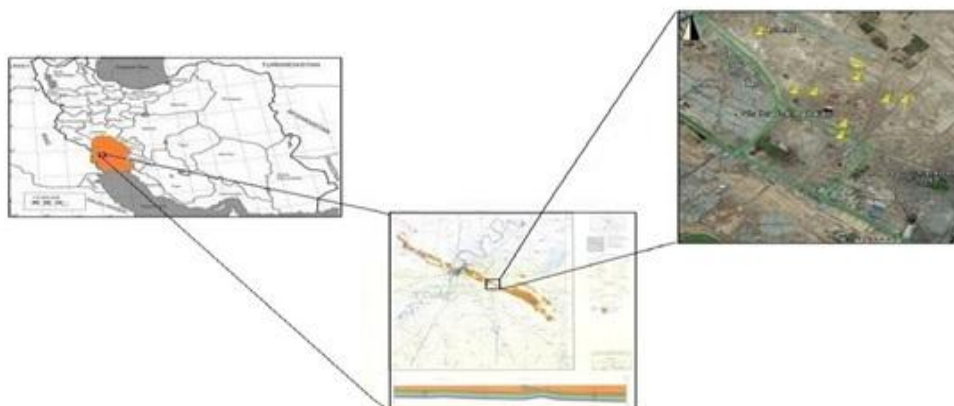
Sample preparation and analysis

Briefly, 0.1 g of each homogenized sample was digested by triacid attack (HF-HClO₄-HNO₃) in a Teflon vessel and heated in a microwave oven at 180 °C for 10 min. The digested solution was diluted to a known volume with double distilled water, then it was analyzed for metals by ICP-OES (PerkinElmer's Optima 8300). Precision was achieved by triplicate analysis of the same sample and standards.

Statistical Analysis

For conducted correlation analysis and one-way ANOVA, using the SPSS 20.0 (SPSS Inc., Chicago, IL, USA) (21).

Figure 1) Location of Ahvaz II industrial estate and sampling stations



Assessment of metal contamination Geoaccumulation index (I-geo)

To evaluate the magnitude of contaminants in the soil profile and intensity of heavy metal pollution at different depths of the soil, I-geo was computed according to the abundance of species in the source material to found in the Earth's crust and the equation 1 was used to calculate the I-geo (22):

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad (\text{Eq. 1})$$

Where C_n is concentration of element, B_n is geochemical background value and 1.5 is background matrix correction factor due to the lithogenic effects.

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

Table 1) Geo-accumulation index for contamination levels in soil (22)

Value	Class	Pollution intensity
<0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strong to extremely polluted
>5	6	Extremely polluted

Contamination factor (CF)

Another approach to estimate the level of contamination in soil is to compute the contamination factor (CF), using the equation 2 (23):

$$Cf = \frac{C_n}{\text{mean } B_n} + \text{one } S.D. \quad (\text{Eq. 2})$$

Table 2) Contamination factor and level of contamination (24)

Contamination Factor (Cf)	Level of Contamination
Cf < 1	Low contamination
1 ≤ Cf < 3	Moderate contamination
3 ≤ Cf < 6	Considerable contamination
Cf > 6	Very high contamination

Results

The mean soil concentrations of heavy metals (mg kg⁻¹) in the soil samples of Ahvaz II industrial estate are summarized in Table 3. Results showed that the mean soil concentrations ranged within 870-1144 for Mg, 188-300 for Mn, 93-199 for Ni and 9-15 for Sn. Also the mean concentrations of all metals in S1 station (distance of 300 m from the source of pollution) were higher than other stations.

The results for comparison of the natural and anthropogenic pollution contribution in soil samples of Ahvaz II industrial estate (Table 4) showed that the contribution of anthropogenic pollution in soil samples is more than the contribution of natural pollution.

The computed I-geo and Cf values are presented in tables 5 and 6, respectively. According to the results, I-geo values for Mg, Mn, Ni and Sn fall in class '1' and indicating the soil quality is unpolluted to moderately

polluted for all stations. Also the Cf values for Mg and Mn fall in class '0' and indicating low contamination, the Cf value for Sn fall in class '1' and indicating moderate contamination, the Cf value for Ni falls in the classes of '1' and '2', indicating moderate to considerable contamination.

The results of Pearson correlation coefficient shows that the elemental pairs Mg/Mn, ($r=0.96$, $p<0.05$), Mg/Ni, ($r=0.78$, $p<0.05$), Mn/Ni,

($r=0.89$, $p<0.05$), Sn/Mg, ($r=0.95$, $p<0.05$), Sn/Mn, ($r=0.96$, $p<0.05$) and Sn/Ni, ($r=0.88$, $p<0.05$) have strong correlations with each other (Table 7). Also cluster analysis of heavy metals in soil samples of Ahvaz II industrial estate are shown by a dendrogram in figure 2.

Table 3) Mean concentration of heavy metal in soil samples of Ahvaz II industrial estate (mg kg⁻¹)

Sampling sites	Mean Concentration±SD			
	Mg	Mn	Ni	Sn
1E	1092±182.9 ^{d*}	279±44.5 ^{de}	153±27.7 ^e	13±2.2 ^d
2E	879±111.3 ^a	188±31.9 ^a	93±14.6 ^a	9±1.8 ^a
1N	1127±98.3 ^e	290±37.6 ^e	161±34.4 ^f	14±2.5 ^e
N2	932±109.8 ^b	217±51.8 ^c	105±22.9 ^c	10±1.9 ^b
1W	1032±82.7 ^c	259±40.3 ^d	138±31.4 ^d	11±3.5 ^c
2W	924±100.3 ^b	209±28.1 ^{bc}	101±20.1 ^c	9.9±1.4 ^{ab}
S1	1144±112.2 ^e	300±56.6 ^f	199±42.2 ^e	15±3.1 ^f
S2	912±77.8 ^b	201±29.3 ^b	98±11.30 ^b	9.50±1.3 ^{ab}
Blank	870±101.5 ^a	286±40.5 ^e	140±29.8 ^d	11±3.1 ^c
Mean concentration	1008.11	246.33	131.95	11.39
**Average shale	15000	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 (25)

Table 4) Natural and anthropogenic pollution in soil samples of Ahvaz II industrial estate

Element	Anthropogenic %	Geopogenic %
Mg	89.50	10.50
Mn	81.88	18.12
Ni	79.67	20.33
Sn	51.39	48.61

Table 5) Geo-accumulation index of heavy metals in soil samples of the Ahvaz II industrial estate

Sampling site	Mg	Mn	Ni	Sn
E1	0.014	0.066	0.61	0.44
E2	0.011	0.044	0.37	0.30
N1	0.015	0.068	0.64	0.47
N2	0.012	0.051	0.42	0.33
W1	0.013	0.061	0.55	0.36
W2	0.012	0.050	0.40	0.33
S1	0.015	0.070	0.80	0.50
S2	0.012	0.050	0.39	0.31
Blank	0.011	0.067	0.56	0.37

Table 6) Contamination factor of heavy metals in soil samples of the Ahvaz II industrial estate

Sampling site	Mg	Mn	Ni	Sn
E1	0.07	0.33	3.05	2.20
E2	0.05	0.22	1.87	1.50
N1	0.07	0.34	3.20	2.35
N2	0.06	0.25	2.10	1.67
W1	0.06	0.30	2.76	1.83
W2	0.06	0.24	2.03	1.65
S1	0.07	0.35	3.98	2.50
S2	0.06	0.24	1.95	1.58
Blank	0.05	0.34	2.80	1.88

Table 7) Pearson correlation coefficient for heavy metals

Element	Mg	Mn	Ni	Sn
Mg	1	0.96**	0.78**	
Mn		1	0.89**	
Ni			1	
Sn	0.95**	0.96**	0.88**	1

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

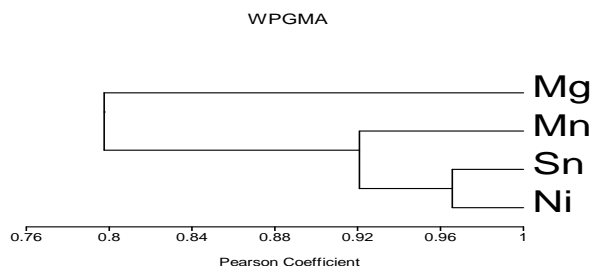


Figure 2) Cluster analysis of heavy metals in soil samples of Ahvaz II industrial estate

Discussion

Mean concentrations of Mg, Mn, Ni, and Sn obtained from this study generally decreased with increasing the distance from the source of pollution. The overall contamination of soils at the area of the study, based on the I-geo values indicate that soil samples were unpolluted to moderately polluted with Mg, Mn, Ni, and Sn. Also the overall contamination of soil samples based on Cf values indicate that soils were low contamination with Mg and Mn, moderately contaminated with Sn, but showed moderate to considerable contamination with Ni. In the case of the degree of contamination, the windward soils fall under considerable contamination.

According to the Pearson correlation coefficient, strong correlations signify that each paired elements have common anthropogenic origin contamination sources. However, it seems that Sn content in the surface soils was controlled by both natural (geochemical processes) and anthropogenic sources. Also the data indicate that some of the sampling stations, especially S1, are relatively higher concentration levels of metals Mg, Mn, Ni, and Sn in the surface soil; therefore more extensive sampling and analysis would be necessary to provide more data in trace metal speciation in this region to establish the potential environmental impact.

Conclusion

Based on the results of this study, the portions of all metals bounded to anthropogenic phase

were higher than those which had been 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 meters from the source of pollutants was the most level. Based on the geo-accumulation index values, the soil in the Ahvaz II industrial estate can be classified as unpolluted to moderately polluted for all assessed metals. Contamination factor showed that the soil had low contamination for Mg and Mn. Also for Ni is moderate contamination to considerable one and for Sn is moderate. Therefore it can be concluded that with increasing the distance from the source of pollution, the accumulation of contaminants in the soil decreased. Dendrogram of cluster analysis (Figure 2) shows that there is a strong relationship among all metals based on Pearson correlation coefficient, especially between Ni and Sn; also both of them with Mn. Because the Ni originates from the oil sources, it can be resulted that Mn and Sn originate from oil sources, too. Therefore, industrial activities and exploitation of oil reservoirs are the main causes of pollution in that area.

Finally, according to the results, it can be concluded that such information would also be necessary to determine the sources of elevated levels of trace elements which were analyzed; as well as provide more accurate baseline data which can be used by authorities in their impact assessment and future planning of activities in Ahvaz II industrial estate of Iran.

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