

Natural and Anthropogenic Source of Heavy Metals Pollution in the Soil Samples of an Industrial Complex; a Case Study

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ABSTRACT

Background: Soil serves as a major reservoir for contaminants as it can bind to various chemicals. The aim of this study was to evaluate the levels of some metals (Cd, Cu, Fe and V) in soil samples collected from different stations of Ahvaz Industrial Complex II to determine the natural and anthropogenic contribution of metal in the soil.

Methods: This was an experimental study that carried out in 2013. Soil samples were obtained from 9 stations and were subjected to bulk digestion and chemical partitioning. Concentrations of Cd, Cu, Fe and V in soil were determined by ICP-OES. Contaminant factor (CF) and geo-accumulation index (I-geo) were used to evaluate the soil pollution in the samples. ANOVA, Duncan Multiple Range and Pearson correlation coefficient matrix tests was used to analyze the data.

Results: According to I-geo results, the soil samples of the Ahvaz Industrial Complex II could be classified as strongly to very strongly pollute for Cd and it was unpolluted to moderately pollute for Cu, Fe and V. The amount of anthropogenic pollution was more than that of natural sources and the anthropogenic order of metals pollution was Fe (88%)> Cu (83%)> Cd (75%)> V (61%).

Conclusion: Metals concentrations are the highest at a distance of 300m from the pollution source. V, Cu and Cd pollutants are probably originated from oil industries.

Keywords: Environmental Pollution; Metals, Heavy; Soil Pollutants.

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INTRODUCTION

Trace metal contamination is important due to its potential toxicity for the environment and human beings [1]. The role of heavy and trace elements in the soil system is increasingly becoming an issue of global concern. Soil constitutes a crucial component of rural and urban environments [2] and the sources of these contaminants in soil mainly include natural occurrence derived from parent materials and human activities. Anthropogenic inputs are associated with industrialization as atmospheric

deposition, waste disposal, waste incineration, urban effluents, traffic emissions, fertilizer application and long-term application of wastewater in agricultural lands [3, 4]. Apart from the source of heavy metals, the physicochemical properties of soil also affect the concentration of heavy metals in soil [5]. Understanding heavy metal accumulation in soil, the origin of these metals and their possible interactions with soil properties are priority objectives in environmental monitoring [6]. Heavy metals and trace elements are also a matter of concern due to their non-biodegradable

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nature and long biological half-lives [7, 8]. Organic matter and pH are the most important parameters controlling the accumulation and the availability of heavy metals in soil environment [5].

Elements are distributed throughout soil and sediment components and interact with them in various ways such as ion exchange, adsorption, precipitation, and complexation but they are not permanently fixed by soil and sediment [9]. Sequential extraction can provide information about the identification of the main binding sites, the strength of element binding to the particulates and phase associations of trace elements in soil [10]. Following this basic scheme, some modified procedures with different sequences of reagents or operational conditions have been developed [11-15]. Heavy metal accumulation in soil is of concern in agricultural production due to adverse effects on food quality (safety and marketability) and crop growth (due to phytotoxicity) [16, 17]. The heavy metals are health hazards either indirectly; by consuming vegetables grown on contaminated soils, or directly by inhaling dust or drinking contaminated water [18]. Metals such as Cd and Cu are cumulative poisons. These metals cause environmental hazards and are reported to be exceptionally toxic [19]. Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on different parts of the vegetables exposed to air from polluted environments [20]. Nearly half of the mean ingestion of Cd through food is due to plant origin [fruit, vegetables and cereals].

Heavy metals may enter the human body through dust inhalation, direct ingestion of soil and consumption of food plants grown in metal contaminated soils [21]. In addition, people may come in contact with heavy metals via their jobs in industrial, pharmaceutical or agricultural sections. Children can also be poisoned as a result of playing in contaminated soil. Symptoms vary, depending on the nature and 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 [22].

The aim of this study was to evaluate the levels of some metals (Cd, Cu, Fe and V) in soil samples collected from different stations of Ahvaz Industrial Complex II to determine the natural and anthropogenic contribution of metal in soil of Ahvaz Industrial Complex II.

MATERIALS AND METHODS

This experimental study carried out in 2013. The study area was Ahvaz Industrial Complex II that located in 6th km Southeast of Ahvaz City (48°46'31" longitude and 31°18'56" latitude; an approximate altitude of 17 meters above the sea level) with active units in the industrial complex including the exploitation, desalination and gas compression units. Soil samples were collected in 4 cardinal directions at two distances [300 and 600m] with three replicates. In addition, a sample was obtained from the north western with a distance of 1800m from the source of contamination as control sample (Figure 1).

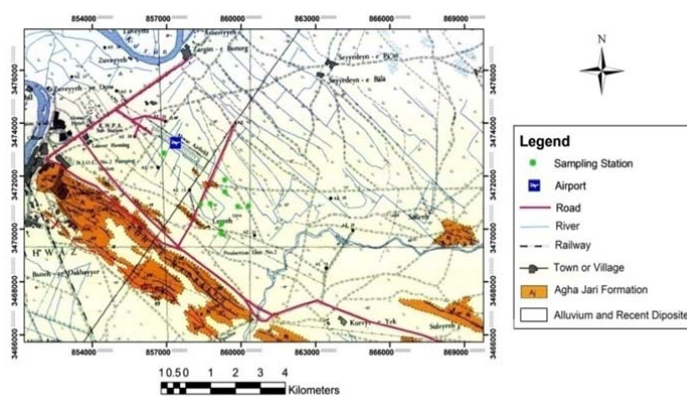


Figure 1. Sampling stations of Ahvaz Industrial Complex II, Khuzestan Province, Iran.

The soil samples were obtained with a hand auger from top soil between depths of 15-30cm. The first 15cm of top layer was not sampled to avoid surface contaminants. The

blank sample was obtained from top soil at 1800m distance from source pollution site. Soil samples were collected with a polyethylene scoop and stored in plastic bags. Then they were air-dried and passed through a 2mm plastic sieve to remove gravel and rocks and was kept in plastic bags. Briefly, 0.1g of each homogenized sample was digested by three-acid attack (HF/HClO₄/HNO₃) in a Teflon vessel and was heated in a microwave oven at 180°C for 10min. The digested solution was diluted to a known volume with double distilled water, and then it was analyzed for metals by ICP-OES. Precision was achieved by triplicate analyses of the same sample and standards. Correlation analysis was conducted using the SPSS 15 (SPSS Inc.; Chicago, IL, USA) statistical package. I-geo and CF were used to identify the association between metals and evaluate the soil pollution.

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

$$I_{geo} = \log_2 [C_n / (1.5B_n)]$$

Where, C_n is the concentration of element 'n', B_n is the geochemical background value and 1.5 is the background matrix correction factor due to lithogenic effects. The geo-accumulation index (I-geo) scale consists of seven grades or classes (0 to 6) ranging from unpolluted to highly polluted; CF<1=Low, 1≤CF<3=Moderate, 3≤CF<6=Considerable, 6≤CF=Very high contamination.

To estimate the amount of pollution in soil samples we compute the contaminant factor (CF) using the following formula [23]:

$$CF = \text{metal concentration in soil} / \text{background values of the metal}$$

Table 1. Natural pollution, anthropogenic pollution, geo-accumulation index and the amount of contaminant factor in soil of Ahvaz Industrial Complex II.

Stations	V	Cu	Cd	Fe
Natural pollution (%)				
E1	41.04	19.18	18.80	11.24
E2	27.19	13.53	37.47	17.34
N1	41.77	19.51	19.97	12.66
N2	38.49	15.50	24.85	11.74
W1	40.58	14.97	18.49	8.05
W2	36.66	14.45	28.82	13.24
S1	48.20	22.48	22.24	13.70
S2	35.14	14.71	29.81	13.03
Blank	37.87	20.97	42.89	5.67
Anthropogenic pollution (%)				
E1	58.96	80.82	81.20	88.76
E2	72.81	87.47	62.53	82.66
N1	58.23	80.49	80.03	87.34
N2	61.51	84.50	75.15	88.26
W1	59.42	85.02	81.51	91.95
W2	63.34	86.55	75.18	87.76
S1	51.80	77.32	77.76	86.30
S2	64.86	85.29	70.19	86.97
Blank	62.12	79.03	58.11	94.32
Geo-accumulation index (I-geo)				
E1	0.074	0.175	7.52	0.09
E2	0.035	0.140	4.78	0.08
N1	0.075	0.178	7.94	0.09
N2	0.055	0.159	5.79	0.08
W1	0.072	0.164	6.88	0.09
W2	0.050	0.154	5.26	0.08
S1	0.077	0.188	8.42	0.10
S2	0.045	0.148	4.98	0.08
Blank	0.077	0.142	4.50	0.09
The amount of contaminant factor (CF)				
E1	0.37	0.88	37.60	0.45
E2	0.18	0.70	22.33	0.40
N1	0.37	0.90	39.73	0.46
N2	0.27	0.80	28.96	0.42
W1	0.36	0.83	34.43	0.42
W2	0.25	0.77	26.33	0.41
S1	0.38	0.94	42.13	0.47
S2	0.23	0.74	24.93	0.40
Blank	0.11	0.21	22.50	0.42

Where CF is the mean content of metals from at least five sampling sites and is the pre-industrial concentration of the individual metal.

Cluster analysis was one of the multivariate analyses used in this study. Correlation analysis, which is one of the approaches of Explore software, was used to achieve the similarity coefficients and dendrograms. Then it was used to assign the similarity of the samples. Finally Ipoll index was compared with the intensity of the contamination.

Statistical grouping of the concentrations of each element in the different samples of soil was analyzed by ANOVA and Duncan Multiple Range tests. Pearson correlation coefficient matrix was used for pair elemental analysis.

RESULTS

The mean of heavy metal concentrations in the soil of Ahvaz industrial complex II estate ranged from 23.14 ± 3.22 to $50.12 \pm 5.23 \text{ mg kg}^{-1}$ for V; 31.85 ± 3.12 to $42.46 \pm 3.54 \text{ mg kg}^{-1}$ for Cu; 6.70 ± 1.10 to $12.64 \pm 1.95 \text{ mg kg}^{-1}$ for Cd; and 18980.0 ± 255.0 to $22456.0 \pm 414.0 \text{ mg kg}^{-1}$ for Fe.

There were significant differences within and between most of the evaluated samples ($p < 0.05$). Natural and anthropogenic source of pollution, I-geo and contaminant factor (CF) values based on the average shale are presented in Table 1. Cd/Cu ($r = 0.98$), Cd/Fe ($r = 0.91$), Cd/V ($r = 0.69$), Cu/Fe ($r = 0.92$), Cu/V ($r = 0.66$) and Fe/V ($r = 0.79$) elemental pairs are significantly correlated with each other ($p < 0.05$).

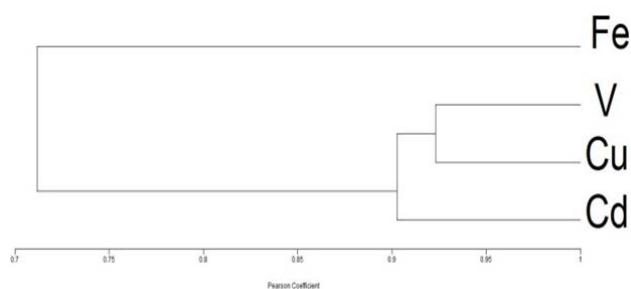


Figure 2. Cluster analysis of heavy metals in Ahvaz Industrial Complex II.

According to the result of cluster analysis, there was a strong relationship among all metals (Pearson coefficient > 0.7), that Cu had high similarity coefficient with V; also Cd had high similarity coefficient with V and Cu, but there was negative high coefficient with Fe (Figure 2).

DISCUSSION

The present results show that permethrin is highly toxic to Zebra cichlid (*Cichlasoma nigrofasciatum*). The toxicity of permethrin on *C. nigrofasciatum* increased with increasing

concentration and exposure time. When the fish were exposed to $7.5 \mu\text{g/l}$ permethrin, only 23.33% died after 96h, whereas all the fish (100%) died after 48h when exposed to a concentration of $60 \mu\text{g/l}$ permethrin. In addition, the 24, 48, 72 and 96h LC₅₀ values of permethrin on *C. nigrofasciatum* were calculated as 38.07, 22.57, 19.96 and $17.55 \mu\text{g.l}^{-1}$, respectively. Başer et al. [18] found out a 48h LC₅₀ value for permethrin in guppy (*Poecilia reticulata*) of $245.7 \mu\text{g.l}^{-1}$. The 96h LC₅₀ values of permethrin in *Morone saxatilis*, *Pimephales promelas*, *Salmo salar* and *Gambusia affinis* were 15.6, 16, 12 and $15 \mu\text{g.l}^{-1}$, respectively (Quoted from 18) which are highly comparable to our results. The inability of fish to rapidly hydrolyze permethrin may result in an overall low rate of detoxification and this could be a factor in the fish sensitivity to permethrin [11, 16].

The calculated 24, 48, 72 and 96h LC₅₀ values of mercury chloride, using a static bioassay system to zebra cichlid, were 333.45, 198.43, 163.37 and $140.38 \mu\text{g.l}^{-1}$, respectively. Our results demonstrate that mercury is highly toxic to *C. nigrofasciatum*. The LC₅₀ values of HgSO₄ for *Capoeta fusca* at 24, 48, 72, and 96h of exposure were 0.32, 0.28, 0.26, and 0.24 mg.l^{-1} , respectively [19]. The 96h LC₅₀ values of mercury in *Clarias gariepinus*, *Cyprinus carpio*, *Barbus conchoniensis*, *Clarius batrachus* and *Etroplus maculatus* were 600, 930, 181, 510 and $130 \mu\text{g.l}^{-1}$, respectively (20, 21, Quoted from 22). The degree of susceptibility of zebra cichlid to lower concentrations of mercury may be attributed to differences in the physiological response of fish to this pollutant.

No mortality was observed in fish exposed to sub-lethal concentrations of permethrin and mercury chloride as well as control group during the experimental period. Increased mucus secretion, dark skin pigmentation, loss of appetite, bleeding at the base of the fins and eye balls, behavioral changes such as tremors,

lethargy, unbalanced swimming, swimming in surface water and extreme irritability were important changes observed in fish exposed to permethrin and mercury chloride during The results showed that the I-geo value for Cu, V and Fe fell in "class 1" indicating unpolluted to moderately polluted soil, and the I-geo value for Cd was in "class 6" (very strongly polluted) for all stations except E2 and S2 stations that were 600m from the pollution source which is categorized as "class 5", indicating strongly to very strongly polluted.

The CF value for Cu, V and Fe fell in "class 0" indicating low contamination and the CF value for Cd was in "class 3" for all stations, indicating very high contamination factor.

There was strong relationship among all metals (Pearson coefficient > 0.7), especially between V and Cu and both of them with Cd. As V is an oil pollution index, it can be concluded that Cu and Cd could have originated from these sources, too. So anthropogenic pollution is more important than natural pollution of soil.

Ghiyasi determined the origin and concentrations of heavy metals in agricultural lands around an aluminum industrial complex [26]. In their research lithogenous origin of Zn, Sn and Cr was emphasized, while this relation was not seen for Ni and Cd. Asaah and Abimbola examined pollution in the surface soils of the Bassa industrial zone using I-geo and the results showed that soils in this area were moderately to very highly polluted [27]. Sekabira determined heavy metal pollution in an urban stream sediments and its tributaries [28]. Factor analysis revealed three sources of pollutants as explained by three factors (75.0%); 1. mixed origin or retention phenomena of industrial and vehicular emissions, 2. terrigenous and 3. dual origin of zinc (vehicular and industrial).

CONCLUSION

The concentration of metals at 300m from the pollution source is the highest. Soil of the Ahvaz Industrial Complex II can be classified as

strongly to very strongly pollute for Cd and it is unpolluted to moderately pollute for Cu, Fe and V. Soil samples have very high contamination factor for Cd and low contamination factor for V, Cu and Fe. The amount of all metals bounded to soil due to anthropogenic sources is higher than that of natural ones, especially the heavy industries in the area. There is strong relationship among all metals especially between V and Cu and both of them with Cd. Because V originates from oil industries therefore it can be concluded that Cu and Cd could have originated from these sources, too. Industrial activities, mining and exploitation of oil reservoirs are the main cause of pollution in the area.

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