Assessment of Copper and Zinc Contamination in Soils of Industrial Estates of Arak Region (Iran)

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ABSTRACT

Background: Contamination of the environment due to heavy metals is a major concern to human life and the environment. This study was conducted to investigate and quantify the copper and zinc concentrations in industrial estates soil in Arak, Iran.

Methods: Four industrial estates were considered for the experimental design, including Arak 1, Arak 2, Arak 3, and Ghotbe Sanaati. For preliminary understanding of soil heavy metals pollution in industrial estates, the concentrations of zinc and copper in the soil are analyzed and investigated to evaluate their concentration and environmental quality based on the contamination factor.

Results: The results indicated the soils had been polluted by heavy metals due to industrial processes that concentrate these metals in the soil. Copper concentrations varied from 15.69 to 49.55 mg/kg. Zinc concentrations were found to be between 23.02 and 144.17 mg/kg. The highest concentration of Zn was found in Arak 3 region which may be due to industrial activities while the highest concentration of Cu was observed in the soil of Arak 1 region that may be due to proximity of this industrial estate to Arak city. The findings of the contamination factor showed that the heavy metals are accumulated in the soil of industrial estates that are considered low risk for contamination with zinc and copper.

Conclusion: The achievements of this research showed the location of the industrial estate, proximity to highways and main roads, and the area of green space of industrial estates are important factors in determining heavy metals concentration.

Keywords: Arak, Copper, Industrial Estates, Soils, Zinc.

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INTRODUCTION

Industrial estates (IEs) are characterized by clustering of industries designed to meet compatible demands of different organizations within one location [1]. According to UNIDO, an industrial estate (IE) can be defined as a tract of land developed and subdivided into plots according to a comprehensive plan with provision for roads, transport, and public utilities for the use of a group of industrialists [2]. In fact, industrial estates (IEs) are specific areas zoned for industrial activity to facilitate the growth of industries and to minimize their environmental impacts. However, most of the solid wastes and waste waters are discharged into the soil and water bodies and thus ultimately pose a serious threat to human and routine functioning of the ecosystem. A wide range of chemicals are used at facilities within the estates, including many organic compounds as well as many metals and their compounds [3]. Among pollutants, heavy metals have been the subject of particular attention because of their long-standing toxicity when exceeding specific thresholds. As a consequence of these industrial activities, large amounts of wastes are generated. These wastes contain heavy metals, such as copper, zinc, cadmium, lead, and mercury, as well as arsenic, at levels that exceed the critical limits.

Heavy metals are naturally occurring in the Earth's crust. Many of these elements are biologically essential and are introduced into aquatic and terrestrial environments through various anthropogenic activities [4]. Main anthropogenic sources of heavy metals exist in various industrial point sources, e.g. present and former mining activities, foundries, smelters, and other diffuse sources, such as piping, constituents of products, combustion of by-

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products, traffic, and industrial and human activities [5]. Soils are considered “recipients” of heavy metals from a large variety of anthropogenic source. Thus, they can be considered good indicators of metals pollution. In addition, they are critical environments where rock, air, and water interface. Consequently, they are subjected to a number of pollutants due to different anthropogenic activities, such as industrial, agricultural, transport, etc [6, 7]. The chemical composition of soil, particularly its metal content is environmentally important since toxic metals concentration can reduce soil fertility and increase input to food chain which leads to the accumulation of toxic metals in food and, ultimately, endangerment of human health. Hence, their detailed study is of great significance. Among the metals, copper (Cu) and zinc (Zn) are essential for human. Chronic metabolic disturbances may result from excess or deficiency of these metals. Moreover, copper and zinc are essential elements for higher plants but at the same time they are potential environmental contaminants. Their sources range from the electrical industry, transport or mechanical engineering, construction, and civil engineering. Copper and zinc may enter the soil through fertilizers, organic wastes, and pesticides applications. Sewage sludge usually contains significant amounts of Cu and Zn and can be a source of these metals in the soil [8]. Worldwide, several studies have evaluated heavy metals contamination in soils [9-13], but very little is known about the concentration of heavy metals in IEs' soils. Copper (Cu), lead (Pb), cadmium (Cd), and zinc (Zn) are the principal metals of concern in environmental surveys because they are often the main metal constituents of air pollutants and known toxicities to biota [14]. To date, little research on soil pollution in IEs has been conducted. Therefore, four IEs (Arak 1, Arak 2, Arak 3 and Ghotbe Sanati [GS]) in Arak city were chosen for this study. There are seven major industry groups in Arak industrial estates. The objectives of this study included the investigation of the concentrations of zinc (Zn) and copper (Cu) in the surface soil throughout IEs and the evaluation of degree of soil pollution in terms of metals contamination.

MATERIALS AND METHODS

Study Area

The study area (Arak city) is located in the southern part of Markazi province, central Iran. Arak is an industrial city and, in fact, one of the industrial centers of the country. Markazi IEs corporation was registered in 1989. Four IEs in Arak city were selected for this research. A sketch map of the location of the sampling sites is shown in Figure1**.** Four IEs near Arak city known as important IEs- Arak 1 (Serahi Khomein), Arak 2 (Eybakabad), Arak 3 (Kheirabad), and Ghotbe Sanati- were chosen to be included in the study. Arak 1 IE (Serahi Khomein: 34°4'4"N 49°46'32"E) is located 5 km far from Arak city, an important chemical industry centre 48.6 hectares wide. Arak 2 IE (34°17'5"N 49°41'7"E), also called Eybakabad, is located 17 km for from the city on Arak-Farmahin Road. This IE is 331 hectares wide. Arak 3 IE (34°9'21"N 49°58'49"E) is commonly known as Kheirabad due to its proximity to Kheirabadi village. It is about 30 km distant from the city. This area is 1344 hectares wide. Ghotbe Sanati (GS) IE is also in proximity of Arak 1 IE.

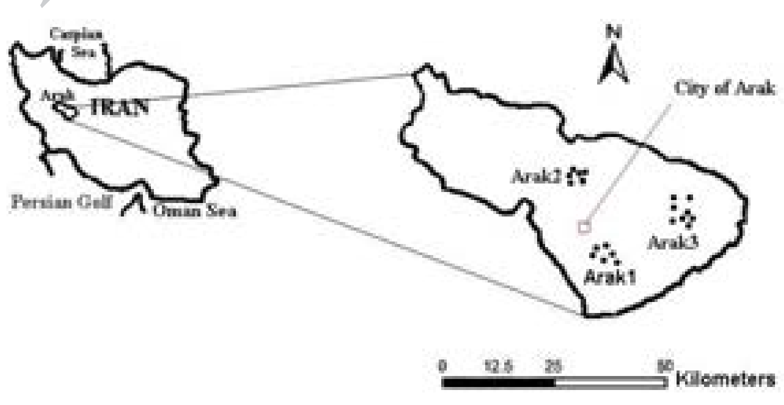

Figure1. Map of the study area, showing the locations of sampling points for surface soils.

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Soil Sampling and Analysis

The total number of soil samples was 22 (Arak 1 and Arak 2: six samples each, Arak 3: eight samples, and Ghotbe Sanati: two samples). The samples were collected in zip lock polythene bags. All samples were collected with a stainless steel spatula and kept in PVC packages. At each sampling point, five to nine sub-samples, with 20×20 cm surface, were taken and then mixed to obtain a bulk sample. Figure 1 shows the location of soil samples collection in the study area.

The samples were air-dried for several days at 25°C (room temperature) and sieved through a 2 mm sieve prior to analysis. Fractions smaller than 2 mm were grounded by a mortar and pestle to make fine powders (<149 µm). Soil pH was measured in water using a soil-to-water dispersion ratio of 1: 5. Soil samples (1 g) were digested with a mixture of HNO3 (7.5 mL), HClO4 (5 mL), and HF (2.5mL). The mineral residues were diluted with deionized water to 50 ml in a volumetric flask and stored in a fridge at 4°C before analysis [3]. The total contents of Cu and Zn in the digested solution were measured by flame atomic absorption spectrometry (FAAS).

To verify quality assurance and quality control (QA/QC), the precision and accuracy of all of the methods were determined by analyzing the two standard reference materials (1633b Coal Fly Ash and 2709 San Joaquin Soil) obtained from the National Institute of Standards and Technology (NIST). Recovery was between 94% and 108%. Each sample was analyzed in triplicates. The instrument's limit of detection for Cu and Zn were 0.025 and 0.5 mg/kg, respectively.

Statistical Analysis

Statistical analyses were conducted using Microsoft Excel 2007 and SPSS for windows version 18. The Kolmogorov-Smirnov test was used to check the normality of the data and the analysis of the experimental data was carried out using one-way ANOVA, Duncan's test, and Pearson's correlation matrix. One-way analyses of variance (ANOVA) were used to determine significant differences among the industrial estates. Then, Duncan's test was used to determine which of IEs were significantly different from others. Pearson's correlation coefficients were used in order to find the correlation between the metals and soil pH.

Ethical Considerations

Ethical issues were considered during data collection and throughout the study.

Contamination Factor (CF)

Contamination factor (CF) is one of the indices of pollution that was proposed by Hakanson [15]. This factor gives an indication of the level of contamination. CF is the ratio obtained by dividing the concentration of each metal in the soil by the baseline or background value (concentration in unpolluted soil). CF is used to classify the level of contamination of metals in the soil samples. It is calculated using the following formula:

$$CF=C_0/C_n$$

Where C_0 is the mean content of metals in at least five sampling areas, and Cn is the concentration of elements in the Earth's crust or reference value and baseline level. In this study, the continental crustal average is used as C_n [16, 17]. Hakanson [15] divided the contamination factor into four categories based on their intensities on a scale ranging from 1 to 6 (Table1).

RESULTS

PH and Heavy Metal Concentrations

The analytical results of the PH and heavy metal (Cu and Zn) concentrations (minimum, maximum, mean and standard deviation) for the 4 IEs are presented in Table 2. Soil PH values were in a narrow range from 6.15 to 9.02 with an average of 7.94, suggesting the neutral to weak alkaline quality of the tested soils. Accordingly, the metal mobility was lower in the slightly alkaline range (6.15- 9.02) (Table 2). The total metals concentrations in the soil samples were 15.69-49.55 mg/kg with mean value of 28.90 mg/kg for Cu and 23.02-144.17 mg/kg with mean value of 78.51 mg/kg for Zn in all IEs in the study area. The highest concentration of Zn was found in Arak 3 region (144.17 mg/kg). The highest concentration of Cu was observed in Arak 1 region (49.55 mg/kg). Table 3 depicts the correlation coefficient matrix, listing Pearson's product moment correlation coefficient. A significant correlation (P<0.01) was found

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between Zn and Cu (r=0.59) while a negative correlation was observed between green space area of IEs and heavy metals.

Contamination Factor of Copper and Zinc in the Soils

In this study, CF was calculated based on the ratio of the contamination in the industrial estates soils to the Earth's crust or mean worldwide values. The results of the quantification of metal contamination of the soil samples using contamination factors are shown in Table 6. Contamination factor of copper ranged between 0.28 and 0.90 with a mean factor of 0.52, considering the Earth's crust values. CF of Zn ranged from 0.32 to 2.05 with a mean factor of 1.12, considering the Earth's crust values. CF of Cu ranged from 1.12 to 3.53 with an average value of 2.06, considering values of mean worldwide. CF of Zn ranged from 0.37 to 2.32 with a mean of 1.26, considering values of mean worldwide.

Comparison between the Four Industrial Estates

Analysis of variance (one-way ANOVA) was used to compare the mean metal concentrations among the industrial estates (Table 4). As it can be seen, there was a statistically significant difference among the industrial estates. The results of Duncan's test showed that soil Cu and Zn contents of Arak1 industrial estate is significantly different from the other two estates (Table 5).

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Table 1. Classification of contamination factor values.

C_f	pollution
$C_f<1$	Low contamination factor indicating low contamination
$1\leq C_f<3$	Moderate contamination factor
$3\leq C_f<6$	Considerable contamination factor
$C_f\geq 6$	Very high contamination factor

Table 2. Summary statistics for heavy-metal concentration (mg/ kg) in topsoils.

	IE_1			IE_2			IE_3			IE_{GS}		IE_s		
	Min	**Max**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**	**Min**	**Max**	**Mean**
Zn	81.15	117.07	94.90	23.02	93.97	56.4633	51.79	144.1	82.75	74.86	82.11	23.02	144.17	78.51
Cu	30.56	49.55	37.82	18.89	29.35	24.14	15.69	31.05	24.18	27.97	42.57	15.69	49.55	28.90
pH	6.65	9.02	7.89	7.79	8.31	7.99	7.62	8.38	8.06	6.95	7.79	6.65	9.02	7.94

Table 3. Pearson correlation coefficients between heavy metal and pH concentrations in soil samples.

		Zn	Cu	pH
Metals	Zn	1		
	Cu	0.59**	1	
	pH	-0.08	0.27	1

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

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Table 4. One-way ANOVA of top-layer soil heavy metals contents in 3 industrial estates.

		Sum of Squares	df	Mean Square	F	Sig.
Zn	Between Groups	4673.402	2	2336.701	3.903	0.04
	Within Groups	10177.394	17	598.670		
	Total	14850.797	19			
Cu	Between Groups	783.366	2	391.683	11.444	.001
	Within Groups	581.844	17	34.226		
	Total	1365.210	19			

Table 5. Results of Duncan test for compare three IEs.

Is	IE_1	IE_2	IE_3
Zn	94.90^{a}	56.46^{b}	82.75^{ab}
Cu	37.82^{a}	24.14^{b}	24.18^{b}

a and b denote they have statistical significance at probability levels of <0.05;
a and a or b and b denote they have no statistical significance.

Table 6. Contamination Factors (C_f) using mean worldwide and the Earth's Crust values for heavy metals in soils from the study area.

Background Value	Industrial Estate	Zn			Cu		
		Min	Max	Mean	Min	Max	Mean
Earth Crust	IE_1	1.15	1.67	1.35	0.55	0.90	0.68
	IE_2	0.32	1.34	0.80	0.34	0.53	0.43
	IE_3	0.73	2.05	1.18	0.28	0.56	0.43
	IE_{GS}	1.06	1.17	1.15	0.50	0.77	0.63
	IE_s	0.32	2.05	1.12	0.28	0.90	0.52
Mean Worldwide	IE_1	1.30	1.88	1.53	2.18	3.53	2.70
	IE_2	0.37	1.51	0.91	1.34	2.09	1.72
	IE_3	0.83	2.32	1.33	1.12	2.21	1.72
	IE_{GS}	1.20	1.32	1.26	1.99	3.04	2.51
	IE_s	0.37	2.32	1.26	1.12	3.53	2.06

DISCUSSION

Concentrations of the metals were substantially higher than the background values (the Earth's crust and mean worldwide values), suggesting possible anthropogenic pollution. Copper concentrations of soil samples are mainly due to geogenic and anthropogenic activities. Natural concentration of Cu in soils depends primarily on the geochemistry of the parent material [18]. Copper which is a highly reactive metal is commonly used in a wide variety of process industries. This results in the presence of large quantities of this element in their discharge. The high concentration of copper may be associated with electrical and mechanical working. The other potential sources of copper pollution are metallurgical and metal finishing, corrosion inhibitors in cooling and boiler systems, drilling mud's catalysts, primer paints, fungicides, copper plating and pickling, corrosion of copper piping, copper releases from vehicle brake pads, architectural copper, vehicle fluid leaks and dumping, domestic water discharged to storm drains, etc [19]. The high content of Zn in soil may result from the atmospheric deposition from a factory which manufactured different zinc compounds. Zn and Cu may also originate from mechanical abrasion of vehicles, as they are used in the production of brass alloy itself and come from brake linings, oil leak sumps, and cylinder head gaskets [20]. Al-Khashman concluded that the high correlation between Cu and Zn represents the role of anthropogenic activities,

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such as traffic movement, furniture, aluminum, and steel industries, and tire wear, in Karak Industrial Estate, Jordan [4]. These main sources of heavy metals, such as Cu and Zn, in soils are also present in the IEs of Arak. The high correlations between soil metals may reflect the fact that these heavy metals had similar pollution level and similar pollution sources. It can also be concluded that the sources of Cu and Zn in the soils of IEs mainly originate from industrial activities and automotive emissions. Moreover, the levels of the metals in some of the examined samples and the small magnitude of correlation coefficients obtained from the correlation analysis between the metals and the soil properties indicate the anthropogenic rather than the lithogenic origin of these metals since lithogenic metals show higher correlation with soil properties [21, 22]. Nevertheless, this inconsistent pattern of heavy metals concentration is a common phenomenon observed in soils. Other studies reported the absence of consistent relationships between heavy metals concentrations and clay content, OM, carbonate content, PH, and EC [22, 23]. Considering these variations, it is difficult to discriminate sources of these metals precisely. A negative correlation was found between agreen space areas of IEs and heavy metals. IEs with less green area have higher levels of metals. This confirms the role of green space areas in reducing air and soil pollution.

The three studied IEs differed significantly in the concentration of heavy metals (Cu and Zn) in their soil. Mean concentration of metals (Zn and Cu) in soil was highest in the samples taken from the Arak 1 region. This may be due to the proximity of this industrial estate to Arak city (5 km). Copper (Cu), lead (Pb), cadmium (Cd), and zinc (Zn) are the principal metals of concern in environmental surveys because they are often the main metal constituents of air pollutants and have known toxicities to biota [14].

As revealed by Table 6, some of the sampling points had Cu and Zn contamination factors (CFs) higher than 1. This implies that these sites are polluted with Cu and Zn. The likely sources may be mainly anthropogenic activities, such as industrial activities. The comparison with the Earth's crust and mean worldwide values reveals some degree of heavy metals contamination. According to the contamination factor classification of Hakanson [15], the soils under study were considerably contaminated with Zn and Cu. The Earth's crust and mean worldwide values were used as background values in this study because regional geochemical background values for these elements were not available. To obtain more reliable results, the background value of this area must be determined.

CONCLUSIONS

This study focused on the application of CF in interpreting the degrees of Cu and Zn contamination and pollution of soils within the IEs environments. The results of this investigation show that soils in the IEs are contaminated with heavy metals at the levels exceedingly above the background (The Earth's crust and worldwide) concentrations. This may give rise to various health hazards. The results obtained from the CFs confirm that soils taken from four areas under study are contaminated. Based on the obtained data, the surface soil of the IEs is contaminated with some heavy metals (Zn and Cu), most probably due to industrial pollution and sewage effluent. On the other hand, it can be stated that the relationship between copper and zinc in the soils indicates that these metals emanate from the same source such as industrial activities. Hence, there should be provisions to measure toxic metals in industrial effluents before dumping them into soil or water. It is also important to check the discharging water of IEs after treatment to ensure that standard values are satisfied and these toxic pollutants are not released into the environment. Moreover, based on the findings of this study, metal pollution from IEs may be a threat to the inhabitants' health. It is recommended to policy makers to support possible remedial actions which will safeguard the environment and human health. Although Cu and Zn are micronutrients, their high concentrations in soils may be poisonous to micro-organisms, higher plants, and fauna. In general, plants tolerate soil concentrations between 2 and 40 mg/kg Cu (dry weight) and between 10 and 100 mg/kg Zn (dry weight) [24].

Using bioremediation techniques such as phytoremediation is recommended. It is concluded that the pollution with heavy metals

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of zinc and copper in IEs is moderately high. Studies with more samples are necessary for validating these results.

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