

Assessment of Accumulation and Human Health Risk of Trace Elements in the Vicinity of Industrial Estates, Central Iran

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Background & Aims of the Study: Regarding to development of industry, soil contamination has become a serious problem in many countries, such as Iran. The aim of the present work was the illustration of the accumulation of potentially harmful trace elements and the potential risk which is posed to human health in surface soils of three industrial estates of Aran-o-Bidgol city, Isfahan province of Iran.

Materials & Methods: Altogether, 24 composite soil samples were collected at depths 0-20 cm from industrial estates of Helal, Sobahi and Ansar located in Aran-o-Bidgol in September and October 2014. Element contents (Cd, Pb, Ni, Zn and Cu) were extracted by 3 acids digestion (HF-HNO₃-HClO₄). Concentrations of Cu, Pb, Zn and Ni in soil extracts were analyzed by Flame Atomic Absorption Spectrometry, whereas Cd was measured by Graphite Furnace Atomic Absorption Spectrometry. The accumulation and non-cancer risk of trace elements were investigated of these industrial states soils.

Results: The mean contents of Cd (0.81 mg/kg), Pb (13.41 mg/kg), Ni (30.14 mg/kg), Zn (53.85 mg/kg) and Cu (14.15 mg/kg) were higher than the uncontaminated background values. The average values of Pb, Ni, Zn and Cu at Ansar industrial site were higher than other industrial sites. Igeo for Cd, Pb, Ni, Zn and Cu were found in the range of 2-2.80, -2.26 - 3.33, 0.5-2.54, 0.47-2.49 and 0.44-4.01, respectively. The highest non-cancer risk was belonged to Pb (0.3 and 0.01) while the lowest was Zn (0.008 and 0.0002) for child and adult, respectively.

Conclusions: Pollution index indicated that industrial estate soils were 'moderately contaminated' or 'moderately to heavily contaminated' by Cd, Pb, Ni, Zn and Cu. The non-cancer risk levels of sampling sites were lower than the regulatory limits. Also, it can be concluded that, non-cancer risks for adults were lower than children.

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Background

Soil is a non-renewable dynamic natural resource that is essential to human life and serves as the most important sink for toxic ingredients like trace elements (1,2). There have been great concerns about the contamination of hazardous elements due to rapid industrialization and urbanization during the recent decades (3-6). Trace elements via urban soils can intake into the human body

through three ways, ingestion, inhalation and dermal absorption, accumulate in fatty tissues, and subsequently affect the nervous, endocrine and immune system; also, hematopoietic function and normal cellular metabolism (7,8). In evaluating anthropogenic contaminations, more attention should be paid to understanding the status, quantity and dispersion of the pollution in the ecosystem. There is the need for more detailed information about the accumulation and levels of human exposure to

trace elements for responsible development and to maintain human health (9-11).

Several studies have been carried out on trace elements contaminations in industrial soils of Iran (12-18). There have been very few studies about the exposure risk level and potential health effects due to trace elements, especially for industrial soils till now (9,17).

Aran-o-Bidgol city is an important industrial area in Isfahan Province of Iran that has become rapidly industrialized and urbanized in recent decades. There are lots of industrial activities, including petrochemical production, metal smelting and pressing, cotton and wool textile mills, the manufacture of chemicals, paints, plastics and trace element emissions from these activities threatens the environment and inhabitants' health in the area.

Aims of the study:

The objective of the present study was the contents estimation of trace elements in surface soils of the industrial estates of Aran-o-Bidgol city, to evaluate the enrichment degree of metals (Cu, Pb, Zn, Ni and Cd) by regional background values and the geo-accumulation index to assess non-carcinogenic health impacts on adults and children due to the ingestion, inhalation and dermal contact of these soils.

Materials & Methods

Research area

Aran-o-Bidgol city (50° 15' - 52° 29' E, 33° 30' - 34° 27' N) with an elevation of 912 m and area of 6,051 Km² is situated in northeast of Kashan city, Isfahan province of Iran. This area characterized by hot summers and cold windy winters. The wind direction predominantly was from northeast to southwest. The industrial estates of Helal, Sobahi and Ansar are located in the study area. This industrial zone in recent decades experienced rapid developments and cluster of industries.

Soil Sampling and Chemical Analysis

A total number of 24 surface soil (0-20 cm) samples were collected from the industrial

estates of Helal, Sobahi and Ansar located near the Aran-o-Bidgol. The longitudes and latitudes of each site were recorded, using GPS. At every sampling area, five subsamples in top soils were mixed together. Distribution of sampling points is shown in Figure 1. In the laboratory, soil samples were first air-dried at room temperature and then passed through a 2 mm plastic sieve to remove large size particles, plant leaves and other waste materials. These samples were sealed in zip lock polythene bags and stored at ambient laboratory conditions until analysis. Soil was digested with a 5:2:3 mixture of HNO₃-HClO₄-HF (19). In the final step, the acid digested extracts were diluted to 50 ml with ultrapure water in a volumetric flask and stored in a refrigerator at 4°C before the analysis. Total element contents of Cu, Pb, Zn and Ni were determined, using flame atomic absorption spectroscopy (FAAS, Shimadzu AA-670G, Japan). The Cd concentration was measured, using graphite furnace atomic absorption spectroscopy (GFAAS, Shimadzu AA-670G, Japan). Satisfactory analytical techniques were obtained for the Montana II Soil standard reference material (SRM 2711); (41.70 mg/kg for Cd, 114 mg/kg for Cu, 1162 mg/kg for Pb, 20.6 mg/kg for Ni and 350.4 mg/kg for Zn). Reagent blanks and analytical duplicates were also included with each batch of samples (20) and the recoveries for considered elements were approximately 81-98%.

Human Non-cancer Risk Evaluation

To characterize the potential non-cancer risks, the risk assessment model developed by US EPA was conducted (21-23). The average daily dose (ADD) received via various exposure pathways were calculated based on the equations (1)-(3)

$$ADD_{\text{ingestion}} = C_{\text{Soil}} \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (1)$$

$$ADD_{\text{inhalation}} = C_{\text{Soil}} \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (2)$$

$$ADD_{\text{dermal}} = C_{\text{soil}} \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (3)$$

Where ADD_{ing} , ADD_{inh} and ADD_{derm} are the daily intake of exposure to elements (mg/kg day) ingested, inhaled or absorbed through the skin, respectively. Other exposure factors and values of parameters for non-cancer risk are listed in Table 1.

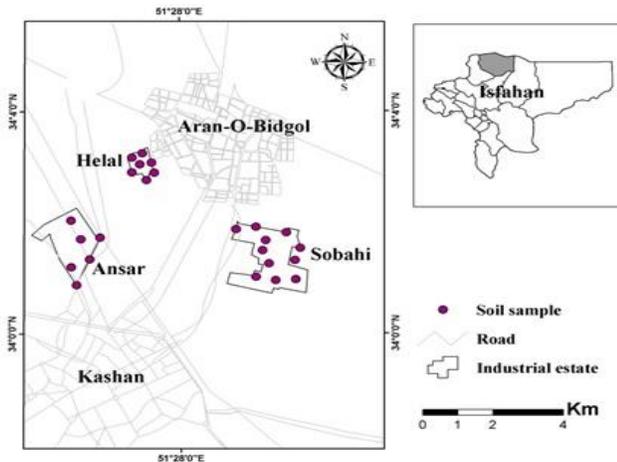


Figure 1) Situation of Aran-o-Bidgol city in Isfahan Province, industrial estates and distribution of sampling sites in soils of the study area

The reference dose (RfD) is a benchmark dose from each daily route for each trace element (mg/kg day). The hazard quotient (HQ) is the ratio of the daily exposure of element (ADD) to its corresponding reference dose (RfD).

Hazard Index (HI) defined by sum of the HQ value of each exposure pathway for each element. It was calculated according to equation (4) (21,22,24).

$$HI = \sum HQ_i = \sum \frac{ADD_i}{RfD_i} \quad (4)$$

There is significant concern for the adverse health effects if the HQ exceeds 1, whereas $HQ \leq 1$ indicates no adverse health effects (22,23). The total non-cancer risk (HI) is the combination of HQ via three exposure pathways for single element. If the level HI is less than one, the individual receptor is unlikely to experience non-cancer risks. If HI exceeds more than unity, it would be a chance for potential non-cancer effects (24).

Table 1) Input assumption parameters to derive the intake value and RfDs and SF for the risk assessment

Parameters	Unit	Value	
		Children	Adults
C_{soil}	mg/kg		
IngR	mg/day	200	100
InhR	m^3/day	7.63	12.8
EF	Day/year	350	350
ED	Year	6	24
BW	kg	15	55.9
AT	days	365 ED	365 ED
PEF	m^3/kg	1.36×10^9	1.36×10^9
SA	cm^2	1600	4350
AF	mg/cm day	0.2	0.7
ABS	Unitless	0.001	0.001
RfD _{ingestion}	mg/kg day	Cd (1E-03), Pb (3.5E-03), Ni(2E-02), Zn (3E-01), Cu(4E-02),	
RfD _{inhalation}	mg/kg day	Cd (1E-03), Pb (3.52E-03), Ni (2.06E-02), Zn (3E-01), Cu (4.02E-02)	
RfD _{dermal}	mg/kg day	Cd (1E-05), Pb (5.25E-04), Ni (5.40E-03), Zn (6E-02), Cu (1.2E-02)	

Evaluation of the Degree of Soil Contamination

Geo-accumulation index was used to assess the degree of elemental contamination in the soil samples, and calculated, using the following equation (5):

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5 B_n} \right] \quad (5)$$

Where C_n is the concentration of a given element "n" in the soil, B_n is the geochemical background value of a given element "n" (25) and the factor 1.5 is used to account the possible variations in the background values. The I_{geo} is applied to determine the influences made by human activities on soil contamination

levels. Muller, 1969 distinguished seven classes of trace elements pollution (26):

($I_{geo} \leq 0$) practically uncontaminated; ($0 < I_{geo} < 1$) uncontaminated to moderately contaminated; ($1 < I_{geo} < 2$) moderately contaminated; ($2 < I_{geo} < 3$) moderately to heavily contaminated; ($3 < I_{geo} < 4$) heavily contaminated; ($4 < I_{geo} < 5$) heavily to extremely contaminated, and ($5 \leq I_{geo}$) extremely contaminated (26). The background values in this study were estimated by samples from relatively pristine sites.

Results

Descriptive Statistics

Table 2) Descriptive statistics of element concentrations (mg/kg) and the *Igeo* of trace elements in surface soils from different industrial estates located around of Aran-o-Bidgol city

industrial estates	Measure	Cd	Pb	Ni	Zn	Cu	<i>Igeo</i> (Cd)	<i>Igeo</i> (Pb)	<i>Igeo</i> (Ni)	<i>Igeo</i> (Zn)	<i>Igeo</i> (Cu)
Helal (n=7)	Mean	0.70	12.35	23.43	52.03	14.43	2.21	1.15	1.31	1.28	2.49
	Max	0.80	27.90	36.50	66.35	22.30	2.41	2.53	2.09	1.65	3.35
	Min	0.60	5.65	13.60	37	3.18	2	0.23	0.67	0.80	0.54
	SD	0.09	7.79	10.89	9.22	7.11	0.19	0.82	0.67	0.26	1
	CV (%)	12.85	63.07	46.47	17.72	49.27	8.59	71.30	51.14	20.31	40.16
Sobahi (n=11)	Mean	0.86	10.96	25.14	44.94	8.77	2.51	1.09	1.36	0.95	1.56
	Max	1.05	15.05	47.95	115.53	20.45	2.80	1.64	2.48	2.45	3.23
	Min	0.65	5.45	12.15	29.40	2.95	2.11	0.18	0.50	0.47	0.43
	SD	0.12	3.71	13.65	25.30	7.20	0.21	0.57	0.75	0.59	1.17
	CV (%)	13.95	33.85	54.29	56.29	82.09	8.36	52.29	55.14	62.10	74.99
Ansar (n=6)	Mean	0.84	19.17	47.13	72.29	23.70	2.48	1.19	2.46	1.70	3.40
	Max	0.93	48.53	49.95	119.35	35.23	2.62	3.33	2.54	2.49	4.01
	Min	0.68	1	43.88	51	17.23	2.17	-2.26	2.35	1.27	2.98
	SD	0.08	17.58	2.27	26.58	6.78	0.16	2	0.07	0.47	0.38
	CV (%)	9.52	91.70	4.81	36.76	28.60	6.45	168.06	2.84	27.64	11.17
Total (n=24)	Mean	0.81	13.41	30.14	53.85	14.15	2.42	1.13	1.62	1.23	2.29
	Max	1.05	48.53	49.95	119.35	35.23	2.80	3.33	2.54	2.49	4.01
	Min	0.60	1	12.15	29.40	2.95	2	-2.26	0.50	0.47	0.44
	SD	0.12	10.04	14.63	24.12	9.13	0.23	1.09	0.78	0.56	1.21
	CV (%)	14.81	74.86	48.54	44.79	64.52	9.50	96.46	48.14	45.52	52.83

Non-cancer Hazard Evaluation

In this research, the contents of elements were employed to determine the probabilistic of non-cancer risk on human body via different routes (ingestion, inhalation and dermal absorption) of soil. In order to evaluate the risk, the average daily doses (ADDs), hazard quotients (HQs) and hazard index (HI) of the investigated elements were estimated for both receptor groups and the results are summarized in Table

Table 2 presents the statistical summary of total concentrations of the trace elements for industrial top soils. Results indicated that Cu, Pb, Zn, Ni and Cd (14.15, 13.41, 53.85, 30.14 and 0.81 mg/kg, respectively) have higher average compared with their soil background contents (2.17, 4.08, 21.11, 8.55 and 0.15 mg/kg, respectively). The Pb, Ni, Zn and Cu contents in the industrial state of Ansar were more than other industrial estates. The CV of trace elements in industrial soils decreased in the order Pb (74%) > Cu (64%) > Ni (48%) > Zn (44%) > Cd (14%).

3 and Figure 2. Among all studied elements, the mean daily dose of Zn via ingestion for each receptor group resulted in the highest ADD value when considering three exposure pathways in the industrial estates (Table 3). In all industrial estates, the HQ values from ingestion, inhalation, and dermal contact for all investigated elements were less than 1, in both receptor groups.

Table 3) The average daily intake (ADD) of elements and non-carcinogenic (hazard quotient from three exposure routes) for two population groups in different industrial estates located around of Aran-o-Bidgol city

Helal												
ADD _{ingestion}		ADD _{inhalation}		ADD _{dermal}		HQ _{ingestion}		HQ _{inhalation}		HQ _{dermal}		
Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	
Cd	3.1E-05	1.3E-06	2E-09	3.9E-07	6.2E-07	4E-08	3E-02	1E-03	2E-06	3E-04	6E-02	3E-03
Pb	6E-04	2.3E-05	3.6E-08	4E-09	1.1E-07	7E-07	19E-02	6E-03	1E-11	1.1E-12	2.1E-12	1.3E-11
Ni	1E-03	4.4E-05	6.8E-08	7.6E-09	2.1E-06	1.3E-06	6E-02	2E-03	3.2E-10	3.7E-11	3.9E-10	2.5E-10
Zn	2E-03	9.7E-05	1.5E-07	1.7E-08	4.7E-06	3E-06	9E-03	3E-04	5E-07	5.6E-08	7.7E-09	4.9E-09
Cu	8E-04	2.7E-05	5.1E-06	7.9E-06	1.3E-06	8.2E-07	2E-02	6E-04	1.3E-08	2E-08	1.1E-08	6.8E-09
Sobahi												
ADD _{ingestion}		ADD _{inhalation}		ADD _{dermal}		HQ _{ingestion}		HQ _{inhalation}		HQ _{dermal}		
Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	
Cd	4.8E-05	1.6E-06	2.5E-09	4.8E-07	7.7E-07	4.9E-08	4E-02	1E-03	2.5E-06	4E-04	7E-02	4E-03
Pb	6E-04	2E-05	3.2E-08	3.6E-09	9.7E-08	6.2E-07	17E-02	5E-03	9E-12	1E-12	1.9E-12	1.2E-11
Ni	1E-03	4.7E-05	7.2E-08	8.2E-09	2.2E-06	1.4E-06	6E-02	2E-03	3.5E-10	4E-11	4.1E-10	2.6E-10
Zn	2E-03	8.4E-05	1.3E-07	1.5E-08	4E-06	2.6E-06	8E-03	2E-04	4.3E-07	4.9E-08	6.7E-09	4.3E-09
Cu	4E-04	1.6E-05	3.1E-06	4.8E-06	7.8E-07	5E-07	1E-02	4E-04	7.7E-09	1.2E-08	6.5E-09	4.1E-09
Ansar												
ADD _{ingestion}		ADD _{inhalation}		ADD _{dermal}		HQ _{ingestion}		HQ _{inhalation}		HQ _{dermal}		
Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	
Cd	4.7E-05	1.6E-06	2.4E-09	4.6E-07	7.5E-07	4.8E-08	4E-02	1E-03	2.4E-06	4E-04	7E-02	4E-03
Pb	1E-03	3.6E-05	5.5E-08	6.2E-09	1.7E-07	1.1E-06	3E-01	1E-02	1.6E-11	1.8E-12	3.2E-12	2.1E-11
Ni	2E-03	8.8E-05	1.4E-07	1.5E-08	4.2E-06	2.7E-06	13E-02	4E-03	6.5E-10	7.4E-11	7.8E-10	5E-10
Zn	4E-03	1E-04	2.1E-07	2.3E-08	6.4E-06	4.1E-06	1E-02	4E-04	7E-07	7.8E-08	1.1E-08	6.8E-09
Cu	1E-03	4.4E-05	8.3E-06	1.3E-05	2.1E-06	1.3E-06	3E-02	1E-03	2.1E-08	3.2E-08	1.8E-08	1.2E-08

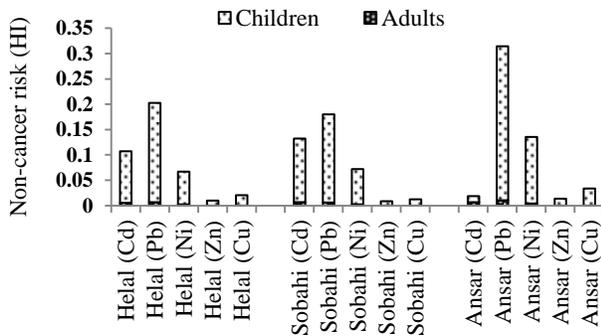


Figure 2) Total exposure hazard index (HI) from ingestion, inhalation and dermal contact for adults and children in different industrial estates located around of Aran-o-Bidgol city

As shown in Figure 2, we found that probabilistic non-cancer index values of Cd, Pb, Ni, Zn and Cu for both receptor groups were less than one. In the present study, the highest non-cancer risks were belonged to Pb (0.3 and 0.01) while the lowest were related to Zn (0.008 and 0.0002) for child and adult, respectively. Therefore, Pb caused the highest non-carcinogenic risk. Among three studied industrial estates, the hazardous index of Ni,

Cu, Zn and Pb belongs to the Ansar area which was the highest.

Evaluate the Pollution Intensity of Elements Using Geo-accumulation index

The basic information of Igeo corresponding to five trace elements measured in the industrial regions is summarized in Table 2. The Igeo ranged from 2 to 2.80 (mean 2.42) for Cd, -2.26 to 3.33 (mean 1.13) for Pb, 0.5 to 2.54 (mean 1.62) for Ni, 0.47 to 2.49 (mean 1.23) for Zn and 0.44 to 4.01 (mean 2.29) for Cu.

The percentage of class distribution of pollution assessment for soil trace elements with Igeo are illustrated in Figure 3. All soil samples in the Ansar industrial estate and the Sobahi industrial estate were moderately to heavily contaminate by Cd. The mean Igeo value for Cu in Ansar industrial estate was 3.40 and more than 66% of soil samples were heavily contaminated by Cu. The Igeo values of Ni indicated moderately to

heavily contamination in all Ansar soil samples (Figure 3).

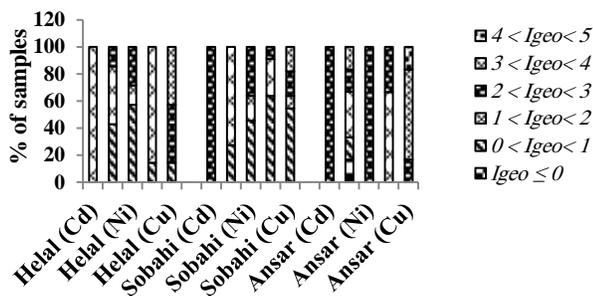


Figure 3) The results of geo-accumulation index classes of trace elements in topsoils of industrial estates located around of Aran-o-Bidgol city

Discussion

The corresponding relationships between coefficient of variation (CV) values of soil elements are given as follows: $CV \leq 20\%$ (low variability); $21\% < CV \leq 50\%$ (moderate variability); $50\% < CV \leq 100\%$ (high variability); and CV above 100% (exceptionally high variability) (17). The large CV for Pb and Cu indicated that the concentration of these elements was differed greatly with respect to different sites. The coefficient of variation (CV) values was moderate degree of variability for Ni and Zn, suggesting non-homogeneous distribution of these elements.

The mean of Cd concentrations found in our industrial samples (0.81 mg/kg) was lower than those reported elsewhere; for example, Solgi et al., 2012 (mean 1.26 mg/kg) and Parizanganeh et al., 2010 (mean value 3.46 mg/kg) (13,14). However, according to Hashemi et al., 2016, the mean Cd concentration in steel factory soils of the North of Iran was 0.71 mg/kg which is lower than the mean content in our industrial soil samples (27). Pb (mean 13.41 mg/kg) values in industrial soils were significantly lower than those in other industrial areas, such as Parizanganeh et al., 2010 (mean 128.50 mg/kg) and Naimi and Ayoubi, 2013 (mean 99.4 mg/kg) (13, 15). The current mean Ni concentration (30.14 mg/kg) in the industrial area of Aran-o-Bidgol was lower than those

recently reported for a number of industrial sites e.g. Naimi and Ayoubi, 2013; Solgi et al., 2012 (14, 15). Zn (mean 53.85 mg/kg) values were lower than the levels previously found in areas affected by most Iranian industries, such as Naimi and Ayoubi, 2013 (mean 101.1 mg/kg) and Nezhad et al., 2015 (mean 1716 mg/kg) (15, 17). Nonetheless, the concentration of Zn was higher than that reported by Ravankhah et al., 2017 (mean value 52.23 mg/kg) (28). In the present study, the mean Cu concentration (14.15 mg/kg) in our industrial samples was almost similar to Ravankhah et al. study, 2017 (mean 14.29 mg/kg) in brick kiln soils of Aran-o-Bidgol (28). The Cu concentration (14.15 mg/kg) was lower than the levels recently found in other industrial zones of Isfahan province (15) (21.1 mg/kg).

The exposure route that has the highest contribution to the non-cancer risk for each receptor group appears to be ingestion of trace elements except Cd (dermal contact). It indicated that non-dietary ingestion of soil was the most important exposure pathway; this has also been found in other studies (29-31).

By comparing the non-cancer index levels for children and adults, it can be concluded that children were more susceptible to the non-cancer effects of trace elements (Figure 2). Moreover, among the studied elements, Pb showed the highest HI value for both children and adults. These results were also reported by Rastegari Mehr et al., 2017 (25).

The average Igeo values decreased in the order of $Cd > Cu > Ni > Zn > Pb$. The mean Igeo obtained for Cd and Cu indicated moderately to heavily contamination, while Pb, Ni and Zn had moderate enrichment in soils of the studied area.

Conclusion

The results of the study showed the mean element concentrations in industrial estates soils surrounding the Aran-o-Bidgol industrial district were not high, but elements, especially

Cd and Cu, were enriched at some specific sites. Overall, in the industrial estates of Aran-o-Bidgol district, the soil trace elements exposure was below the threshold limit to the public. As results of this investigation, children have higher non-cancer levels than adults, which indicating children were more susceptible to the trace elements. In our study, Pb in soil samples had the priority concern as it had the highest hazardous index. Among the industrial regions, the industrial estate of Ansar suffered from the most serious trace element contamination. This is because the soil accumulation level in region dominated by different industries. Among these industries, iron and steel mills, textile industries, galvanizing industries, electric and electronics manufacturing, and cement plants are dominant. To protect the ecosystem of Aran-o-Bidgol industrial district, researchers and local government should take efficient control to those anthropogenic sources and characterize the related health risks associated with industrialization.

Footnotes

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Conflict of Interest:

The Authors have no conflict of interest.

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