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Environmental risk assessment and source apportionment of heavy metals in soils and natural plants surrounding a cement factory in NE Iran

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ABSTRACT

Introducing different heavy metals (HMs) into the environment through cement production has been recognized as a serious concern globally. The present study was carried out to assess the environmental risk of chromium (Cr), nickel (Ni), lead (Pb), and cadmium (Cd) pollution in the soil and plants surrounding the Shahrood Cement Factory, Northeast Iran. A total of 35 surface soil samples (0–10 cm) and 23 natural plant samples were collected. After preparation, the soil samples and plant tissues were analyzed for their total concentration of Cr, Ni, Pb, and Cd. In addition to normal statistical analyses, the inverse distance weighting (IDW) method was applied to prepare the thematic distribution maps. The results showed that the total Cr, Ni, Cd, and Pb soil concentrations ranged from 4.19 to 21.74, 2.11 to 41.20, 0.77 to 4.23, and 2.72 to 54.50, respectively. Comparing the soil content of the studied HMs with their national threshold values revealed that except for Cd in limited locations, other HMs were substantially lower than their permissible limits, indicating that the area was not polluted. The spatial distribution maps of selected HMs suggested an anthropogenic source for elevated Pb and Cd soil concentrations, whereas Cr and Ni soil concentrations were influenced by both natural and anthropogenic factors. Furthermore, the relatively high Pb concentrations in the plant tissues implied the role of car exhaust in introducing this pollutant into the environment. Even though the environmental risk of HMs in the studied area currently appears to be low, preventing the adverse impacts of cement production in this area requires further precautions.

1. Introduction

As the world's population grows, the resultant rapid urbanization and growing transport intensity accompanied by industrial and agricultural operations have led to environmental pollution that has become a global concern. Among the various parts of the environment, the soil is of specific importance because mankind relies on healthy soil directly or indirectly for its existence [16,17]. Even though it provides a unique medium for agricultural production, soil can also be considered as a filter for different pollutants, which mainly originate from anthropogenic activities [12]. Numerous environmental studies have indicated a considerable decline in soil quality following the accumulation of organic or inorganic pollutants in soil [3,4,5,7,8,11,13,21,24,25]. Accordingly, identifying the possible natural or anthropogenic sources of hazardous pollutants and their contribution in introducing the pollutants into the soil is of great substance. Considering the fact that cement factories have a relatively high potential for environmental pollution [3], they should be given special attention to prevent serious damage to the environment, especially in developing countries where the number of cement factories is currently increasing [19]. It has been reported that cement factories could be a potential source of different heavy metals (HMs), particularly some dangerous and carcinogenic ones like chromium (Cr), nickel

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(Ni), cadmium (Cd), and lead (Pb) [4,13,17,24]. Given the multiple known ways that heavy elements are transferred from polluted soils to the human food chain [12], monitoring soil contamination is crucial, especially the soil surrounding cement factories. There is no doubt that elevated concentrations of these naturally hazardous elements in different parts of the human body may result in nervous system diseases, severe respiratory distress, lung and skin cancers, and even death [25]. Depending on some important factors like the chemical composition of the raw materials used in cement factories or the regional or national environmental regulations, the dust produced by cement factories in various parts of the world may contain different amounts of heavy metals. These metals are deposited in the soil at varying intervals depending on the prevailing wind speed and direction, as well as particle size through cement dust and chimneys of factories [4,7,24]. It should be noted that soils naturally contain some heavy metals, and the contribution of industrial activities in the accumulation of toxic metals in the soil at relatively low rates may not necessarily lead to soil degradation [12]. In other words, in terms of soil pollution, industrial activities like cement production may be accomplished without threatening human health. On the other hand, the aerial uptake of some heavy metals by the aboveground parts of the plants grown in the vicinity of cement factories may necessitate special attention to control the entering of hazardous pollutants into the human food chain [5,13,21]. Cement is currently considered as the most common material for infrastructural growth and building thanks to its affordability and availability [17]. Considering the rising number of cement factories across Iran that meet not only the domestic needs but also the increasing export demands, environmental risk assessment of soil pollution in the land surrounding cement factories is of great importance. The Shahrood Cement Factory was established in 1984 in a non-residential area, 12 kilometers from the city of Shahrood. More than 500 people are directly involved in producing cement in this industrial complex, and its nominal capacity is about 6000 tons of cement per day. Most of the raw materials, comprising of marl and calcite, are extracted from the surrounding lands. Currently, little information is available about the environmental pollution risk of heavy metals associated with cement production in this area. The main objective of this study was to assess the environmental risk of heavy metals in the soil and endemic plants near the Shahrood Cement Factory by determining the spatial variations of Cr, Ni, Cd, and Pb with respect to the distance from the factory.

2. Materials and methods

The area under investigation is located between 54º 52ʹ and 54º 55ʹ E and 36º 28ʹ and 36º 30ʹ N at an altitude of 1570 meters above sea level (Figure 1). This area has a semiarid climate with an average annual temperature of 14.1 ºC and rainfall of more than 200 mm. The predominant wind direction is from the northwest to the southeast and, less commonly, to the east [8]. The lands directly adjacent to the cement factory mainly include bare lands covered with natural plants, whereas apricot and peach are being cultivated at further distances. Among the natural plants in the studied area, *Euphorbia macroclada* is the dominant species and considered as an indicator for assessing the HMs risk in the natural plant community.

Fig. 1. Geographical location of the study area along with its satellite image [9].

A total of 40 soil sampling locations were systematically distributed in the lands surrounding Shahrood Cement Factory, based on a regular grid sampling method of 250 * 250 meters. Among these locations, five samples were not taken as they were located inside the factory. Thus, 35 soil surface samples (0–10 cm) were collected. Besides, 23 plant samples were collected from the sampling locations that were covered with the mentioned plant species. The soil samples were air-dried, passed through a 2 mm sieve, and digested with a solution of $HCl\text{-}HNO_3$ [22]. Similarly, plant materials were washed well with distilled water and dried at 65 ºC for 48 hours. The powdered (passed through a 0.4 mm sieve) plant samples were subjected to digestion in a solution of 70 % aqua regia (HNO3 + concentrated HCl) and 30 % H_2O_2 [23]. The soil and plant digested solutions were analyzed for their total concentration of Cr, Ni, Cd, and Pb via atomic absorption spectroscopy AA-670. The data were statistically analyzed using the Statistical Package for the Social Sciences (SPSS), version 19.0. The Kolmogorov-Smirnov test was used to test the normal distribution of the data at the confidence level of 95%. A correlation analysis was applied to determine the relationships between the investigated HMs. The Inverse distance weighting (IDW) method was used to predict the values of the studied HMs in un-sampled locations. The spatial distribution maps were prepared using ArcGIS (version 10.3).

3. Results and discussion

3.1. Statistical analysis

Table 1 represents the descriptive statistics of the studied HMs concentrations in the soil samples. The selected metal concentrations in the studied soils were generally low. Examining the common statistical indices revealed a substantial change in the selected HMs content among the sampling locations so that the total soil concentrations of Cr, Ni, Cd and Pb varied between 4.19 and 21.74, 2.11 and 41.20, 0.77, and 4.23, 2.72 and 54.50 mg/kg, respectively (Table 1). The mean soil concentration of the selected elements decreased in the order of Ni > Pb > Cr > Cd.

Table 1. Selected heavy metals concentration in the studied soils (mg/kg).

Variable	Mean	Minimum	Maximum	Median	Standard deviation	Coefficient of variation; CV (%)	K-S *p*[a]
Cr	10.98	4.19	21.74	10.58	4.82	43.85	0.07
Ni	21.39	2.11	41.20	21.64	8.71	40.69	0.11
Cd	1.87	0.77	4.23	1.59	1.03	55.13	0.01*
Pb	18.06	2.72	54.50	14.87	12.78	70.74	0.00*

[a] K-S *p*: The significance level of Kolmogrov-Smirnov normality test and * means significant at $p < 0.05$.

The investigated elements experienced inconsistent levels of variability, indicated by the different CV percentages (Table 1). It is widely accepted that CV values of HMs that arise out of natural processes like rock weathering are relatively lower compared to those caused by anthropogenic activities [10]. Accordingly, it appears that in relation to the Cr and Ni concentrations in the soil, the higher CV percentages obtained for Cd, and more importantly Pb, may imply that these two pollutants are more impacted by the cement production in the studied area. In line with these findings, the results obtained from performing the Kolmogorov-Smirnov normality test were considered significant at a probability level of P=0.05 for Cd and Pb but insignificant for Cr and Ni (Table 1). Table 2 shows the mean values reported in the literature for soils located near cement factories around the world.

Table 2. Chemical composition of soils impacted by cement factories worldwide (mg/kg).

Pb	Cd	Ni	Cr	Country	Reference
18.06	1.78	21.39	10.98	Iran	This study
1.41	0.76	1.82	11.91	Nigeria	[17]
55.00	5.00	-	22.18	Jordan	[3]
32.19	-	-	119.00	Spain	[4]
19.32	-	29.09	76.44	Nigeria	[14]
56.27	-	139.07	115.77	Iran	[13]
19.80	1.70	5.90	-	Iraq	[1]
13.13	-	245.26	-	Ghana	[11]

According to the results presented in Table 2, the mean values of soil HMs concentration reported in previous researches are largely different, possibly due to the inexorable differences in some factors such as sampling depth and the distance of sampling locations from the pollution source. Investigating the spatial distribution of the Pb, Cr, and Ni concentration in the soil near a cement factory, Jafari et al. [11] reported that the concentration of the selected heavy metals in the topsoil was significantly higher than that of subsurface soil layers. Similarly, while performing a correlation analysis of soil metal concentrations with distance from the adjacent cement factory gate, Olatunde et al. [17] found some strong relationships for Cd (r = −0.65), Ni (r = −0.71), Pb (r = −0.0.86) and Zn (r = −0.63).

3.2. Spatial distribution of selected heavy metals

The spatial distribution of the total soil concentration of the selected HMs is presented in Figure 2. The spatial distribution of Cr and Ni concentrations in the soil were not strongly influenced by the cement factory, as their highest values were not found in the soils directly adjacent to the factory. This observation might be logically supported by the fact that the raw materials used in this industrial complex for producing cement are mainly extracted from the nearby lands. Consequently, it appears that in relation to the anthropogenic activities, natural factors more effectively control the distribution of these elements in the area under investigation. In line with these findings, it has been reported that the spatial distribution of Pb [21], Pb and Hg [4], Ni and Mn [24], and Cr [17] in the soil were poorly correlated with the distance from the adjacent cement factories.

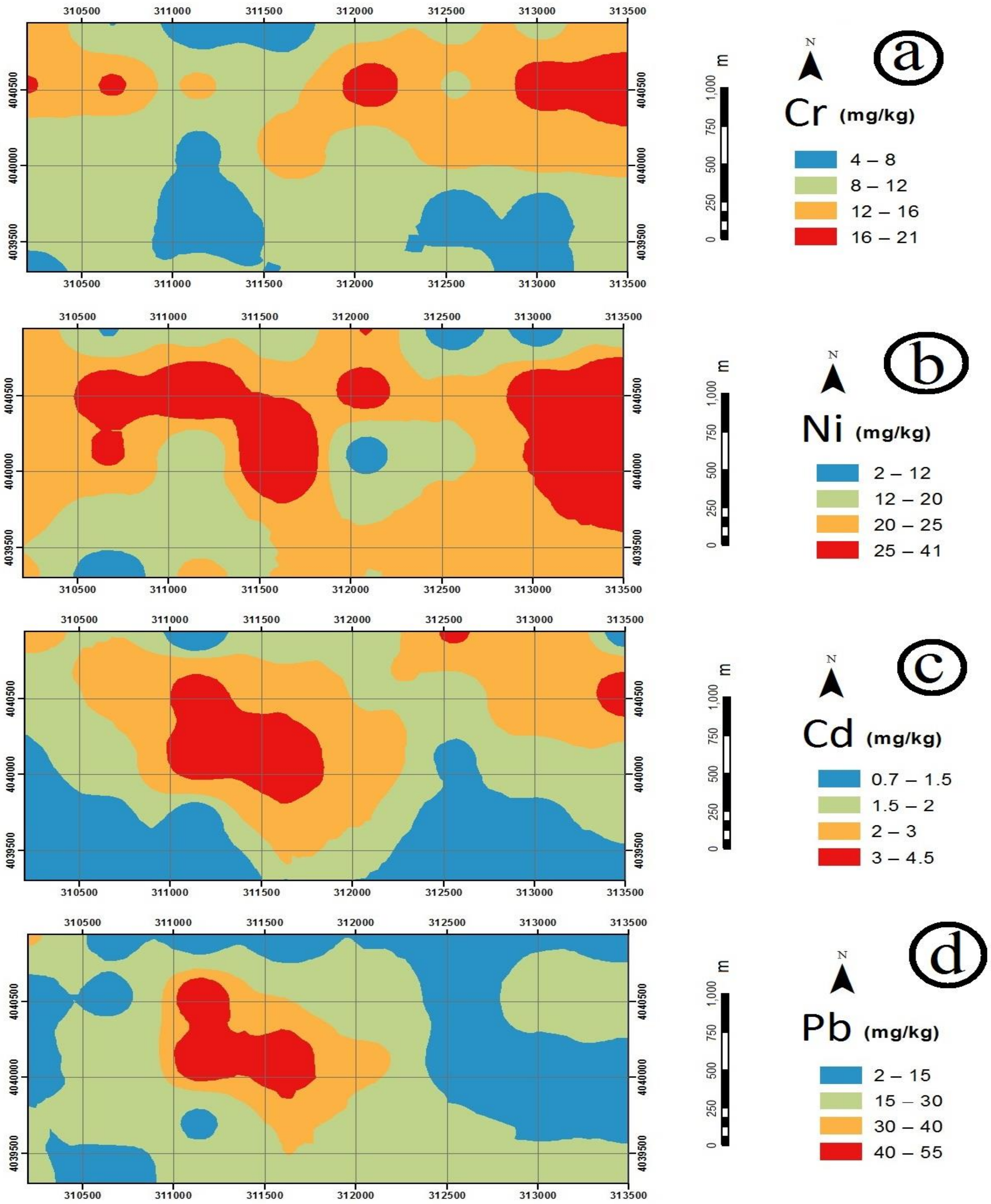

Fig. 2. Spatial distribution of soil Cr (a), Ni (b), Cd (c) and Pb (d) concentration (mg/kg) in the studied area.

As shown in Figure 2, the spatial distribution of the Cd and Pb soil concentration followed a similar pattern so that the highest soil Cd and Pb concentrations were found just across the factory gate, whereas their lowest contents were observed in the southern parts of the studied area. It may indicate that the prevalence of these two pollutants in this area is mainly caused by the Shahrood Cement Factory, in which cement production requires not only huge amounts of metal-containing raw materials but also burns a substantial amount of fossil fuels. In this regard, the spatial distribution of Zn, Cd and Cu [3], Cd [21], and Pb, Cr, Ni and Zn [11] in the adjacent soils correlated with the distance from the cement factories. Furthermore, since the studied area included the Sharood-Gorgan road, another anthropogenic activity, namely automobile exhaust, may partly contribute to introducing Pb and Cd into the nearby soils. In line with these results, Zhang et al. [25] reported that apart from the smelter dust as the dominant source governing soil Cd distribution in an area in China, car exhaust and agricultural fertilizers contributed equally in increasing Cd content in the investigated soils. Similarly, by mapping the spatial distribution of Pb, Zn, and Cr soil concentration in an area near a cement plant in Nigeria, Ogunkunle and Fatoba, [16] declared that cement production was the only source of Zn and Cr in the studied soils,; while Pb might have originated from both the cement factory and the vehicular activities.

3.3. Risk assessment of soil pollution with heavy metals

Since there is no known biological function for most of the HMs, cement production may impact the soil quality through the introduction of various HMs into the soil [3]. Nevertheless, the accumulation of specific HMs in the soil at relatively low rates may occur without any significant detrimental impact on the environment [12]. It is widely accepted that heavy metals affect environmental components when their concentration exceeds a certain threshold value [20]. Accordingly, in relation to the common statistical analyses, comparing the soil HMs concentration in any given area with their threshold values could provide more reliable information about the environmental risk associated with soil pollution. In the current study, the threshold values proposed by the Department of Environment of Iran [6], which are generally higher than other national or international permissible limits of heavy metals in soils, were considered as the criterion for the environmental risk assessment (Table 3). It is worth mentioning that these thresholds have been proposed considering the limited bioavailability of most of the heavy elements in naturally alkaline soils of the country.

Table 3. The proposed threshold values for selected heavy metals (mg/kg) [6].

Element	Cr	Ni	Cd	Pb
Threshold value (mg/kg)	64.0	50.0	3.9	300.0

A comparison of the numeric values obtained for the soil HMs concentration (Table 1) with their exclusive threshold values (Table 3) indicates that except for Cd, other pollutants may not threaten the soil quality in the studied area. Almost all of the area could be considered as unpolluted in terms of the investigated HMs except for a small part of the studied area, in which the soil Cd concentration exceeded the permissible limit. In similar research, Kolo et al. [13] reported that except for Cr, the HMs concentrations in the soil adjacent to a cement plant in Nigeria were lower than their background values provided in the Canadian soil quality guidelines. The concentrations of various HMs in the soil around a cement factory in Iran were found to be much higher than the USEPA standards [11]. Al-Husseini [2] reported that the concentration of Cd and Ni in the soil around a cement factory in Iraq was lower than their permissible limits.

3.4. Risk assessment of plant community pollution with heavy metals

Descriptive statistics of the studied HMs concentrations in the plant samples are presented in Table 4. The mean concentrations of the investigated HMs in the plant samples fall in the order of Pb > Ni > Cr > Cd, with the values of 26.29, 11.61, 4.08, and 0.29, respectively. It has been previously reported that simple relationships between the HMs contents in plants and their total concentrations in soils are rarely found in natural soil systems [18]. Comparing the studied HMs concentration in the soil (Table 1) and plants (Table 4) suggests that the concentration of most of the studied elements in the plant tissues is directly commensurate to their soil concentrations. Such similarity may indicate that considerable parts of the HMs contents in the plant were taken up from the underlying soil. As far as Pb is concerned, its average concentration in the plant tissues is substantially higher than its soil concentration, suggesting that other alternative sources like aerial uptake may contribute to introducing Pb into the plant's aboveground parts. In other words, high Pb concentration in the studied plants can be attributed to the release of Pb-containing particles produced by combustion of leaded gasoline through automobile exhaust. Nejadkoorki and Nicholson [15] declared that air quality is directly influenced by both spatial and temporal differences in industrial activity. However, the precise apportionment of HMs between different interchangeable sources definitely requires more in-depth investigation.

Table 4. Selected heavy metals concentration in the studied plant samples (mg/kg).

Variable	Mean	Minimum	Maximum	Median	Standard deviation	Coefficient of variation (%)	K-S p[a]
Cr	4.08	<DL[b]	9.25	4.50	2.70	66.17	0.00*
Ni	11.61	<DL	27.54	9.77	8.55	73.67	0.00*
Cd	0.29	<DL	2.40	<DL	0.62	213.98	0.00*
Pb	26.29	2.87	55.00	22.30	16.23	61.75	0.00*

[a] K-S p: The significance level of Kolmogrov-Smirnov normality test and * means significant at $p < 0.05$.

[b] lower than the detection limit of the atomic absorption spectroscopy

Given the key role of field crops in food security, some international organizations like the Food and Agriculture Organization of the United Nations (FAO) provide threshold values for most of the prevalent pollutants in these plants [20]. When it comes to natural plants, to the best of our knowledge, there are no widely accepted permissible limits for HMs concentration. Therefore, it cannot be judged for certain that the investigated plant species should be classified as polluted or unpolluted in terms of the studied HMs.

3.5. Correlation analysis

Pearson's correlation analysis was performed between the selected HMs (Table 5). The results presented in Table 5 clearly imply that the studied HMs are highly correlated so that except for the correlation coefficient between soil Pb and soil Cr concentrations, other correlation coefficients calculated for every couple of selected HMs were significant either at the 0.01 or 0.05 probability level. Such an observation may be ascribed to the fact that the selected HMs have a considerable chemical similarity to each other, which lead to these elements to be found concomitantly [12].

Table 5. Correlation coefficients between the selected heavy metals in the studied area.

Heavy metal	Cr	Ni	Cd	Pb
Cr	1	0.603**	0.523**	0.232
Ni		1	0.388*	0.359*
Cd			1	0.711**
Pb				1

* and ** represent significant correlation at the level of 0.01 and 0.05, respectively

Among the correlation coefficients calculated, the highest value was obtained when the Pb and Cd soil concentrations were compared. Confirming the results of the spatial distribution of these elements (Figure 2), it might imply that Cd and Pb mainly originated from the same sources in the studied area. In line with these findings, it has been reported that Pb, owing to its substantial chemical resemblance to Cd, may be simply substituted for this hazardous element in soil exchange sites [20]. In a similar research, the positive, significant correlation between Pb and Cu was indicative of a common source for both elements [16].

4. Conclusions

The metal concentrations in the studied soil were generally low, and the mean concentrations of the investigated HMs in the soil decreased in the order of Ni > Pb > Cr > Cd with the values of 21.29, 18.06, 10.98, and 1.78, respectively. Except for Cd in limited locations, the studied HMs did not exceed their national threshold values, suggesting that the area under investigation was not considered polluted. Examining the spatial distribution of the studied HMs with respect to the distance from the cement factory revealed that the Cr and Ni soil concentrations were influenced by a combination of natural factors and anthropogenic activities; whereas, the different activities concerning cement production in the studied area were recognized as the main factor governing soil Cd and Pb concentrations. The higher Pb concentrations in the plant tissues compared to the soil highlights the role of aerial uptake of Pb-containing, exhaust-induced particles by the aboveground plant parts.

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