

Investigation of heavy metals concentration in soil around a Pb-Zn mine and ecological risk assessment

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Abstract

Background: Soil pollution with heavy metals seriously threatens soil quality, food safety, and human health. This study was conducted to determine the soil pollution level and ecological risk assessment of different heavy metals in agricultural soils around Nakhlak Pb-Zn mine, located in Anarak district, Nain county of Isfahan province.

Methods: A total of 50 soil samples were collected from agricultural land around Nakhlak mine and analyzed to determine the concentrations of Pb, Cd, Zn, Ni, Cu, and Mn. The geo-accumulation index (I_{geo}), enrichment factor (EF), and potential ecological-risk index (Er) were used to assess the level of soil pollution with heavy metals.

Results: The mean concentrations of Pb, Cd, Zn, Ni, Cu, and Mn were 355, 2.72, 347, 26, 36, and 505 mg/kg, respectively, which were higher than the background values of world soils. Based on the I_{geo} index, the study area was moderately to heavily contaminated with Pb and Zn, uncontaminated to moderate contaminated with Cd and Cu, and uncontaminated with Mn and Ni. According to the EF values, the study soil was moderately contaminated with Mn, Ni, and Cu, significantly contaminated with Cd and Zn, and highly enriched with Pb. The RI values showed a moderate level of heavy metals contamination in the study soil.

Conclusion: According to the results, the ecological risk of heavy metals for ecosystem in agricultural lands around Nakhlak Pb-Zn mine is moderate. However, the contamination status should be considered periodically.

Keywords: Soil, Lead, Zinc, Risk assessment, Pollution

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Introduction

Environmental pollution is a serious problem in many parts of the world, especially in developing countries, such as Iran (1). The most important pollutants in the soil are heavy metals, acid rain, and some organic matters, such as mineral oil, petroleum products, pesticides, and sewage sludge (2). In recent years, environmental contamination with heavy metals has become big concern because of their toxicity properties (3). The decomposition of heavy metals in nature is not fast, and they can stay in the soluble form for a long time (4). Heavy metals enter human body via different sources such as food, drinking water, soil ingestion, and air (5). Some of heavy metals, such as Cu, Se, and Zn have effective impacts on human health. However, they are also harmful at high concentrations. Some other heavy metals, such as Pb, Co, Cd, As, and Cr are considered as harmful heavy metals (6). These metals have adverse effects on the normal function of human

body and may contribute to the development of different diseases, especially in children and pregnant women (7,8). In this regard, it has been reported that contact with heavy metals-contaminated soil and consumption of vegetables with high concentrations of heavy metals reduced human life expectancy by 9–10 years in Copsa Mica and Baia Mare, Romania (9).

Overall, the soil contamination with heavy metals occurs naturally or due to the anthropogenic activities, such as mining, smelting, and metal extraction from ore (10). Mining activities and ore processing creates some residuals, waste waters, and dust, that contaminate the surrounding environment. The results of many studies in different countries indicated higher concentrations of heavy metals in air, soil, water, and agricultural products of the mine-affected areas compared to those of the none mine-affected areas (11–14). Also, it has been reported that the number of people suffering from diseases, such



as cardiovascular, bladder, liver, kidney, nervous system, blood and bone diseases is very high in the mine-affected areas (15,16).

Anarak district is a representative area of mining activities (Nakhlak Pb-Zn mine) in Nain county, central part of Iran (Figure 1). Expansion of mining activities in this region can contaminate the soil. Therefore, the objectives of this study were to 1) determine the Pb, Cd, Zn, Cu, Ni, and Mn concentrations in the surface soils of agricultural lands around Nakhlak Pb-Zn mine, 2) assess the ecological risk of heavy metals in the study area, and 3) identify the soil pollution levels by these heavy metals in the study area. To our knowledge, this study is the first one that assessed the pollution and ecological risk of heavy metals in agricultural soil nearby a Pb-Zn mine in Nain county, central part of Iran.

Materials and Methods

Study area

Nakhlak mine (33° 33' 47" North, 53° 50' 42" East, 1440 m above sea level), located in 45 Km of Anarak district in Nain county, central part of Iran (Figure 1). A total of 50 surface soil samples (1 kg) were collected from the top layer (0–30 cm) of agricultural lands around the mine. At each site, three subsamples were collected to make a composite sample.

Evaluation of environmental risk

Index of geo-accumulation (I_{geo})

The geo-accumulation index (I_{geo}) was applied to estimate the pollution level of heavy metals, and determine the intensity of human activities on environmental pollution (17). This factor was determined using Eq. (1).

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (1)$$

where C_n is the measured concentration of each heavy metal and B_n is the local geochemical background value of heavy metals. The constant 1.5 is adopted because of natural fluctuation of baseline data (10,18). Due to the lack of geochemical background values for the study area, the background values of the world soils were used. According

to the I_{geo} values, soil pollution with heavy metals was classified into 7 groups as the following (18,19).

Uncontaminated ($I_{geo} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$), moderately contaminated ($1 < I_{geo} \leq 2$), moderately to heavily contaminated ($2 < I_{geo} \leq 3$), heavily contaminated ($3 < I_{geo} \leq 4$), heavily to extremely contaminated ($4 < I_{geo} \leq 5$), and extremely contaminated ($I_{geo} > 5$).

Enrichment factor

In environmental studies, especially when both of natural and human (external) factors affect the soil heavy metals content, enrichment factor (EF) can be used to determine the level of human activities on soil heavy metals concentration. This parameter is calculated using Eq. (2) (20,21).

$$EF = \frac{(C_n/C_{ref})_{sample}}{(B_n/B_{ref})_{crust}} \quad (2)$$

where C_n and C_{ref} are the concentrations of the considered heavy metal and the reference element in the sample, respectively, B_n and B_{ref} are the mean concentrations of the elemental component and the reference element in the crust, respectively (22). In this study, Fe was chosen as the reference due to its high concentration and stability in the crust.

EF is divided into five groups: minimal enrichment (< 2), moderate enrichment ($2 \leq EF < 5$), significant enrichment ($5 \leq EF < 20$), very high enrichment ($20 \leq EF < 40$), and extremely enrichment ($EF \geq 40$) (14).

Evaluation of potential ecological risk

The potential ecological risks of total heavy metals toxicity (RI) was calculated using Eq. (3) (23,24).

$$RI = \sum_{i=1}^n E_r^i \quad (3)$$

$$E_r^i = Tr^i \times \frac{Ci}{Cr}$$

where Tr is the toxic response factor for a special heavy metal, this factor was 30, 5, 1, 5, 5, and 1 for Cd, Cu, Mn, Ni, Pb, and Zn, respectively (25,26). Ci is the metal



Figure 1. Study area (Nakhlak mine) in Nain county.

concentration, C_r is the background value of heavy metal in soil, E_r is the individual potential ecological risk factor, RI is a composite index that indicates the potential ecological risk of total heavy metals in soils, and n is the total number of the estimated heavy metals (27-29). RI is generally classified in four groups: low risk ($RI \leq 150$), moderate risk ($150 < RI \leq 300$), considerable risk ($300 < RI \leq 600$), and high risk ($RI > 600$) (14,24).

Statistical analysis

The descriptive statistics of heavy metals concentration was calculated using SPSS statistical package version 22 (SPSS Inc., Chicago, IL, USA). The CV of each heavy metal was used to determine the degree of variability within the concentrations of a metal in soil samples according to Table 1 (4).

Chemical analysis

To determine the soil heavy metals concentration, the samples were digested by $\text{HF-HNO}_3\text{-HClO}_4$, and then, analyzed by an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500a, USA).

Results

The descriptive statistical analyses of the studied heavy metals are shown in Table 2. The estimated I_{geo} values are deciphered in Figure 2. The highest and the lowest mean of I_{geo} values were belonged to the Pb and Mn, respectively. The I_{geo} values for Mn (82%) and Ni (76%) in the study soils were smaller than zero. The Cu I_{geo} values in most samples were smaller than one. The Pb I_{geo} values with the mean of 2.56 ranged between 3.51 and 0.67. The mean values of I_{geo} for Zn and Cd were 2.1 and 0.8, respectively (Figure 2).

Table 1. The degree of variability within the concentrations of a metal in soil samples based on the CV percentage

CV	Degree of Variability
CV<20%	Low variability
21%<CV<50%	Moderate variability
50%<CV<100%	Moderate variability
CV>100%	High variability

Table 2. Descriptive statistics of the heavy metals concentrations (mg/kg) in agricultural soil around Nakhlak mine

Element	Minimum	Maximum	IEQS ^b	Mean	Median	CV	Background Value ^a
Pb	51.36	642.54	300	354.97	410.23	50	32
Cd	0.85	4.962	3	2.72	2.65	34	1
Zn	25.54	598.24	500	347.92	409.34	51	64
Mn	102.45	785.36	600	505.02	478.3	29	473
Ni	11.67	48.74	110	26.42	24.52	40	20
Cu	18.3	58.61	200	36.47	37.34	25	18.5

^a Background values of world soils (30).

^b Allowable contents of potential toxic elements for agricultural soils with pH>7 given according to the Iranian Environmental Quality Standard (IEQS) (31).

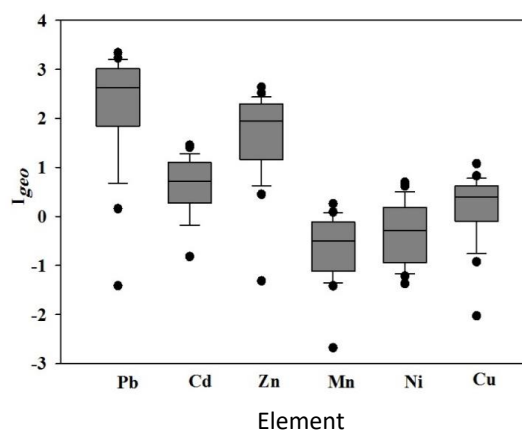


Figure 2. Boxplot of Geo-accumulation index (I_{geo}) for heavy metals studied in the agricultural soil samples around the Nakhlak mine.

The EF values of heavy metals are shown in Figure 3. The highest and the lowest EF belonged to Pb and Ni. The EF values of Zn in most soil samples were higher than five (Figure 3). The mean of EF values of Cd was 5.91. Other heavy metals showed minimal enrichments (Figure 3). The E_r values of the heavy metals studied are shown in Figure 4. The mean values of E_r for heavy metals followed the order of $\text{Cd} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Zn} > \text{Mn}$. The E_r values of Cd with the mean of 81.64 ranged between 39.6 and 120. The E_r values of Pb with the mean of 55.46 ranged between 85.16 and 10.05. The E_r values of Zn, Cu, Ni, and Mn were very low (Figure 4). The potential ecological risk index (RI) of total heavy metals in soils was 160, which shows the moderate ecological risk of heavy metals in the study area.

Discussion

The mean concentrations of heavy metals studied were higher than their background values (Table 2), but their concentrations, with the exception of Pb concentration, were lower than their corresponding values proposed by IEQS, which indicates that the mining activities have a considerable influence on the Pb concentration in the soil. Abouian Jahromi et al performed a qualitative mapping of surface soil contamination around Irankouh Pb-Zn mine in Isfahan and reported that the concentrations of Pb,

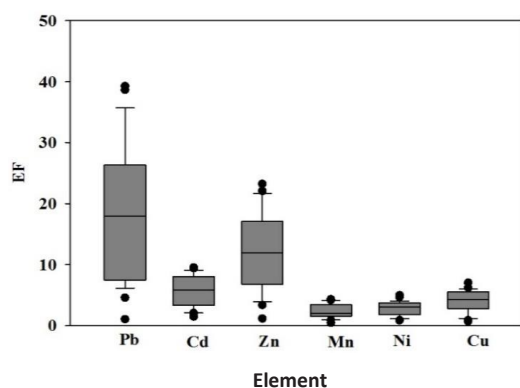


Figure 3. Boxplot of enrichment factor (EF) for heavy metals studied in the agricultural soil samples around the Nakhlak mine.

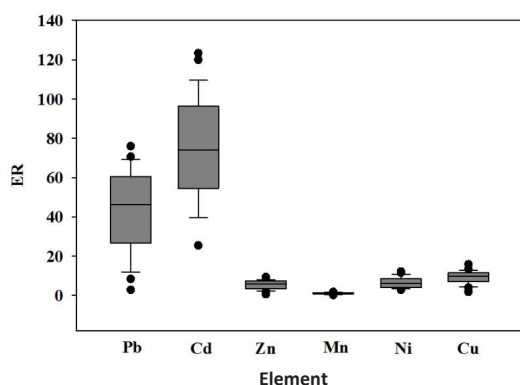


Figure 4. Boxplot of Er for heavy metals studied in the agricultural soil samples around Nakhlak mine.

Cd, and Zn in surface soils around Irankouh mine were significantly higher than those in the soils of the world. They mentioned that mining activity greatly influenced the concentration of these heavy metals in surface soils around Irankouh mine. On the other hand, they reported that the Cu concentration in the surface soils of the study area was lower than that in the world soils (32).

The CV of each heavy metal is an indicator to determine the degree of variability within the concentrations of a metal in soil samples. According to Tables 1 and 2, the CV for Cd, Mn, Ni, and Cu showed a moderate degree of variability, while the CV for Zn and Pb indicated a high degree of variability, suggesting the non-homogeneous distribution of Zn and Pb concentrations, which could be due to either mining activities and/or geological properties.

The I_{geo} values of heavy metals showed that the study soils are uncontaminated or slightly contaminated by Mn and Ni, as the I_{geo} mean values of Mn and Ni were negative (18,19). The I_{geo} mean value of Cu in soil samples was smaller than 1, which according to Ho et al. (18) and Bhuiyan et al (19), it is suggested that the agricultural soil around Nakhlak mine is uncontaminated to moderately contaminated by Cu. The I_{geo} values for Pb in about 25% of the soil samples were higher than 3 and in more than

50% of the samples were higher than 2.5. This indicates the heavily contamination of the study soils by Pb. Also, the mean of Zn I_{geo} value showed that the study soil is moderately to heavily contaminated with Zn (Figure 2). Overall, the results of heavy metals I_{geo} values in the soil samples suggest that the soil in this area is contaminated by the Pb and Zn derived from anthropogenic sources such as mining activities (33). On the other hand, the mean I_{geo} value of Cd (0.8) indicates that the soil is lowly to moderately contaminated with Cd. Soil contamination with Cd in this area could be due to the same geological properties of Zn and Cd. In this regard, Anju and Banerjee investigated the associations of Cd, Zn, and Pb in soils from a Pb and Zn mining area in Zawar, India, and reported that the Zn and Cd concentrations were closely correlated (34).

Ahmadi Doabi et al investigated the I_{geo} values of Ni, Cu, Zn, and Cr in agricultural soil of Kermanshah province and reported that the heavy metals contamination is considerable in Kermanshah. They also reported that Zn and Cu in the agricultural soils of the study area may be due to anthropogenic activities, but Ni and Cr are mainly affected by geological properties and partly influenced by anthropogenic activities (31). Abouian Jahromi et al evaluated the I_{geo} values of different heavy metals in surface soils around Irankouh Pb-Zn mine and reported that the surface soil around Irankouh mine is heavily to extremely contaminated with Cd and Zn ($4 < I_{geo} \leq 5$), extremely contaminated with Pb ($I_{geo} > 5$), and uncontaminated with Cu ($I_{geo} \leq 0$) (32).

The findings of EF were consistent with those of I_{geo} values. According to the results of this study and based on the Jia et al classification (14), about 45% of the soil samples were very high enriched with Pb ($EF > 20$), and the other samples were significantly enriched with Pb ($5 < EF \leq 20$). The EF values of Zn in 90% of the soil samples were higher than 5 (Figure 3), suggesting significant enrichment of Zn in these samples. The EF values of Cd in 55% of the samples were between 5 to 9, suggesting significant enrichment of Cd, and in other samples, they were between 2 to 5, indicating moderate enrichment with Cd. Other heavy metals studied showed minimal enrichments based on the Jia et al classification (14) (Figure 3). Similar to the findings of I_{geo} values, significant enrichments of Pb and Zn, as well as moderate enrichments of Cd, may be due to the influence of anthropogenic activities. Ahmadi Doabi et al reported low to moderate contamination of Zn, Cu, and Cr, and high enrichment of Ni by anthropogenic inputs, indicating serious pollutions of soil by Ni in agricultural soils of Kermanshah province, west of Iran. However, the agricultural soil in Kermanshah is lowly or moderately contaminated by Zn, Cu, and Cr (31).

According to the Er values and based on the studies by Jia et al (14) and Hu et al (24), the Cd concentration in 10, 40, and 50% of the soil samples showed low ($Er < 40$), moderate ($40 < Er < 80$), and considerable ($Er > 80$) potential

ecological risk, respectively. Also, the Pb concentration in 73% of the samples showed moderate potential ecological risk ($40 < ER < 80$), and its concentration in the remaining samples, showed low potential ecological risk ($ER < 40$). Zn, Cu, Ni, and Mn had low potential ecological risk, suggesting that these heavy metals do not have adverse effects on the ecosystem (31,35). The RI values in about 74% of the samples were higher than 150 (Figure 4), suggesting the moderate ecological risk of heavy metals for ecosystem in agricultural lands around Nakhlak Pb-Zn mine ($150 < RI < 300$).

It has also been reported that the ecological risk of heavy metals was very high around Irankouh Pb-Zn mine, however, this index was moderate in Abnil village close to the Irankouh mine (32).

In general, the geo-accumulation index and EF values are used to determine the effect of anthropogenic sources on heavy metals accumulation, but the Er and RI values are used to estimate the potential risk of heavy metals for ecosystem (36). Therefore, despite the high anthropogenic sources of Zn in the study area, it is not still at health-threatening levels. In contrast, Pb and Cd with high and moderate effects of anthropogenic sources on their accumulation, seriously threaten human health and ecosystem quality.

Conclusion

According to the results, the concentrations of heavy metals studied in the soil samples were higher than the world background values. The EF values indicated a very high enrichment for Pb, significant enrichment for Zn and Cd, and moderate enrichment for the other heavy metals. Based on the I_{geo} values, the study area was moderately to heavily contaminated with Pb and Zn, uncontaminated to moderate contaminated with Cd and Cu, and uncontaminated with Mn and Ni. According to the EF values, the study soil was moderately contaminated with Mn, Ni, and Cu, significantly contaminated with Cd and Zn, and highly enriched with Pb. According to the Er values, Cd and Pb in the study samples have moderate and considerable potential risk for ecosystem. The evaluated RI value showed moderate ecological risk of heavy metals for ecosystem in agricultural lands around Nakhlak Pb-Zn mine.

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Ethical issues

The author hereby certify that all data collected during the research are as expressed in the manuscript, and no data from the study has been or will be published elsewhere separately.

Competing interests

The authors have declared that they have no conflict of interests.

Authors' contributions

All authors contributed in data collection, analysis, and interpretation. All authors reviewed, refined, and approved the manuscript.

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