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Heavy metal concentration of soils affected by Zn-smelter activities in the Qeshm Island, Iran

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Abstract

In this study, concentrations of heavy metals in soils around a Zn-smelter in Qeshm island, Iran, are investigated. Calculated geoaccumulation index (Igeo), contamination factor (Cf), and contamination degree (Cdeg) values indicate surface soil contamination by toxic metals (As, Cd, Pb, and Zn). The results also indicate that most contaminated areas are located in the vicinity of the smelter and waste pile. However, concentrations of soil metals decrease with increasing distance from the pollution sources. Results from a potential ecological risk assessment indicate high risk in areas around the smelter. Statistical analysis also confirms the role of the Zn-smelter in soil contamination in the study area.

Keywords: Zn-smelter; Environmental effects; Heavy metals; Soil pollution; Potential ecological risk

Introduction

There are many different sources of heavy metal contaminants, including mining and metallurgical industries [1]. In addition to vegetation destruction and erosion of cultivated land caused directly by mining and smelting activity, the release of heavy metals is a serious threat to the environment [2; 3; 4]. Heavy metals are known to have adverse effects on human health, mostly because of their persistence and toxicity [1].

Since the industrial revolution smelters have polluted their surroundings by heavy metal dust emissions. Although; dust inhalation is primarily dangerous for human health, heavy metal dust also concentrates in soils and may become a secondary environmental danger in two respects: (1) contamination of crops and vegetables, when soils are used for agriculture; and (2) contamination of groundwater by metal migration [5].

Lead/Zn smelting is a major source of contaminant metals to the environment, and has resulted in soil pollution, with adverse ecological impacts [6]. Furthermore, non-ferrous metal production is the largest source of atmospheric As, Cd, Cu, In and Zn [7].

The concentrations of metals in the surface soil and size of the contaminated area; distance from the smelter plant, and the period of soil exposure to heavy metals contamination, as well as concentration, depend on numerous factors, such as: the concentration, size distribution, rate and duration of emission of airborne particles from the smelter chimney stack, the stack height, atmospheric stability, wind speed and direction, and terrain configuration [8].

Qeshm Island with a surface area of 1504 square kilometers is the largest island in the Persian Gulf, located between N 26° 32′ to 27° 00′ , E 55° 16′ to 56° 17′ . The Island is located just a few kilometers south of

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the mainland of Iran, near the provincial city of Bandar Abbas. Elevation of the island varies between zero to 380 m above sea level. The climate is warm and average annual temperature is 26˚C, and average annual precipitation is 153 mm. The dominant wind directions is from NE to SW and N to S with a speed range of 3.5 to 5 m/s in autumn and 5.5 to 8 m/s in winter [9].

A Zn smelting and reclamation plant on Qeshm is located 45 km from Qeshm city and 25 km from Bandar Abbas (N 26˚ 53′ , E 55˚ 52′) , between Dargahan and Laft. The smelter is 10 km from the village of Laft, at an elevation of 8.84 m above sea level. The smelting plant started operation in 1998 and is now an important Zn producer in Iran. Annual production is 20,000 tons of zinc ingots.

The objectives of the present work are: 1. to assess the extent of soil heavy metal pollution in the vicinity of the smelter; 2. to assess the ecological risk of heavy metals in soil by using an ecological risk index.

Materials and Methods

Sampling was carried out from May to June 2011. Soil surface samples (0 to 5 cm depth) were collected around the smelter [Figure 1]. To study the effect of atmospheric emissions on soil pollution, most samples were taken in the prevailing wind direction. Surface samples were collected from various distances from the smelter, and every sample consisted of 4-5 subsamples within an area of 1 m². A control sample was also collected, approximately 20 km from the smelter, to determine the influence of dust deposition on soil heavy metal accumulation.

The soil samples were air dried at room temperature, passed through a 2-mm sieve, and ground in an agate mortar and pestle. The < 2 mm fraction; was analyzed

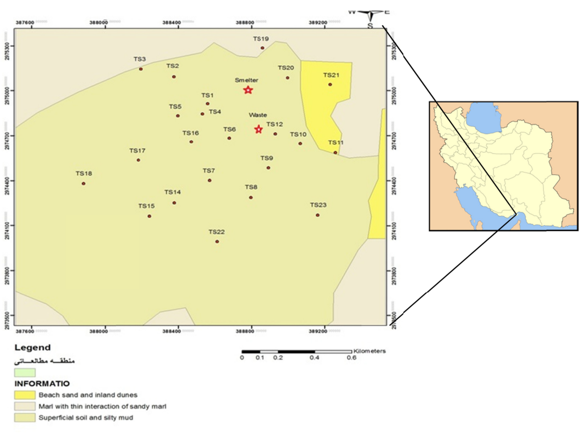

Figure1. Location of the study area showing sampling point location

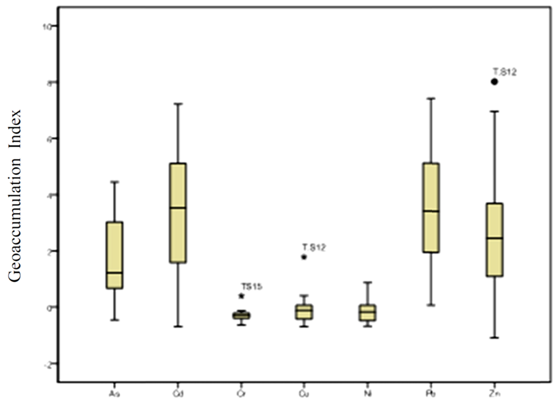

Figure 2. Box-plot of Igeo for topsoil samples

by hydrometric methods to determine soil texture. Soil pH was determined in a 1:2.5 (W:V) soil : deionized water suspension that was stirred for 15 min. The total organic carbon in soil samples was determined by the Walkley and Black method (Mc-Cleod 1975). Ground soil samples were analyzed using the ICP-MS method for metals (As, Cd, Cu, Ni, Pb and Zn) and ICP-OES for Cr and major cations (Fe, Al and Mg). The analyses were carried out in an accredited Australian laboratory (Amdel limited labs ISO 9001). Replicate samples were analyzed to assure precision.

The extent of soil contamination was expressed as the; geoaccumulation index (Igeo) [10], contamination factor (Cf), degree of contamination (Cdeg) [11; 12; 13], and potential ecological risk index (RI) [6; 11; 14; 15; 16]. These indices were calculated using the following equations:

$$Igeo = \log 2 \, (Cn / 1.5Bn)$$

where Cn is the concentration of element in soil samples, and Bn is the geochemical background value in the crust, 1.5 is the background matrix correction factor due to lithologic effects. In this study, metal concentrations in the control sample were used as background. The results of the Igeo values are shown in Figure 2.

$$Cf = Cni / Cno$$

where Cni and Cno, refer to mean concentration of each metal in soil and the pre-industrial soil, respectively. In the present study, Cno was assumed to be metal concentration in the control sample.

The sum of contamination factors for all elements examined represents the contamination degree (Cdeg) of the environment:

Table 1. Concentrations of trace elements in soil samples, sandy soils and global range in non-polluted soils

	Max	Min	Mean	Median	Sandy soil	World range	Control point
As	204	6.8	50.21	21.6	4.4	1-15	6.2
Cd	223	0.92	40.45	17.4	0.37	0.07-1.1	0.99
Cr	141	69	89.09	88	47	5-120	72
Cu	71.6	12.9	21.04	19.1	13	6-60	13.9
Ni	161	55	82.82	78	13	1-200	59
Pb	1620	9.9	254.98	101.85	22	10-70	6.3
Zn	34600	62.8	3312.95	735.5	45	17-125	89
OC%	0.74	0.09	0.37	0.38			0.76
pH	8.21	6.58	7.61	7.70			7.78

Table 2. Contamination factor and Contamination degree of soil samples

	As	Cd	Pb	Zn	Cr,Cu,Ni	C_{deg}	Decription of C_{deg}
TS1	9.0	28.9	37.8	22.1	1.5	102.4	Very high
TS2	3.1	4.8	8.5	4.5	1.1	24.2	Considerable
TS3	2.9	4	8.8	3.4	1	22.2	Considerable
TS4	17.1	51.5	70.6	44.4	1.5	188.1	Very high
TS5	3.5	13.1	14.1	8.1	0.9	41.6	Very high
TS6	21.3	138.4	96.5	58.5	1.5	3192	Very high
TS7	5.2	29	22.2	11.8	1.3	72.1	Very high
TS8	2.1	3.4	3.4	1.8	1.3	14.7	Moderate
TS9	2.6	7.5	5.8	3.2	1.2	22.7	Considerable
TS10	12.9	54.4	52	8.5	1.4	131.9	Very high
TS11	2.4	31.6	8.5	5.3	1.3	51.8	Very high
TS12	21.8	225.2	149.2	38.9	3	444.3	Very high
TS14	1.8	5.3	18.2	2.5	1.2	31.3	Considerable
TS15	3.5	14	12.3	8.4	1.7	43.4	Very high
TS16	9.1	34.7	32.8	17.3	1.4	98.1	Very high
TS17	2.4	4.5	5.1	3.7	1.1	19.1	Considerable
TS18	1.5	2.2	2.4	1.3	0.9	10.6	Moderate
TS19	7.7	21.1	28.4	17.7	1.3	79	Very high
TS20	32.9	158.6	257.1	18.6	2	473.1	Very high
TS21	12.3	63.9	52.1	19.3	1.4	151.7	Very high
TS22	1.9	1.7	2.7	0.9	1.1	10.7	Moderate
TS23	1.1	0.9	1.6	0.7	1.1	7.5	Low

$$Cdeg = \sum Cf$$

Table 2 shows results and classification of contamination factor and contamination degree.

$$RI = \sum Ei = \sum Ti \times Cf$$

Where RI is the potential ecological risk index for the study area; Ei is the potential ecological risk factor for a given pollutant (i); Ti is the ‘‘toxic-response’’ factor for a given pollutant as calculated by Hakanson(1980), i.e., Cd = 30, As = 10, Cu = Ni = Pb = 5, Cr = 2, Zn = 1; Cf is the contamination factor for a given substances.

Statistical analysis

The descriptive statistical parameters were calculated with SPSS software version 17. For application of the One-Sample Kolmogorov-Smirnov Test, the data distribution was abnormal, so the correlations between heavy metals were assessed by Spearman correlation analysis. Factor analysis was performed by evaluating the principal components and computing the eigenvectors to determine the common pollution sources. The rotation of principal components was carried out by the Varimax method.

Results and Discussion

Metal concentration in soil samples

Table 1 shows minimum, maximum, median, mean and range of total concentrations of trace elements in soil samples together with the mean concentrations in surface sandy soils [17]. The global ranges in non-polluted soils [17] are also represented together with some soil physicochemical properties.

Fluxes of elements depend greatly on the physical and chemical properties of soils. Indeed the pH and Eh of the soil solution can modify metal mobility [5]. Relatively high pH and organic matter content as well as higher clay fractions limit metal mobilization [18]. According to Table 1, soil pH varies in range of neutral to alkaline, so mobility of heavy metals was expected to be limited.

However, the concentrations of As, Cd, Pb and Zn in soil samples exceed both the elemental concentrations for sandy soils, and the global range concentrations. Table 1 also indicates that the concentrations of heavy metals in the surface soil of the smelting region were substantially higher than those in reference site.

The geoaccumulation indices of As, Cd, Cr, Cu, Ni, Pb and Zn around the smelter [Fig.2] indicate heavy contamination with Cd, Pb and Zn; and moderate contamination with As; and no contamination with Cr, Cu and Ni.

Table 2 illustrates calculated contamination factor (Cf) and contamination degree (Cdeg) for measured heavy metals in soil samples.

According to Table 2 contamination factors are moderate to very high for As, Cd, Pb and Zn, and moderate for Cr, Cu, Ni. In general, the contamination factors of heavy metals in the present study are ordered as follows:

Cd > Pb > Zn > As > Cu > Ni > Cr

According to contamination degree by individual metals, soil samples show moderate to very high overall contamination.

Table 3 lists the ecological impacts of elemental contamination to the soil.

To represent spatial variation of Ei classes a series of maps were produced for each element using ArcGIS software version 9.3. Figure 3 shows clearly that the highest risk factor (Ei) levels belong to those stations close to the smelter and especially the waste pile (TS12 and TS20). Contaminant concentration decreases with distance from the smelter, particularly in the upwind direction. According to calculated risk factor (Ei) values, the degree of risk for each heavy metal is as follows:

Table 3. The result of potential ecological risk assessment for the surface soil

	E_i(As)	E_i(Cd)	E_i(Cr)	E_i(Cu)	E_i(Ni)	E_i(Pb)	E_i(Zn)	RI	Description of ecological risk
TS1	90.3	866.7	2.5	8.7	7.8	188.9	22.1	1187	Very high
TS2	31.1	144.5	2.6	5.1	4.7	42.3	4.5	234.8	Moderate
TS3	28.7	120.3	2.0	6.2	4.7	43.9	3.4	209.2	Moderate
TS4	170.9	1545.4	2.5	8	8.2	353.2	44.4	2132.8	Very high
TS5	34.7	393.9	1.9	4.6	4.6	70.4	8.1	518.4	Considerable
TS6	212.9	4151.5	2.4	7.1	9.3	482.5	58.5	4924.4	Very high
TS7	52.2	869.7	2.3	6.9	6.8	111.1	11.8	1060.8	Very high
TS8	21.4	102.4	2.6	7.1	6.3	16.9	1.8	158.7	Moderate
TS9	26.3	224.2	2.3	6.8	5.7	28.9	3.2	297.5	Moderate
TS10	129	1633.3	2.2	7.8	6.9	260.3	8.5	2048	Very high
TS11	23.9	948.5	2.6	6.3	6.7	42.8	5.3	1036.1	Very high
TS12	217.7	6757.6	2.7	25.7	13.6	746	38.9	7802.3	Very high
TS14	17.9	158.8	2.4	5.6	5.8	91.3	2.5	284.3	Moderate
TS15	35	421.2	3.9	7.8	8	61.7	8.4	546	Considerable
TS16	90.8	1042.4	2.4	7.4	7.5	164.3	17.3	1332	Very high
TS17	23.9	134.5	2.5	5.5	5.3	25.6	3.7	201.1	Moderate
TS18	15.3	67.3	2.1	4.9	4.7	12.2	1.3	108	Low
TS19	77.6	633.3	2.7	6.5	6.5	142	17.7	886.5	Very high
TS20	329	4757.6	2.7	9.9	12.6	1285.7	18.6	6416.2	Very high
TS21	122.7	1918.1	2.4	6.9	7.6	260.3	19.3	2337.5	Very high
TS22	19.2	51.8	2.3	6	5.3	13.5	0.9	99.1	Low
TS23	10.9	27.9	2.3	5.1	5.4	7.8	0.7	60.3	Low
C point	10	30	2	5	5	5	1	58	Low

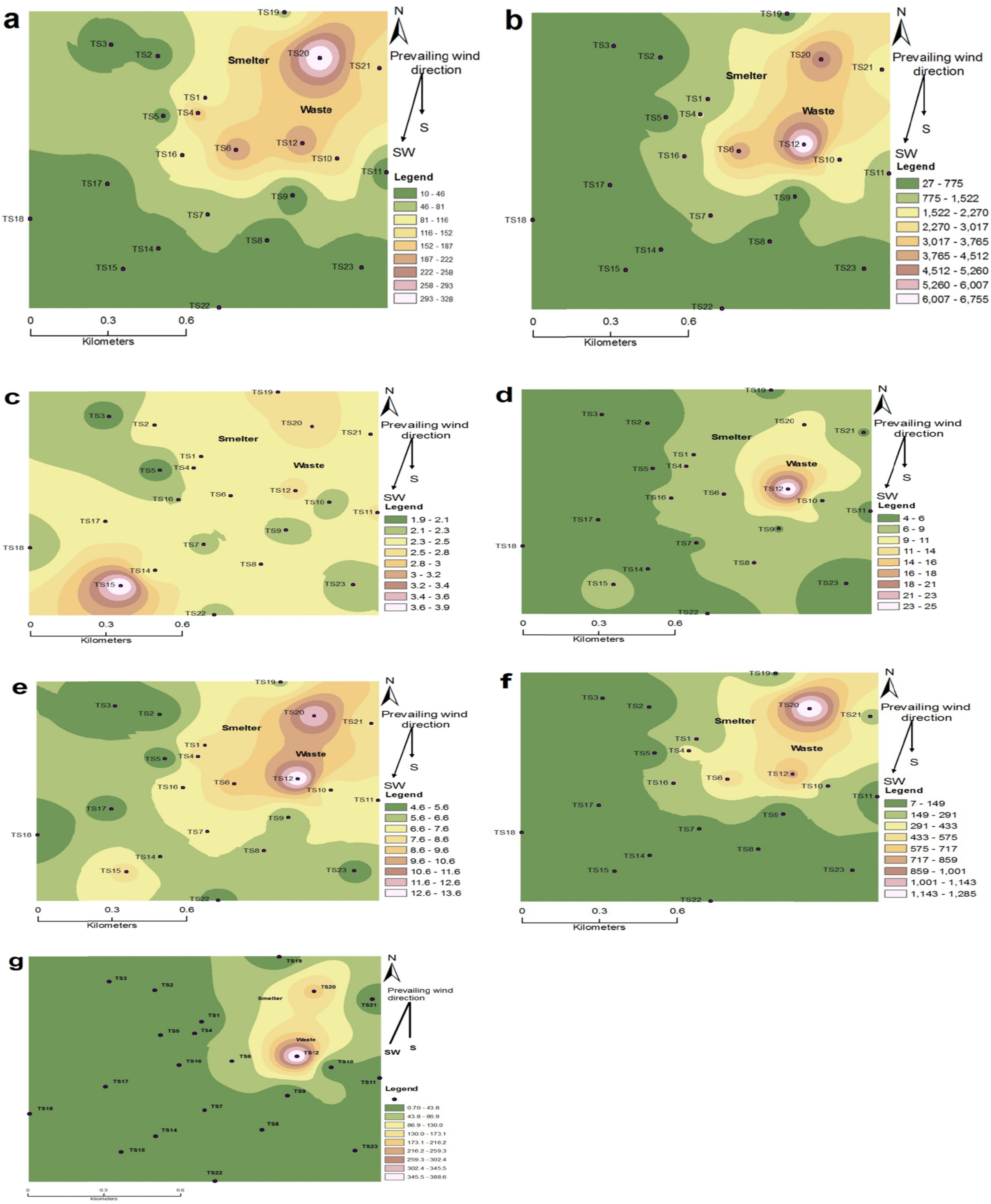

Figure 3. Spatial variation of E_i classes for measured elements. **a** As; **b** Cd; **c** Cr; **d** Cu; **e** Ni; **f** Pb; **g** Zn

Cd = very high ecological risk; As = considerable to high potential ecological risk in areas around the smelting plant; Cr, Ni and Cu = low potential ecological risk; Pb = considerable to very high potential ecological risk; and Zn = low to moderate potential ecological risk.

The contribution of different elements to the potential ecological risk index (RI) decrease in the following order:

Cd >> Pb > As > Zn > Cu > Ni > Cr.

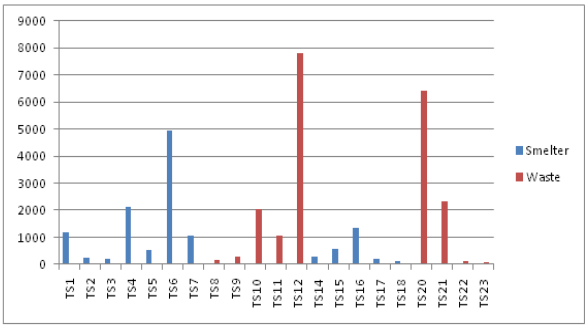

Figure 4. Results of calculated ecological risk index for soil samples

Figure 4 shows measured ecological risk index (RI) values for different sampling points in vicinity of the smelter and waste pile.

Statistical analysis

Spearman,s correlation coefficient [Table 4] shows a significant correlation between As, Cd, Pb and Zn concentrations. A strong positive correlation was observed between Ni and Cu (Ni/Cu: R = 0.911, P < 0.01). However, correlation is the least between Cr and other metals. Moreover, there is a significant negative correlation between the concentration of each metal and distance from the smelter.

Factor loadings, communalities, and variances of the component for the metal concentration in the surface soil samples are given in Table 5. Principal component analysis result reveals that more than 82% of total variance is explained by two factors [Table 5]. The first factor, which explains more than 51% of the total variance, includes As, Cd, Cu, Ni, Pb and Zn, and indicates the " anthropogenic factor" for these heavy metals. The second factor in Table 5, which accounts for more than 31% of the total variance, includes Cr, Fe, Al, Mn, which is concluded to represent the chemical composition of soils. The occurrence of Cr in this group represent the "geogenic factor" for this heavy metal.

Distribution and dispersion of heavy metals in soil samples around the Zn-smelter indicate, that soil contamination in areas adjacent to the smelter and waste pile is high, but concentrations decreased with distance from the smelter. The greatest concentrations of heavy metals occurred at TS12 (in the downwind direction) and TS20 (in the upwind direction) in the vicinity of the waste pile, and TS4 and TS6 in vicinity of the smelter in the downwind direction. These results, confirm the effect of the Zn smelting plant as a main source of substantial but local pollution, as seen in other cases in the world [2; 12; 19].

Although neutral to slightly alkaline soils may be associated with limited metal mobility within the soil,

Table 4. Correlation coefficients between heavy metals and soil characteristics

	As	Cd	Cr	Cu	Ni	Pb	Zn	pH	OC
As	1								
Cd	0.915	1							
Cr	0.365	0.393	1						
Cu	0.777	0.743	0.516	1					
Ni	0.775	0.835	0.580	0.911	1				
Pb	0.940	0.933	0.341	0.748	0.798	1			
Zn	0.957	0.925	0.482	0.747	0.810	0.939	1		
pH	-0.443	-0.304	-0.146	-0.317	-0.291	-0.422	-0.270	1	
OC	0.356	0.356	0.186	0.459	0.463	0.382	0.302	-0.534	1

Table 5. Rotated factor analysis of elements in soils

	F1	F2	Communality
As	0.881	0.184	0.810
Cd	0.971	0.136	0.961
Cr	0.023	0.911	0.831
Cu	0.820	0.192	0.710
Ni	0.896	0.423	0.983
Pb	0.894	0.194	0.837
Zn	0.930	0.112	0.877
Fe	0.226	0.871	0.809
Al	0.452	0.676	0.662
Mn	0.183	0.880	0.808
Percentage of total variance	51.5	31.4	

Extraction method: principal component analysis, Rotated method: varimax.

Table 6. Description of I_{geo}, C_f, C_{deg}, E_i, and RI

Value	Soil quality	Value	Soil quality
$I_{geo} \leq 0$	Practically uncontaminated	$E_i < 40$	Low potential ecological risk
$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated	$40 \leq E_i < 80$	Moderate potential ecological risk
$1 < I_{geo} < 2$	Moderately contaminated	$80 \leq E_i < 160$	Considerable potential ecological risk
$2 < I_{geo} < 3$	Moderately to heavily contaminated	$160 \leq E_i < 320$	High potential ecological risk
$3 < I_{geo} < 4$	Heavily contaminated	$E_i \geq 320$	Very high ecological risk
$4 < I_{geo} < 5$	Heavily to extremely contaminated		
$5 < I_{geo}$	Extremely contaminated		
$C_f < 1$	Low contamination factor		
$1 \leq C_f \leq 3$	Moderate contamination factor	RI < 150	Low ecological risk
$3 \leq C_f < 6$	Considerable contamination factor	$150 \leq RI < 300$	Moderate ecological risk
$6 \leq C_f$	Very high contamination factor	$300 \leq Ri < 600$	Considerable ecological risk
$C_{deg} < 8$	Low degree of contamination	$RI \geq 600$	Very high ecological risk
$8 \leq C_{deg} < 16$	Moderate degree of contamination		
$16 \leq C_{deg} < 32$	Considerable degree of contamination		
$32 \leq C_{deg}$	Very high degree of contamination		

the sandy texture, limited buffering capacity and extensive soil contamination with heavy metals, such as, As, Cd, Cu, Pb and Zn, may facilitate leaching and hence groundwater contamination in time.

Finally, transmission of potentially toxic metals from soil to plants provide a potential pathway for the toxic elements to enter the food chain, with harmful effects on human health. These possibilities, should be investigated in future research.

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