Mobility and ecological risk assessment of heavy metals in soils impacted by hazardous smelting waste

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The present study was carried out in a metals smelting area to identify the phase associations of metals in solid matrix with the application of mBCR procedure of sequential extraction and to assess the elemental mobility, probable bioavailability and their ecological risks in relation to soil contamination levels. pH (5.73–6.85) of the studied soil is acidic to neutral in nature and showed some effects on the distribution pattern related to extent of contamination. The study revealed that the mean Pb (790±112 mg/kg), Cd (21.02±3.26 mg/kg) and As (60.33±6.30 mg/kg) exhibited the high concentration due to the severe impact of smelting activities, which is with high impact than the level III standard of soil quality prescribed in Mainland China (GB15618-1995). The overall percentage of metal content in different fractions is in the sequence of Residual > Oxidixable > Reducible > Exchangeable fraction. Though, an appreciable amount of Pb is fastened in the reducible fraction, Cu and As are tied in the oxidizable fraction and lastly, Cd is in exchangeable fraction. Under changing environmental conditions these non-residual metals may be released back to the surrounding soil environment by various processes of remobilization. The percentage of metal in the exchangeable and carbonate fractions (% F1 for BCR) can be measured by Risk assessment code (RAC), which is used to assess the environmental risks and the potential risk levels of heavy metals like As, Pb, Cd and Cu ranged 4.09–11.52, 10.05–15.26, 29.54–42.08 and 8.50–16.54 and respectively. According to soil pollution indices and risk assessment criteria the metals had the following order: Cd > Pb > Cu > As. The results indicate a high environmental mobility for heavy metals in the studied region which represents high degree of potential risk in ecology.

Keywords: Smelting waste, soil, heavy metals, speciation, mobility, ecological risk.

Introduction

Mining activity, mineral extraction and smelting procedure of non-ferrous metals generate huge amounts of metal-enriched waste products. The waste heaps are accumulated on the soil surface of terrestrial land mass, resulting in the enhancement of toxic components in the soil surface. Metalloids, in combination with metals are accumulated in the soil layers and pose threat to biotic environment. Bio-accumulation process helps the transfer of metal components from solid matrix to the fluid medium and resulting in to magnify in concentration in the food chain and the residual effect poses threat to the ecosystems. Therefore, the soil can be considered as a source and sink of pollution with the capacity to transfer pollutants[1,2]. The study related to heavy metal pollution in soils along with their potential ecological risk assessment is conducted by various workers[3–5]. The eco-toxi-

cological impact of heavy metals and metalloids are the concern because, the metals exhibit persistence, toxico-kinecs, and non-biodegradable fashion in the habitable environment[6,7].

The metals may also be bound in different forms[8] i.e. exchangeable and soluble forms, as material in amorphous forms (Fe/Mn oxides), coupled with sulfides and organic matter or fastened to mineral colanders (residual)[9]. Hazardous solid wastes from metallurgical smelting industries are severe environmental concern. Therefore, the nonferrous metals mining and smelting activities gain more importance due to the concentration of toxic metals and metalloids, their fraction distribution and impact on surrounding soil environment. The study aims on: (i) to characterize the topsoils and subsoils phase associations in region under study in a wide range of anthropogenic contamination with the application

of mBCR sequential extraction; (ii) to identify the profile of metal contamination in different sources and magnitudes in soil layers with the application of various soil pollution indices; (iii) to evaluate the element mobility, potential bioavailability and their ecological risk in relation to soil contamination levels.

Experimental

Materials and methods (Study area, sampling procedure, analytical methods):

In order to obtain the specific objective of the study, soil samples were collected from 8 sites (S1-S8) to analyze the pH, organic matter and total metal content. Topsoil (0–20 cm) and subsoil (30–40 cm) samples were collected from each site. Among the 8 sites (S1-S8) first 4 sites (S1-S4) with relatively high heavy metal concentrations were subjected to estimate the chemical fractions of metals (Pb, Cd and Cu) and metalloid (As) with the application of modified BCR extraction method. The tested soils were collected from arable land in the vicinity of typical smelting area of Zhuzhou city, Hunan province, central China, which belongs to allitic udic ferrisols, and developed from the typical quaternary red clay. Each sample was picked out from a mixture of 3–5 subsamples.

The soils were analyzed for the following properties: pH, soil organic matter (OM), heavy metals (Pb, Cd and Cu) and metalloid (As). The pH has been estimated in the soil extracts (1:2.5 solid/distilled water [w/v]) using a typical glass electrode pH meter. Soil organic matter was determined according to the $K_2Cr_2O_7$ method described by Walkley and Black[10]. Metal fractionations in soil samples were estimated by the modified BCR sequential extraction procedure[11]. To estimate the degree of risk of a metal to the environment the contamination factors (CF) were calculated on the basis of mBCR sequential extraction. In order to evaluate the degree of ecological risk, the risk assessment code (RAC) is calculated as: RAC = the amount of F1/the total concentrations ×100%. In order to calculate different indices (CF, EF, Igeo and PLI), we considered the values of soil background of Hunan province with proposed records of the Chinese Environmental Monitoring Station[12] as the reference values.

To assess the level of contamination, the enrichment factor (as geochemical normalization method) is applied in the study and computed as:

Enrichment factor (EF) = (M/X) sample/(M/X) background

where M = measured metal concentration of the soil sample, X = selected normalizer (reference metal). The (M/X) sample value and (M/X) background value is the ratio of analyzed metal and the normalizer in the target/interest and the background soil, respectively. In this study the iron (Fe) is considered as normalizer as because this inert element shows less anthropogenic contamination in the soil. To explain the level of anthropogenic contamination, a five-category enrichment ranking system[13,14] is followed in the present study.

The geoaccumulation index is calculated by the following equation:

$$Igeo = \log^2 Cn/1.5 Bn$$

where Cn refers to the concentration of measured element in soil and Bn refers to the geochemical background value/ average shale concentration in soil. The factor 1.5 is used as constant and the average shale concentration provided by Turekian and Wedepohl[15] is used as reference value for this study.

The method of PLI, proposed by Tomlison *et al.*[16], is calculated as geometric mean of concentration factor (CF) of each analyzed metal present in the soil.

$$PLI = (CF1 \times CF2 \times CF3 \ldots\ldots\ldots\times CFn)^{1/n}$$

where, n = the number of analyzed metals and CF can be calculated as: CF = Hc/Hb, where Hc denotes the concentration of metals and Hb denotes the background value of metals.

Results and discussion

pH, organic matter and total concentrations of metals in soils:

The total concentrations of Pb, Cd, Cu and As are summarized in Table 1. The pH of soils ranged from 5.73–6.56 in topsoil and 5.87–6.85 in subsoil. Acidic soils (pH < 6.5) account for about 75% in topsoil and 62.5% in subsoil, neutral soils (pH of 6.5–7.5) account for about 25% in topsoil and 37.5% in subsoil. This indicated that the pH for studied soils has a tendency to be less than natural soils. pH controls the exchange of metals from static solid-phase forms to dynamic bioavailable solution phase in soil. The lower pH values in the tested soils may lead to high metal availability in plants in the study area. Organic matter sways the bioavailability of heavy metals in the soil[17], ranged between 14.42–34.64 mg/

Table 1. pH, organic matter and total concentrations of metals in the soil samples

Sites		pH	OM	Pb	Cd	Cu	As
S1	T[a]	5.73	32.86	856	20.63	159	68.85
	S[b]	5.95	25.83	645	16.75	132	61.85
S2	T	5.79	30.41	942	25.99	142	59.65
	S	5.87	15.32	809	21.34	132	48.87
S3	T	6.49	34.64	927	24.95	171	70.53
	S	6.52	19.85	742	20.85	128	64.59
S4	T	6.56	29.95	846	23.62	146	64.21
	S	6.55	14.42	725	22.53	138	58.13
S5	T	6.54	31.55	818	19.31	143	62.67
	S	6.85	20.53	634	16.63	108	56.97
S6	T	5.86	30.32	892	23.45	164	60.57
	S	6.15	18.54	657	17.63	112	52.49
S7	T	6.35	31.96	835	20.97	147	58.33
	S	6.32	19.33	598	14.94	124	49.63
S8	T	5.84	31.75	938	24.89	167	67.32
	S	5.95	17.42	786	21.86	145	60.64
Mean		6.21	25.29	790	21.02	141	60.33
SD±		0.36	7.10	112	3.27	18.3	6.30
Background values of China soils (Hunan province)[c]				29.7	0.13	27.3	15.7
China Environmental Quality Standard for Soils Class III[d]				500	1.00	400	40

[a]T-topsoil; [b]S-subsoil; [c]China Env. Monitoring General Station, (1990); [d]Standard III (GB15618-1995).

kg with an overall mean of 25.29±7.10 mg/kg in the area under study. The concentrations of Cu, Pb, Cd and As in the studied region ranged from 598–942 mg/kg, 14.94–25.99 mg/kg, 108–171 mg/kg and 48.87–70.53 mg/kg with an overall mean of 790±112 mg/kg, 21.02±3.27 mg/kg, 141±18.38 mg/kg and 60.33±6.30 mg/kg respectively. Concentration of heavy metals in total, in contaminated soils under study reflects a variation in the range of soil contamination. The elevated level of total Pb and Cd was observed in S2 and can be due to the recent input of these elements. pH value of the S2 site is low which also may favour the metal mobility. The study in general revealed that the proportion of the total metal concentration was high up in the topsoil than the subsoil.

The Cu concentration did not exceed the standard value (400 mg/kg) (GB15618-1995)[11]. Whereas, the concentrations of Cd, Pb and As in all the sampling sites both in topsoil and subsoil were exceeded the corresponding background val-

ues (500, 1.0 and 40 mg/kg for Pb, Cd and As, respectively) of the soil environmental quality standard in China[18]. It is also important to keep in view that elevated concentrations of metal were observed, both in subsoil and topsoil as because the studied area is situated in the vicinity of metal smelting area. The summarized result revealed that in the studied soils, concentrations of Cu were within range to the soil standard, while Pb, Cd and As were in elevated concentrations in all sample areas. The result showed that the study area bears highly polluted soil profile with hazardous metals. Total metal concentrations were also comparable with background values of China soils (Hunan province) where all the studied metals in all the sampling sites were transcended the background values (29.7, 0.13, 27.3 and 15.7 mg/kg for Pb, Cd and As respectively). Heavy metals are the main environmental concern in the study area as these are regarded as serious pollutants of soil due to their toxicity and environmental persistence in nature.

Pearson correlation and coefficient of variance:

To analyze, assess and find out the relation among properties (pH and OM) of soil and metal contents, Pearson's correlation analysis was carried out with collected data. Correlation process was carried out between pH, OM and various heavy metals in soil samples to assess the leaching possibility and the results are presented in Table 2. There was no positive correlation observed in the Cd ($r = -0.276$), Pb ($r = -0.385$), Cu ($r = -0.379$) and As ($r = -0.018$) concentrations with the pH of the studied soils. Similarly organic matter also showed negative correlations with pH ($r = -0.161$). A significant correlation lies between total concentrations of heavy metals with organic matter content Pb ($r = $ **0.688**), Cu ($r = $ **0.711**) and As ($r = $ **0.698**). The significance in relationships between metal concentrations and organic matter content were further calculated by correlation equation. Correla-

Table 2. Pearson correlation coefficient matrix of analyzed variable

Variables	pH	Pb	Cd	Cu	As	OM
pH	1					
Pb	−0.385	1				
Cd	−0.276	**0.908**	1			
Cu	−0.379	**0.849**	**0.738**	1		
As	−0.018	**0.584**	**0.518**	**0.703**	1	
OM	−0.161	**0.688**	0.431	**0.711**	**0.698**	1

Correlation is significant at the 0.05 level

tion between OM and Cd is not so high (r = 0.431) than the other metals like Cu, because the Cd cannot easily bound with organic matters. The study revealed a strong positive correlation between Cu and OM (r = **0.711**), due to the tendency of high complex formation of Cu for organic matter. Similar observation was also reported by[19] where they found affinity in highest range between Cu and organic matter. On the other hand, Pb-Cd (r = **0.908**), Pb-Cu (r = **0.849**), Pb-As (r = **0.584**), Cd-Cu (r = **0.738**), Cd-As (r = **0.518**), As-Cu (r = **0.703**), showed strong positive correlations, these may be due to their same or similar source input likely resulting from metal smelting activities.

Partitioning of metals in soils:

To evaluate the bioavailability of heavy metals in the studied soils, the mBCR was conducted, and the average concentrations of Pb, Cd, Cu, and As combined with the exchangeable fraction (F1), reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4) in topsoil and subsoil were shown in Fig. 1. The results focussed that the mBCR sequential extraction method used for detecting the speciation of Cd, Pb, Cu and As in different soil samples is accurate and reliable. Chemical fractionation of metals is of immense importance for their probable toxicity and mobility[20] and also useful for distinguishing metals with lithogenic/natural origins from those with anthropogenic origins. The dispersal of metals in the four fractions varies in greater range among the samples.

The association of Pb with the different sequential frac-

tions was observed in this study as follows: I - Exchangeable species (10.05–15.26%), II - Reducible fraction (26.47–29.94%), III - Oxidizable (18.25–21.34%) and IV - Residual fraction (36.19–42.86%). The study revealed that the first 3 extraction (F1, F2 and F3) fractions accounted for a significant part (~60%) of the total Pb concentration. The reducible fraction (F2) only took a minor role for Cd, Cu and As in the studied soil, though in case of Pb this fraction had a significant role (account 29.09% for topsoil and 27.73% for subsoil) in all the soil samples. Fe-Mn oxides are scavengers of heavy metals with immense importance in soils[21]. Ramos *et al.*[22], also suggested that Pb can form stable complexes with Fe and Mn dioxide and may be the reason why reducible Pb is predominating in non-residual fractions in the study area.

The association of Cd with the different sequential fractions was observed in this study as follows: I - Exchangeable species (29.54–42.08%), II - Reducible fraction (9.01–16.45%), III - Oxidizable (4.24–10.24%) and IV - Residual fraction (36.73–53.37%). Cd represented a different exchangeable speciation distribution pattern with respect to the other metals studied. The proportion associated with the acid exchangeable fraction for Cd was higher than the other nonresidual fractions. The high percentage of exchangeable Cd in the studied soil indicated that the bioavailability of Cd was high. A very small amount of cadmium is present in the step III - Oxidizable fraction due to the fact that the low adsorption constant of Cd to organic matter. The high proportion of the chemically reactive forms of cadmium implies a
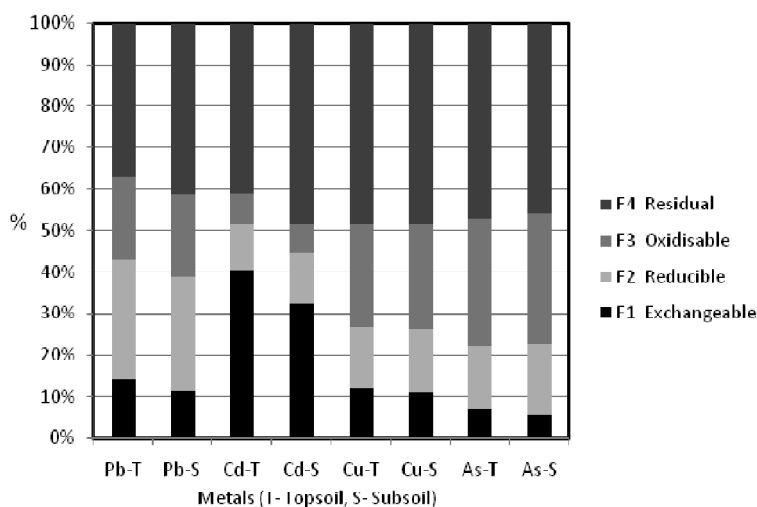

Fig. 1. BCR fractionation profile of Pb, Cd, Cu and As.

high level of ecological risk[23]. Since F1 is considered to be the highest mobile of the four fractions, this speciation distribution flourishes a high environmental mobility for Cd in the studied region which represents serious risk for surrounding ecosystems.

The association of Cu with the different sequential fractions was observed in this study as follows: I - Exchangeable species (8.50–16.54%), II - Reducible fraction (12.39–18.04%), III - Oxidizable (22.40–30.30%) and IV - Residual fraction (35.70–53.30%). Among the first three fractions (nonresidual fractions) of Cu, a major part is complexes to the organic matter with comparable amounts associated with the F1 fraction, F2 and F4 fractions. The fact is that the Cu can easily complex with organic matters because of high formation of organic-Cu compounds[24]. Plants take up copper from the soil solution mainly as Cu^{2+}. Chemical behavior of Cu depends on various geological and pedogenetic processes and on properties of the soil environment (pH, redox conditions and sorption). Other study depicted that the solubility of Cu, as it is calcophilic, is increased under oxidizing conditions, which is mainly bound to sulfides in nature[25]. The results were in accord with the results of other studies[26], that a large proportion of Cu in soil is bound to organic matter.

The association of As was observed with the different sequential fractions in this study as follows: I - Exchangeable species (4.09–11.52%), II - Reducible fraction (11.93–20.17%), III - Oxidizable (28.70–34.04%) and IV - Residual fraction (40.12–52.89%). From the results as shown in Fig. 1, ~50% from the total As within the soils is associated with the non-residual fractions. The proportion order in average of the four fractions for As reduced as F4 > F3 > F2 > F1. Arsenic depicts higher range percentages (mean value) of the oxidizable fraction than other representative metals with 30.84% for topsoil and 31.57% for subsoil respectively, which is at per with the strong potentiality of tagging with the or-

ganic matter for arsenic ion in soils. High concentrations of total arsenic were found in both topsoil and subsoil samples and the fractionation profile indicate that most of the As present in soil have minimum mobility because it is mainly confind to nonlabile fraction. Under changing environmental conditions they may be released back to the surrounding soil. Though, the mobility, bioavailability and activity of heavy metals in the field soils may be greatly affected by acid soils as the study area is under the severe acid rain pollution causes due to presence of H_2SO_4-type components. In case of enhanced oxidation-reduction potential (EH), metal complexes with organic matter could be degraded and leads to a release of soluble metal[27]. This phenomenon therefore, results in a potential environmental disturbance viz. hazard in the soil environment of study area.

Environmental implications:

In order to evaluate the degree of toxicity and risk factors in the environment and bioavailability of heavy metals in the soil, the contamination factors (CF) were calculated. To assess the retention of heavy metals in soil samples the CF was calculated by dividing the sum total of the concentrations of mobile phase metal ions i.e. concentration of non-residual phase to the residual phase[28]. The results of CF in the soil samples are summarized in Table 3. The CF value of Pb, Cd, Cu and As ranged from 1.33–1.76, 0.87–1.72, 0.88–1.81 and 0.89–1.49 respectively. The contamination factors of heavy metals in the study area had the following order as: Pb > Cd ≈ As > Cu for top soil and Pb > As > Cu ≈ Cd for subsoil. The study revealed that Cu and As had relatively lower CF values (<1) in some sites, considered relatively safe for the environment. Though the Pb and Cd exhibited relatively high mean concentration than Cu and As indicate minimum retention time and maximum risk to the environment.

Enrichment factor (EF), Igeo and PLI:

The EF levels of each metal in various sites are enlisted

Table 3. Contamination factors (CF)

Sites	Pb		Cd		Cu		As	
	Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil
S1	1.76	1.50	1.38	1.21	0.92	0.99	1.19	0.99
S2	1.70	1.48	1.37	1.07	0.88	0.89	0.96	1.47
S3	1.67	1.37	1.34	0.87	0.88	1.48	1.30	0.89
S4	1.72	1.33	1.72	1.12	1.81	0.98	1.06	1.49

Table 4. Enrichment factor (EF), geoaccumulation index (Igeo) and pollution load index (PLI) in the studied metals

| | Enrichment factor (EF) | | | | | | | | Geoaccumulation index (Igeo) | | | | | | | | PLI | |
| | Pb | | Cd | | Cu | | As | | Pb | | Cd | | Cu | | As | | | |
	T[b]	S[b]	T	S	T	S	T	S	T	S	T	S	T	S	T	S	T	S
S1[a]	28.82	21.72	158.7	128.9	5.82	4.84	4.39	3.94	4.26	3.86	6.73	6.43	1.96	1.69	1.55	1.39	18.49	15.20
S2	31.72	27.24	199.9	164.2	5.20	4.84	3.80	3.11	4.40	4.18	7.06	6.77	1.79	1.69	1.34	1.05	18.81	16.11
S3	31.21	24.98	192.0	160.4	6.26	4.69	4.49	4.11	4.38	4.06	7.00	6.74	2.06	1.64	1.58	1.46	20.26	16.67
S4	28.48	24.41	181.7	173.3	5.35	5.06	4.09	3.70	4.25	4.02	6.92	6.85	1.83	1.75	1.45	1.30	18.34	16.77
S5	27.54	21.35	148.6	128.0	5.24	3.96	3.99	3.63	4.20	3.83	6.63	6.42	1.80	1.40	1.41	1.27	17.10	14.07
S6	30.03	22.12	180.4	135.6	6.01	4.10	3.86	3.34	4.32	3.88	6.91	6.50	2.00	1.45	1.36	1.16	18.82	14.24
S7	28.11	20.13	161.3	114.9	5.39	4.54	3.72	3.16	4.23	3.75	6.75	6.26	1.84	1.60	1.31	1.08	17.35	13.50
S8	31.58	26.46	191.5	168.1	6.12	5.31	4.29	3.86	4.40	4.14	7.00	6.81	2.03	1.82	1.52	1.36	19.96	17.38
Min	27.54	20.13	148.6	114.9	5.20	3.96	3.72	3.11	4.20	3.75	6.63	6.26	1.79	1.40	1.31	1.05	17.10	13.50
Max	31.72	27.24	199.9	173.3	6.26	5.31	4.49	4.11	4.40	4.18	7.06	6.85	2.06	1.82	1.58	1.46	20.26	17.38
Ave	29.69	23.55	176.8	146.7	5.67	4.67	4.08	3.61	4.31	3.97	6.87	6.60	1.92	1.63	1.44	1.26	18.64	15.49
SD	1.666	2.586	18.44	22.24	0.43	0.46	0.29	0.37	0.08	0.16	0.15	0.22	0.11	0.14	0.10	0.15	1.106	1.445

aSampling site, bT-topsoil, S-subsoil, EF-Enrichment factor, Igeo-Geoaccumulation index and PLI-Pollution load index.

in Table 4. Metal enrichment in the studied soil had the following order: Cd > Pb > Cu > As. Values showed significant increase in topsoil for all metals (Pb, Cd and Cu) and metalloid (As). Further, Cd had the highest EF values (average value 176.8±18.44 for topsoil and 146.7±22.24 for subsoil) among the metals studied. Pb belongs to very high contamination category which ranged from 20.13–31.72. As in the studied soil exhibited moderate contamination. The subsoil of Cu belongs to the moderate contamination category though the topsoil having significant contamination. According to the classification of[29] the value of EF > 0.5–1.5 represents the metal is fully derived from crusted material or natural processes and EF > 1.5 represents the source is might be of anthropogenic. High EF values of all studied metals occurred at the top layer of the profile rather subsurface layer may be due to the industrial activities.

Table 4 also shows the geo-accumulation index for the quantitative estimation of heavy metal accumulation in the research area. The order of participation of different heavy metals on the basis of Igeo followed: Cd > Pb > Cu > As. The geoaccumulation index values for Pb ranged from 3.74–4.40 and corresponded with class 4 (heavily contaminated) and class 5 (heavily to extremely contaminated) values. According to Igeo values the study area is heavily to extremely contaminate by the Cu and moderately contaminated by the As. The Igeo values for Cd ranged from 6.26–7.06 and corresponded with class 6 (extremely contaminated) values. The Igeo value showed much fluctuation in the area under study and the higher values of Igeo for Cd and Pb imply appreciable input from anthropogenic sources.

The values of PLI obtained from the multi-metal contaminated smelting area are summarized in Table 4. The study exhibited a high range of PLI value17.10–20.26 for topsoil and 13.50–17.38 for subsoil indicating that the concentration levels of studied metals exceeded many time than the background values. The PLI values indicated immediate intervention to ameliorate pollution in the study area.

Risk assessment code (RAC):

Meanwhile, the RAC value can be calculated by the percentage representation of metal in the exchangeable and carbonate fractions (% F1 for BCR) and is used to acquire additional insights in evaluation of the environmental risk factors and of metal pollution in sediments or soils[30]. Estimation of bioavailability of metals present in soil is a useful way

to predict the percentage of soil metals readily available for uptake of plants. The first fraction of mBCR extraction depicts weakly bound metals, easily soluble in water or a slightly acidic medium. The soil condition can be termed as in no risk when the F1 BCR fraction is < 1%, a low risk for a range of 1–10%, a medium risk for a range of 11–30%, a high risk from 31 to 50% and a very high risk for F1 percentages > 50%. The results (Table 5) showed that except the topsoil of S3 (11.52%) As represent minimum risk with average RAC values of 7.04% for topsoil and 5.48% for subsoil. Environmental risks in low or medium level were represented for Cu with ranged from 8.50–16.54% for topsoil and 10.65–11.84% for subsoil. The RAC results manifested medium risk (10.05–15.26%) for Pb, though, under changing environmental conditions they may be released back to the surrounding soil environment by various processes of remobilization. On the other side, Cd presents environmental risk in a high range with the mean RAC value for topsoil 40.45% and for subsoil 32.31% should be decided dangerous for urban ecosystems. Finally, the RAC values have applied to classify the elements according to their function of potential hazard as Cd > Pb > Cu > As.

Table 5. Risk assessment codes (RAC) obtained by the extractable F1-BCR

Elements (% exchangeable and carbonate, fraction 1 BCR steps)					
Metal	Soil	S1	S2	S3	S4
Pb	T	14.539	15.256	12.465	14.036
	S	10.814	12.179	10.047	11.524
Cd	T	41.010	42.075	37.557	41.154
	S	32.659	34.442	29.545	32.601
Cu	T	11.662	10.738	8.504	16.536
	S	10.643	11.306	11.678	11.838
As	T	5.279	7.299	11.515	4.087
	S	4.450	5.428	5.610	6.438

Conclusions

The results obtained following conclusions:

(i) pH of the studied soil is acidic to neutral in nature and showed some effects on the distribution pattern related to extent of contamination. The total concentrations of metals and metalloid were remarkably high in the study area in which, the large-scales melting operations are occured in the surrounding regions. The study revealed that the total concentrations of metals in the topsoils are generally higher than those in subsoils.

(ii) The overall percentage of metal content in different fractions is in the sequence of Residual > Reducible > Oxidixable > Exchangeable fraction. Though, a significant amount of Pb is attached to the reducible fraction, Cu and As bound to the oxidixable fraction and Cd is in exchangeable fraction. Under changing environmental conditions these non-residual metals may be released back to the surrounding soil environment by various processes of remobilization. Statistical analysis revealed existence of significant correlation among the studied metals, showed strong positive correlations; these may be due to their same or similar source input likely resulting from metal smelting activities.

(iii) According to soil pollution indices and risk assessment criteria the metals had the following order: Cd > Pb > Cu > As. The speciation distribution and pollution assessment indices indicate a high environmental mobility for studied metals which represents high degree of potential ecological risk. The significance of the metals persist in the study region and their role in imparting ecological effect of that locality required further extensive and exclusive research work with eco-remediation of heavy metals.

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