



# Land Use Based Distribution Pattern, Fractionation forms and Health Risk Assessment of Heavy Metals in Mining-affected Soils of Western Ghat of Goa, India

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## Authors' contributions

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

## Article Information

DOI: 10.9734/IJPSS/2022/v34i232495

## Open Peer Review History:

This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: <https://www.sdiarticle5.com/review-history/92958>

Original Research Article

Received 15 August 2022  
Accepted 21 October 2022  
Published 27 October 2022

## ABSTRACT

Goa is a biodiversity hotspot and a major iron ore producer state in India. The study investigated heavy metal (HM) distribution pattern, fractionation forms under different land use types near an iron mining including health risks associated with different exposure pathways. Georeferenced 38 soil surface samples, 8 soil profile samples and 6 plant samples were collected from three land use types- agriculture cropland, fallow land and natural vegetation. Collected samples were analyzed for HM contamination in inductively coupled plasma atomic emission spectrophotometer (ICPAES). The mean total HM concentration in surface soil exceeded the background value. Weak acid soluble fraction % of metals posed no to medium risk values. Fallow land had higher metal content in surface soil. Principal component (PC) analysis showed Pb, Cd and Cr metals were more associated with mining activity. Vertical distribution pattern of HM accumulation in soil profiles showed a drastic reduction in HM concentration below plough layer in fallow land indicating

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anthropogenic sources of origin. Hazard index (HI) in the descending order were Cd> Cr >Pb. Non-carcinogenic HI value were considerably higher than safe level. Higher organic carbon (OC) and clay content in soil had a tendency to accumulate ample HM in unavailable form due to chelation effect. Soils had higher pool of unavailable residual HM as compared to available. Overall the land uses are in medium risk category and site specific management is requisite of the time to maintain the balance of this fragile ecosystem with anthropogenic activities in long run.

*Keywords: Land use; heavy metals; soil contamination; fractionation forms; rice; health risk.*

## 1. INTRODUCTION

The soil contamination by heavy metals (HM) has remained a widespread problem globally. Pressure on natural resources has aggravated with the dawn of industrial revolution. Sources of the contamination of metals include industry, mining, agriculture, sewage irrigation, metal smelting, vehicular emission etc. However mining and smelting industries are considered to be prime anthropogenic sources of HM contamination in agricultural soil [1,2]. Thus the fate of HMs (Cr, Ni, Cu, Mn, Cd, Pb etc.) in soil near mine sites, dumps and tailing piles pose great threat to the health of the environment [3] including humans. The innate metals from pedogenic/ lithogenic sources are often present in extremely immobile form with lower concentration. But, anthropogenic sources of metals as compared to innate metals are often more active forms in terms of mobility and plant-availability [4-6]. The total trace metals contents in a system seldom provide information about potential risks to the environment [7,8]. So, the fractionation forms of metals determine the bioavailability and mobility [9,10] are an important pool to study. Thus the potential risks associated with elevated HM concentrations arising from anthropogenic activities can be evaluated with the quantification of fractions of total metals that is bioavailable. The HMs mobility and bioavailability in soil is responsible for its potential toxicity. Metal mobility depends upon the phase of occurrence of the metal along with the different processes involving physical and chemical reactions that regulate transformation between phases. Also the persistence and non-biodegradability nature of HM stand it out among other harmful contaminants [11,12]. "Several researchers also reported that mining activity often lead to harmful HM contamination in agricultural soils nearby with uptake and accumulation of HMs in the edible parts and subsequent human exposure" [13-15]. Moreover, there are number of exposure pathways through which human get contaminated with HM, but most important of

them are soil and food. Hence, capturing the information about the concentration of HMs in soil and crops and their dietary exposure are essential for assessing risk to human health. These concentrations exceed acceptable limits thus cause possible threat to health for consumers. The HMs present in soils enters the human system through direct ingestion, dermal contact and inhalation, while through intake of HM contaminated food makes HM entry to the food chain. Some of the toxicological effects showed by HM upon exposure include harm to the internal organs, nervous system and other carcinogenic effects [16,17].

The Goa state in India is rich in both biodiversity and minerals. The state is popular for its fancy beaches and food. The staple food of the state is rice [18]. The Western Ghat's tropical evergreen rainforest is regarded as one of the 36 Biodiversity Hotspots on the Earth. Goa accounts for nearly sixty percent of India's iron ore exports thus considered as an important iron ore producing state in India [19]. are found in Goa. The mining area of Goa comprises of approximately 700 km<sup>2</sup>. "The study area being located at Bicholim taluka is having abundance of quartz-chlorite-biotite/amphibole schist with thin lenses of banded iron formation (BIF), also called Bicholim-Rivona formation, that is predominant in NW-SE direction of Goa state" [20,21]. "In most of the iron ore at Goa the ore to overburden ratio is roughly 1:3 in this region. This means, three tons of overburden material is generated for every ton of ore excavated. This overburden material is heaped into steep and high deposits. Poor management of dumps combined with heavy monsoon leads to the soil erosion from these deposits. This silt-laden water enters the drainage network and apparently move into adjacent low-lying paddy fields, clogging the pores resulting in poor drainage led following" [22]. "Villages of Bicholim block of North Goa owing to mining activity have been subjected to soil degradation. In rural Goa agriculture is a primary source of income; any deterioration of agricultural land has a deep

impact on both livelihood and human wellbeing” [23]. Keeping in view the ecological fragility in this region there is an urgent need to understand the land use based distribution pattern, fractionation forms of HM in soil surrounding the mines as well as the health risk associated with the consumption of rice grown on these soils. Therefore, the objectives of the present study were to: (1) quantify the total concentrations of HMs (Fe, Mn, Zn, Pb, Cd, Cr, Ni and Cu) in three major land use types- natural vegetation, agriculture crop land and fallow land (2) elucidate the influence of soil physico-chemical properties in fallowing of land (3) evaluate bioavailability of HMs in various land use types through fractionation forms analysis and (4) assess human carcinogenic and non carcinogenic health risk through various mode of HM exposure.

## 2. MATERIALS AND METHODS

### 2.1 Site Description

The investigation was carried out in area surrounding an iron mining site of Bicholim Block of Goa state that lies at the foothills of Western

Ghat. The present study area extended from 73° 52' 25"E to 73° 57' 15" E longitudes and 15° 33' 55" to 15°37' 45" N latitudes, covering an area of about 2192 ha (Fig. 1). The land is characterized by undulated topography and tropical monsoon climate with hot humid weather having mean maximum temperature; annual rainfall and relative humidity are of 35°C, 2932 mm and 70%, respectively.

“The soils of study area are mostly lateritic impregnated with alluvium and colluvium deposits at low land. Mean elevation of the study area is ranged from 0 to 168 m above mean sea level indicating the presence of hilly to plain landforms. The iron ore mining is situated along the summit surrounded by forest and scrubs present in the moderately steeply to steeply sloping side slopes. Subsequently at the low lands slopes flattens out and cultivated lands are mostly present in this zone; majority of which were turned into fallow lands as indicated in the land use land cover map due to long term mining deposits accumulation from uphill side that leads to poor soil drainage. The principal crops includes rice, coconut, areca nut, cashewnut, and vegetable crops” [24].

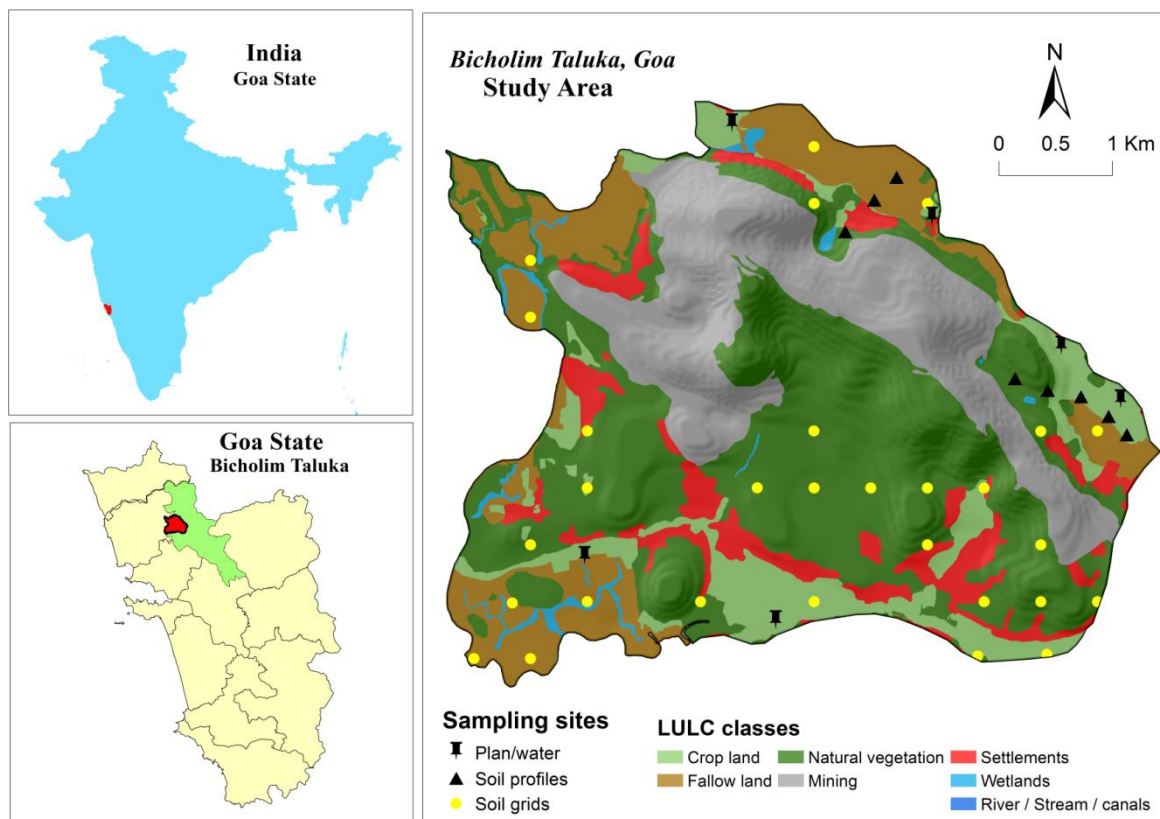


Fig. 1. Study area with sampling points

## 2.2 Sample Collection and Preparation

A total of 38 surface grid samples according to the land use types in the study area were collected considering minimum 500m interval in the month of February, 2017. To determine the regional background concentrations of HMs in soils, an additional ten soil sample were collected from unaffected areas of Bicholim Taluka but far away from study area. There were 21 samples from natural vegetation, 10 from fallow land and 7 samples from agriculture crop land. To study vertical soil samples 8 profiles were selected in different land use types with 3 samples from natural vegetation, 2 from fallow land and 3 from agriculture cropland. Soil samples were collected from the following vertical soil heights 0–30, 30–60 and 60-90 cm. The representative soil samples were collected with core sampler. Sampling locations were recorded during collections by a hand held Global Positioning System (GPS) (Model-Sxtreo WP 60). All samples were placed in polyethylene bags and carried to the laboratory for further processing. Samples were air dried in shade at ambient temperature ( $25 \pm 2^\circ\text{C}$ ) after removal of all the litters, pebbles, and organic debris. Prior to analysis soil physico-chemical properties and HMs, the soil samples (about 2 kg) were dried at room temperature, crushed and filtered through a 100 mesh (0.2-mm) nylon sieve and stored. The rice grain samples were collected from six georeferenced locations from the agriculture cropland in polyethylene bags and carried to the laboratory for further processing. The grain samples were dried in at  $80^\circ\text{C}$ , finely ground crushed and filtered through a 100 mesh (0.2-mm) nylon sieve and stored.

## 2.3 Sample Analysis

The soil reactions (pH) ( in 1:2 soil and water suspension), electrical conductivity (EC) [25] were determined. The soil organic carbon (OC) [26], cation exchange capacity (CEC) [27], bulk density (BD) [28], particle density (PD) (pycnometer) and particle size distribution [29] were also estimated. To determine total HM concentration, soil samples of 0.50 g weight each was digested with concentrated  $\text{HNO}_3$ , HF and  $\text{HClO}_4$  in a ratio of 9:5:3 inside a microwave digester (model Ethos D). Consequently, the total concentration of HMs was determined by a Prodigy (Leeman labs inc.) ICP-AES. Four-step sequential extraction procedure [30] was used to

analyze 38 surface soil samples. Four chemical fractionation forms viz. weak acid-soluble fraction, reducible fraction, oxidizable fraction and residual fractions of HMs were derived. Finely powdered 0.5 g of plant sample was soaked in 10 ml of  $\text{HNO}_3$  overnight and digested at  $50^\circ\text{C}$  temperature in a diacid mixture (5:1  $\text{HNO}_3$ :  $\text{HClO}_4$ ). Subsequently, the total concentration of HMs was determined by a Prodigy (Leeman labs inc.) ICP-AES.

## 2.4 Quality Control

“The sample analysis was done taking three replicates of each sample. The instrument was recalibrated after every 15 samples. For all the assessed samples the percent relative standard deviation (RSD) as obtained with respect to overall precision measurement was less than 10%. Double distilled water was used for preparation of standard solution and sample dilution. To check background interference and for more accurate determination reagent blank samples were also analysed. To prepare working standards of Zn, Cu, Fe, Mn, Pb, Ni, Cr and Cd standard stock solutions of  $1000 \text{ mg kg}^{-1}$  (SRL India) were used following dilution by double distilled water. For analysis of Zn, Cu, Cd, Pb, Cr and Ni working standards of 0.01, 0.05, 0.1, 0.25  $\text{mg kg}^{-1}$  were used; whereas 0.25, 0.50, 1.00, 2.00  $\text{mg kg}^{-1}$  working standards were used for analysis of Fe and Mn in ICP-AES. The recovery percentage was 99.5%” [24].

## 2.5 PC Analysis

To determine the origins of certain HMs in soil based on their contribution in extracted dimensions (Dim) from a set of variables, principal component (PC) analysis was carried out in R statistical programme. To understand variation in many dimensions, data transformation based on rotated orthogonal coordinates was used. Dimensions were obtained based on descending magnitudes of variance as expressed through eigen values.

## 2.6 Health Risk Assessment Methods

The detrimental effects of the environmental pollutants to human health are characterized by the health risks. Equations of daily intake dose via various exposure pathways [31,32] is described in Table 1. The values of Table 1 is explained in Table 2.

**Table 1. Equations of daily intake dose via various exposure pathways**

No.		
1	Soil ingestion	$CDI_{ingestion-soil} = \frac{CSXIRXCFXEFXED}{BW \times AT}$
2	Soil inhalation	$CDI_{inhale-soil} = \frac{CSXPM_{10}XDRAIXPIAAXAFSPXCFXEFXED}{BW \times AT}$
3	Soil dermal absorption	$CDI_{dermal-soil} = \frac{CSXAFXSAAXABSXCFXEFXED}{BW \times AT}$
4	Crop oral intake	$CDI_{crop} = \frac{C_{crop} \times IR_{crop} \times EF \times ED}{BW \times AT}$

Where, CDI: Chronic daily dose intake; CS: Soil HM content in (mg/kg); IR: Ingestion rate of soil (mg/day); CF: Conversion factor (kg/mg); EF: Frequency of exposure (day/a); ED: Duration of exposure (a); BW: Body weight (kg); AT: Average time (day); PM<sub>10</sub>: In ambient air content of inhalable particulates (mg/m<sup>3</sup>); DRAI: Daily rate of air inhalation (m<sup>3</sup>/day); PIAF: Inhaled particulates retention fraction in body; AFSP: In air fraction of soil-borne particulates; AF: Factor of skin adherence (mg/cm<sup>2</sup>); SA: Surface area of skin exposed (cm<sup>2</sup>); ABS: Factor of dermal absorption; C<sub>crop</sub>: Crop HM content in (mg/kg); IR<sub>crop</sub>: Rate of ingestion of crop (g/day).

**Table 2. The values of various parameters**

Parameter	Value of Parameter	References
CS	observed value	
IR	100	[33]
CF	10 <sup>-6</sup>	[34]
EF	350	[34]
ED	30	[34]
BW	60	Average body weight of Indians
AT	365 x 70 (carcinogens) 365x ED (Non- carcinogenic)	[33]
PM <sub>10</sub>	0.063	[35]
DRAI	14.5	[36]
PIAF	0.75	[36]
AFSP	0.5	[36]
AF	0.2	[33]
SA	5408	[33]
ABS	0.001	[33]
C <sub>crop</sub>	observed value	
IR <sub>crop</sub>	199.33	[37]

**2.7 Human Health Risk Assessment**

Health risks in humans are divided into carcinogenic and non-carcinogenic risks. These are mainly caused by diverse contaminants that enter the body through miscellaneous exposure pathways. Carcinogenic risk of an individual pertains to probability of developing any kind of cancer as a result of exposure to carcinogens in a lifetime. Carcinogenic risk can be calculated by the following equation:

$$\text{Cancer risk} = \text{CDI} \times \text{SF} \tag{1}$$

Where, cancer risk is a probability of an individual developing cancer, CDI is carcinogen's chronic daily intake dose (mg/kg/day), and SF: slope factor of carcinogenicity (mg/kg/day) [31]. 42 and 6.3 mg/kg/day are SF for inhalation of Cr and Cd were respectively [38,39]. The total

cancer risk (R) in the possible exposure pathways is the sum of carcinogenic risk of individual carcinogens. The cancer risk of less than 10<sup>-6</sup> can be ignored whereas risk in the range of 10<sup>-6</sup> to 10<sup>-4</sup> is tolerable and a risk exceeding 10<sup>-4</sup> is considered to be unacceptable.

Hazard quotient (HQ) can be described as the non-cancer risk. The ratio of chronic daily intake (CDI) and oral reference dose (RFD) of an individual element is called the hazard quotient and the equation is:

$$\text{HQ} = \text{CDI} / \text{RFD} \tag{2}$$

The oral reference doses were 3.5 x 10<sup>-3</sup>, 0.3, 4 x 10<sup>-2</sup>, 3 x 10<sup>-3</sup>, 1 x 10<sup>-3</sup> and 2 x 10<sup>-2</sup> mg/kg/day for Pb, Zn, Cu, Cr, Cd and Ni respectively; dermal reference doses were 5.25 x 10<sup>-4</sup>, 6 x 10<sup>-2</sup>, 1.2 x 10<sup>-2</sup>, 6 x 10<sup>-5</sup>, 1 x 10<sup>-5</sup> and 5.4 x 10<sup>-3</sup> mg/kg/day

for Pb, Zn, Cu, Cr, Cd and Ni, respectively, and the inhalation reference doses were  $3.52 \times 10^{-3}$ ,  $3.00 \times 10^{-1}$ ,  $4.02 \times 10^{-2}$ ,  $2.86 \times 10^{-5}$ ,  $2.4 \times 10^{-6}$  and  $2.06 \times 10^{-2}$  mg/kg/day for Pb, Zn, Cu, Cr, Cd and Ni respectively [38,40].

Hazard index (HI) is the sum of HQ of all the individual HMs thus HI is used to assess the overall non-carcinogenic risk posed by more than one HM. When the value of HQ or HI is  $<1$ , it is not likely to create any adverse health effects; but if the value exceeds 1, it is no more in the tolerable range, and as the value increases so thus the probability of occurrence of poor health effects.

## 2.8 Statistical Analysis

The statistical analysis was carried out using R statistical software version 4.3.1.

## 2.9 GIS Operations

The study area delineation and sampling design scheme was prepared using ArcGIS version 10.2.2 software.

## 3. RESULTS AND DISCUSSION

### 3.1 Physico-chemical Properties and Total HM Content of Surface Soil

The result of physico-chemical parameters of the surface soil samples are shown in Table 3. The pH of fallow land was significantly higher than agricultural land. There was not much significant difference observed in other soil parameters among the land uses. The soils were slightly acidic in nature with mean pH value in forest, fallow land and agriculture crop land at 5.35, 5.68 and 5.21 respectively. The EC value was in neutral range for all the land uses viz. forest, fallow land and crop land at 0.1, 0.12, 0.18 ( $\text{dSm}^{-1}$ ) respectively. Highest OC (%) was observed in fallow land followed by forest and cropland at 2.1, 1.87 and 1.56 (%) respectively. Fallow lands had higher percentage of finer particles in soil as compared to cropland, where mostly silt portion dominated. The results are in agreement with the soil characteristics of Goa which is highly acidic having high SOC content with fine textured soil [41]. The mean total HM concentration was higher than the background value (Table 4). Among all the metals Fe content was significantly higher in fallow land as compared to agriculture cropland. Similarly, Pb content is significantly

higher in agriculture cropland and fallow land as compared to natural vegetation. In case of Cd, Cr, Ni and Cu metals there was no significant difference observed among the land use types. Overall, fallow land had higher metal content in surface soil as compared to agriculture cropland while soils under natural vegetation elucidated metal concentration falling in between the two land use types. Thus metal content in different land uses in descending order was Fallow > Natural vegetation > Agricultural crop land. The Pearson's correlation matrix showed significantly negative correlation between pH with HMs but positive with OC and clay content of soil. However, in this study pH of fallow land was significantly higher than other land uses. Khaledian et al. [42] reported the rate of metals discharge into solution is lower at low-pH (pH = 4) as compared to mid- pH. So, it may be inferred that metal availability might be more in fallow land as compared to other land uses. Soil variables like pH, OC, soil texture and other parameters like organic matter, cation exchange capacity etc. are involved in influencing the availability of metals [43,44]. Moreover, the soil organic carbon and metal interaction is a complex mechanism involving several sorption theories. Several researchers have also reported a significantly positive correlation between SOC and total HM (Yang et al. 2013; Chen et al. 2016). The SOC content of fallow land is found to be higher than both agriculture cropland and natural vegetation. It has found that as compared to silty or sandy soils the HM content is higher in clay-rich soils [45,46]. The physico-chemical properties of different land use types advocates higher OC with higher percentage of fine textured characteristic of the soil in the whole study area is providing a conducive state for heavy metal accumulation vis a vis clogging of pores due to mine overburden deposition. However higher OC and clay content in fallow land is aggravating this condition. The proper management practices in agriculture cropland is helping in keeping away HM deposition and pore clogging.

### 3.2 Fractionation Forms of HM in Surface Soil

The chemical fractions of Ni, Pb, Zn, Mn, Cr, Cu, Fe and Cd metals in surface soils from three different land use systems are depicted as a percentage of the total metal concentration in Fig. 2. Among the four pools viz. weak acid-soluble fraction, reducible fraction, oxidizable fraction and residual fractions of HMs, residual fractions of all the HM the residual fractions are

in higher side. The residual fractions of Mn were highest among all the metals at 96.59 %. The residual fraction varied from 64.05% to 96.59% in all the three land use types. As compared to agriculture cropland residual fraction was higher in fallow land and natural vegetation but there was no significant difference observed among the land use types. This might be due to various cultivation practices by farmers on agriculture cropland affected the different pools of metals making unavailable fraction to be more available. This is indicative of relatively lower mobility and bioavailability of HM in soil. The fractions of metals that are bound to Fe-Mn oxides (reducible) and sulfide/organic matter (oxidizable) considered potentially bioavailable and under certain conditions they can be released to the environment. The weak acid soluble fraction of both Pb and Cd was found to be below detection limit. Generally to predict environmental risk associated with mobility of labile form of HMs risk assessment code is used. Toxicity gradation in accordance with the percentage of weak acid soluble forms is used to explain the risk associated. If less than 1%: there is no risk; 1–10%: low risk; 11–30%: medium risk; 31–50%: high risk; more than 50%: very high risk [47]. According to the above code, Ni, Pb, Zn, Mn and Fe posed no risk; Cr represented low risk; Cu represented medium risk in all the land use types. The acid-soluble fraction is considered bioavailable phase and found to be most mobile form in soil, showing potential biotoxicity [48], whereas the residual fraction also recognized as the stable fraction in soil system comprising mostly of secondary minerals, has the ability to hold metals within their crystal structure [49]. This high content of residual fraction might be originated from the highly weathered lateritic parent material of Goa with rich deposition of metals [50]. The residual fraction consists mostly of stable metals and over an environmentally related time scale they are not predicted to be released in soil solution [51]. There was no such immediate risk posed by the readily available metals in any land use type but in a time scale release of the reducible and oxidizable pools might alter the present equation.

### 3.3 PC Results

PC approach was validated using KMO (0.615) and Barlett's test ( $p < 0.001$ ). The percentage contribution of individual HMs in first two

Dimensions (Dim) were presented in (Fig. 3a and b) indicated that Dim1 accounting 42.5% variation was represented by Fe, Pb, Cr and Cd (contributions are above red threshold line). The second dimension elucidated 14.8% of variation in the data and was attributed by higher factor loading mainly for Mn, Ni and Cu. The results highlighted that the first dimension might be representing the HM combinations of mostly anthropogenic origin (Fe, Pb, Cr and Cd) followed by Dim 2 representing geogenic origin (Mn, Ni and Cu). Though Fe is a dominant metal of earth crust but the overburden deposits on soil surrounding the active iron mine is contributing more towards anthropogenic pool.

### 3.4 Vertical Distribution of HM in Soil Profile

To understand the deposition pattern and vertical mobility of anthropogenic origin metal Pb, Cr and Cd in soil profile on different land uses was also studied (Fig. 4). In case of Pb all the three land use types showed a steady concentration beneath the soil depth with a slight fluctuation after 30 cm. In case of Cr the fluctuation was more in cropland and natural vegetation. In cropland and natural vegetation the increase in concentration of Cr was observed after 60 cm of soil depth. In case of Cd a gradual increase in concentration was observed upto 60 cm of soil depth which subsided below the depth. Overall, fallow land showed significantly higher metal accumulation than cropland especially in plough layer (upto 30 cm). Agricultural land management practices and absorption of metals by crops may have led to lower metal concentration in plough layer. Moreover, a drastic reduction is noticed in metal concentration (especially in Cr) below 30 cm depth revealed that clogging of pores by mining overburden mixed runoff might be the reason for higher concentration in plough layer followed by sharp decrease in concentration down the depth. In case of natural vegetation the lower concentration of Cd, Cr and Pb at upper surface of 30 cm may be attributed to plant uptake led decrease in concentrations of HM in surface soils. In agriculture cropland the metals followed rather even vertical distribution pattern. The agricultural activities may have blended soils in cropland area causing an even HMs distribution along the soil profiles [52,53].

**Table 3. Soil physico-chemical properties in the surface soils under different land use types of the study area**

Land Use type		pH (1:2.5)	EC (dSm <sup>-1</sup> )	OC (%)	CEC (meq/100g)	Sand (%)	Clay (%)	Silt (%)
<b>Agriculture crop land</b>	Mean	5.21±0.6b	0.18±0.13a	1.6±0.80a	9.7±2.6a	41.8±4.5a	39.9±7.4a	18.2±5.9a
	Min	4.3	0.06	0.8	6.5	35.9	23.1	11.8
	Max	6.7	0.90	2.9	14.7	48.4	46.6	31.3
<b>Fallow land</b>	Mean	5.68±0.6a	0.12±0.06a	2.1±0.78a	11.9±3.9a	39.2±6.1a	44.9±7.9a	16.0±5.8a
	Min	4.2	0.04	0.5	6.2	23.6	34.4	6.4
	Max	6.9	0.26	3.7	19.4	50.0	70.0	30.0
<b>Natural vegetation</b>	Mean	5.35±0.5ab	0.10±0.08a	1.9±0.76a	11.1±2.9a	40.7±4.3a	42.7±8.5a	16.6±5.7a
	Min	4.1	0.04	0.4	4.8	29.33	23.8	4.6
	Max	6.0	0.45	3.5	22.0	52.00	60.3	26.2

a) OC = Organic carbon

b) Values are means ±standard deviations (n = 21, natural vegetation; n = 10, fallow land; n = 7, agriculture crop land)

c) Means followed by the same letter(s) in a column are not significantly different (P <0:05)

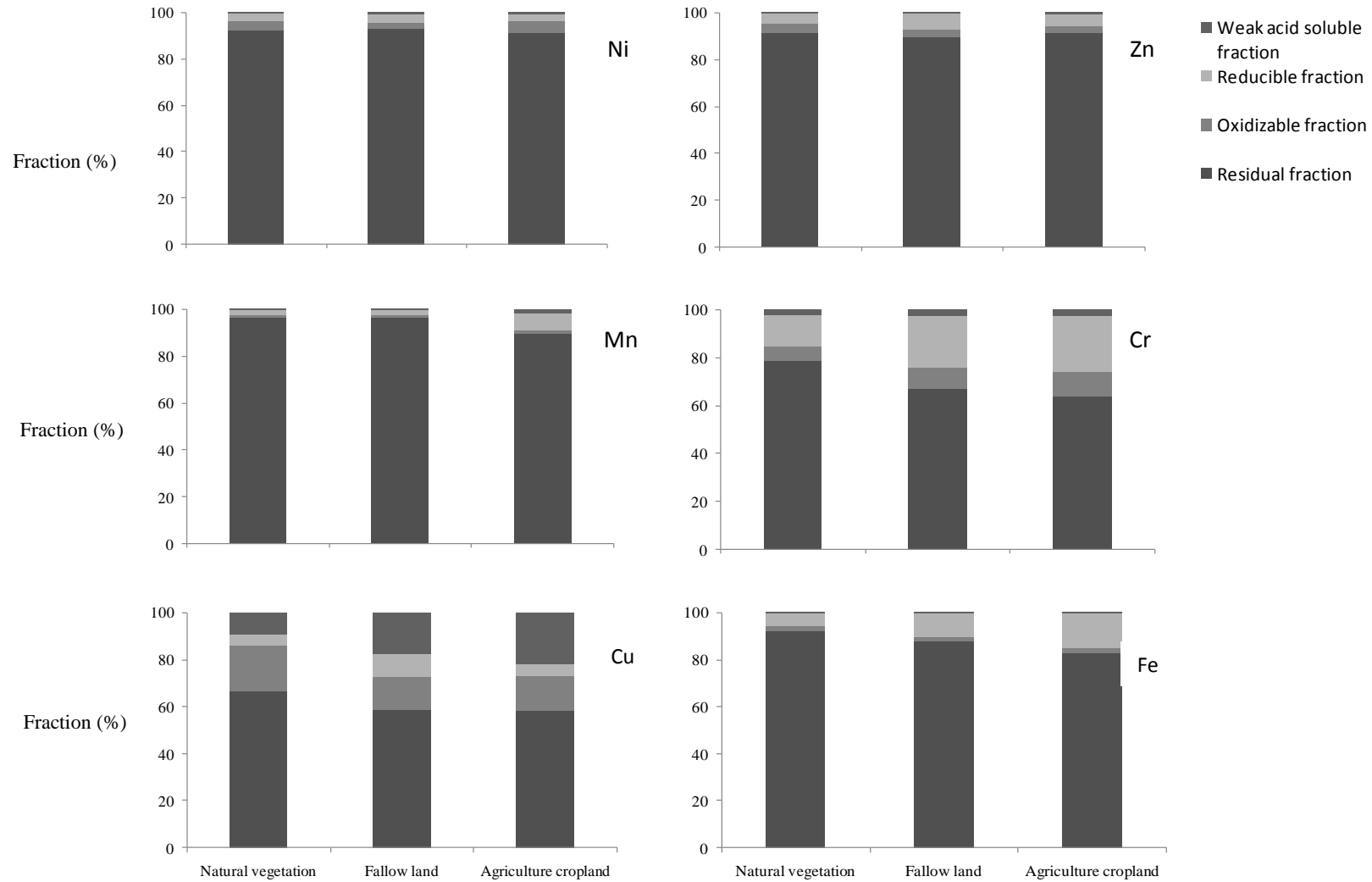
**Table 4. Mean total HM concentration in the surface soils under different land use types of the study area**

Land use	Fe (%)	Mn (mg kg <sup>-1</sup> )	Zn (mg kg <sup>-1</sup> )	Pb (mg kg <sup>-1</sup> )	Cd (mg kg <sup>-1</sup> )	Cr (mg kg <sup>-1</sup> )	Ni (mg kg <sup>-1</sup> )	Cu (mg kg <sup>-1</sup> )
<b>Agriculture crop land</b>	14.09±	755.43±	73.13±	103.43±	26.39±	76.01±	35.23±	124.02±
	2.86a	273.32 a	15.05 a	76.91 a	0.44 a	5.95 a	27.07a	3.03 a
<b>Fallow land</b>	18.42±	1783.80±	74.28±	106.30±	26.61±	71.09±	52.00±	125.94±
	11.31b	1371.98 a	19.79 a	69.09 a	0.65 a	20.17 a	36.8 a	5.36 a
<b>Natural vegetation</b>	17.30±	2148.10±	73.71±	83.35±	25.99±	72.38±	56.81±	128.84±
	11.46ab	2238.26 a	23.37 a	63.71 b	1.32 a	21.06 a	38.40 a	5.92 a
<b>Mean background value</b>	0.45	99.86	32.10	13.49	2.56	39.99	17.38	11.69

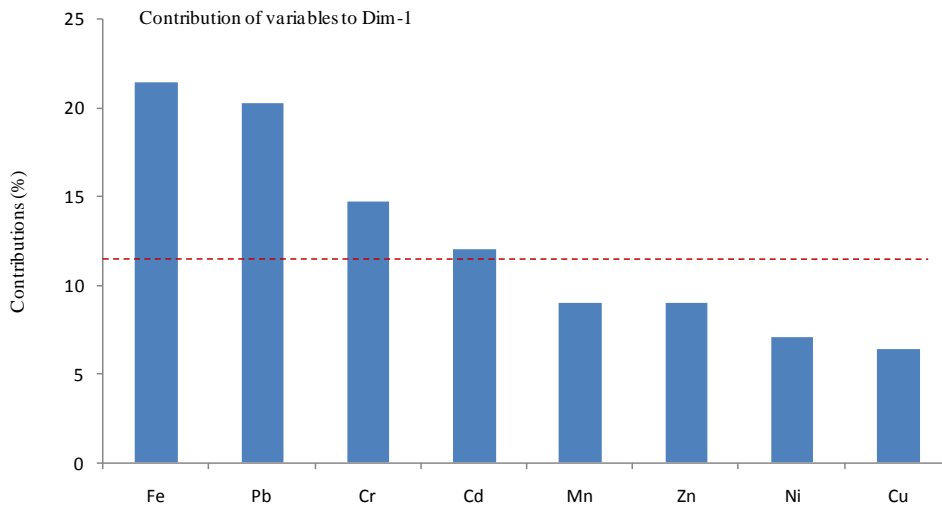
a) Values are means ±standard deviations (n = 21, natural vegetation; n = 10, fallow land; n = 7, agriculture crop land).

b) Means followed by the same letter(s) in a column are not significantly different (P <0:05)

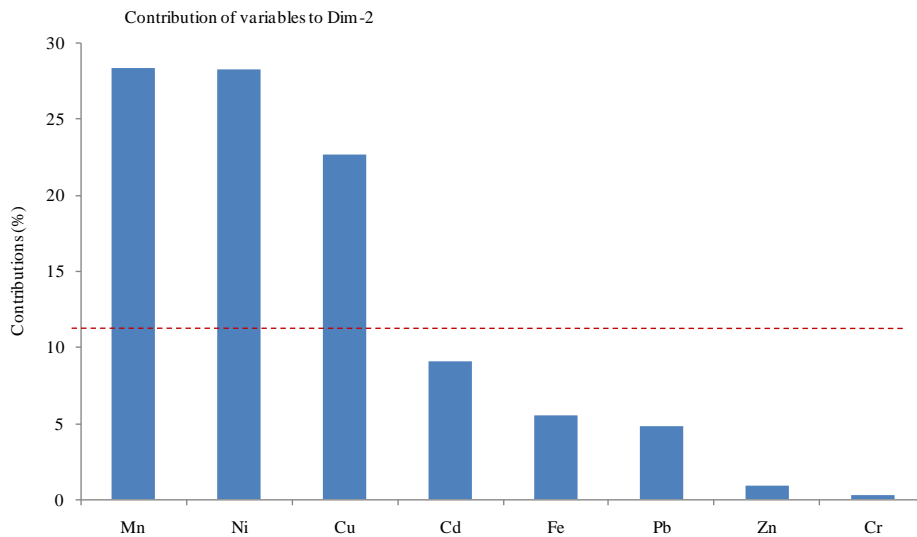




**Fig. 2. Different fractionation forms of heavy metals in the surface soils under different land use types**



**Fig. 3a. Percentage contribution of heavy metals in dimension 1 of PC analysis.**



**Fig. 3b. Percentage contribution of heavy metals in dimension 2 of PC analysis**

### 3.5 Anthropogenic HM in Rice Grain

The anthropogenic HM concentration in the edible part of rice is illustrated in Table 5. Cd, Cr and Pb are the type of metals that have no known physiological activity with high degree of toxicity and are of public health significance [54,55]. Therefore, these three anthropogenic origin priority metals rank among the priority metals [56]. The mean concentration of almost all the three metals in rice grain was near maximum permissible levels (MPL). The mean HM concentrations in the soil of agriculture crop land decreased in the order of Pb>Cr> Cd, while the

HM content in rice grain descended in the order of Pb>Cd> Cr. Though the mean concentration of Pb was higher in both agricultural soil and grain as compared to other priority metals, the actual concentration in grain was very low as compared to the soil. The result is in agreement with other studies reported to have no significant correlation between soil and crop uptake [57,58]. The Pb in soil is dominantly found in insoluble forms such as Pb(OH)<sub>2</sub>, PbCO<sub>3</sub>, Pb(PO<sub>4</sub>)<sub>2</sub> etc. while the soluble form of Pb content is very low. The insoluble Pb compounds are mostly stable metal complexes and chelates. Consequently, this results into low migration rate of Pb from soil

to crops. Hence, the soil surface is mainly suffers from lead pollution and crops grown on it suffers least. Plant response to increased Cd content in soil varies with the soil physico-chemical properties and other plant factors to facilitate uptake [59]. High organic carbon and fine textured soil as observed in our study, generally stabilize Cd in soil and are main factor involved in phytostabilization [53]. High OC in soil causes attenuation and reduced phytoavailability of HMs [60] while the soluble form of Pb content is very low. The insoluble Pb compounds are mostly stable metal complexes and chelates. Consequently, this results into low migration rate of Pb from soil to crops. Hence, the soil surface is mainly suffers from lead pollution and crops grown on it suffers least. Plant response to increased Cd content in soil varies with the soil physico-chemical properties and other plant factors to facilitate uptake [61]. High organic carbon and fine textured soil as observed in our study, generally stabilize Cd in soil and are main factor involved in phytostabilization [53]. High OC in soil causes attenuation and reduced phytoavailability of HMs [60].

### 3.6 Assessment of Health Risk

#### 3.6.1 The daily intake of HMs

The average daily intake of anthropogenic HM Pb, Cd and Cr by the local residents via several exposure pathways is listed in Table 6. It was observed that HM intake through diet was dominant exposure route. While the CDI value showed soil ingestion was found to be the main contributor in the entire pathways of soil exposure. The CDI value in descending order are ingestion > dermal absorption > inhalation. CDI

**Table 6. Various exposure pathways responsible for daily intake of HMs (mgkg<sup>-1</sup>day<sup>-1</sup>)**

Pathway	Cr	Cd	Pb
Soil ingestion	4.27x10 <sup>-5</sup>	1.72x10 <sup>-5</sup>	4.64x10 <sup>-5</sup>
Soil dermal absorption	4.6x10 <sup>-7</sup>	5.9x10 <sup>-7</sup>	5.0x10 <sup>-7</sup>
Soil inhalation	1.46x10 <sup>-7</sup>	5.89 x10 <sup>-8</sup>	1.59 x10 <sup>-7</sup>
Rice diet	0.12	0.14	0.36

**Table 7. Non-carcinogenic hazard quotient (HQ) of HMs via different pathways**

	Pb	Cr	Cd
HQ oral intake	10.28	41.51	136.16
HQ dermal	9.55x10 <sup>-6</sup>	7.70x10 <sup>-3</sup>	1.86x10 <sup>-2</sup>
HQ inhalation	0.45x10 <sup>-6</sup>	4.88x10 <sup>-3</sup>	2.45x10 <sup>-3</sup>
HI	10.28	41.52	136.18

of soil pathways followed same behavior as reported in other studies [61-63].

#### 3.6.2 Health risk assessment

The contribution of all exposure routes to non-carcinogenic risks for the anthropogenic HM is shown in Table 7. As illustrated in daily intake case, HQ through oral intake was the most significant contributor. Among all the HQ of Cd was significantly higher as compared to Pb and Cr, due to high concentration present in edible part of rice and lower RfD value. The HI values of the HMs in the descending order for the metals with data of HQ oral intake are: Cd > Cr > Pb. Since the total non-carcinogenic hazard index (HI) value for all the three metals considerably exceeded the safe level thus the potential non-carcinogenic health risks to local residents due to these metals are a matter of concern. The carcinogenic risk factor was derived for the HMs Cd and Cr except Pb, due to unavailability of carcinogenic slope factors for Pb. The carcinogenic risks (R) were measured only through inhalation mode. The calculated total risk (R) value was 6.5x10<sup>-6</sup>, which comes under the acceptable range of 10<sup>-6</sup> to 10<sup>-4</sup>. So there were no carcinogenic risks out of these metals through inhalation pathway was observed.

**Table 5. Metal concentration in grain of rice (mg kg-1)**

Metals	Cd	Cr	Pb
Mean	0.20	0.18	0.53
SD	0.02	0.10	0.04
Min	0.19	0.13	0.48
Max	0.24	0.38	0.57
Standard value (MPL)*	1	0.2	0.2

\*Li et al. [64]

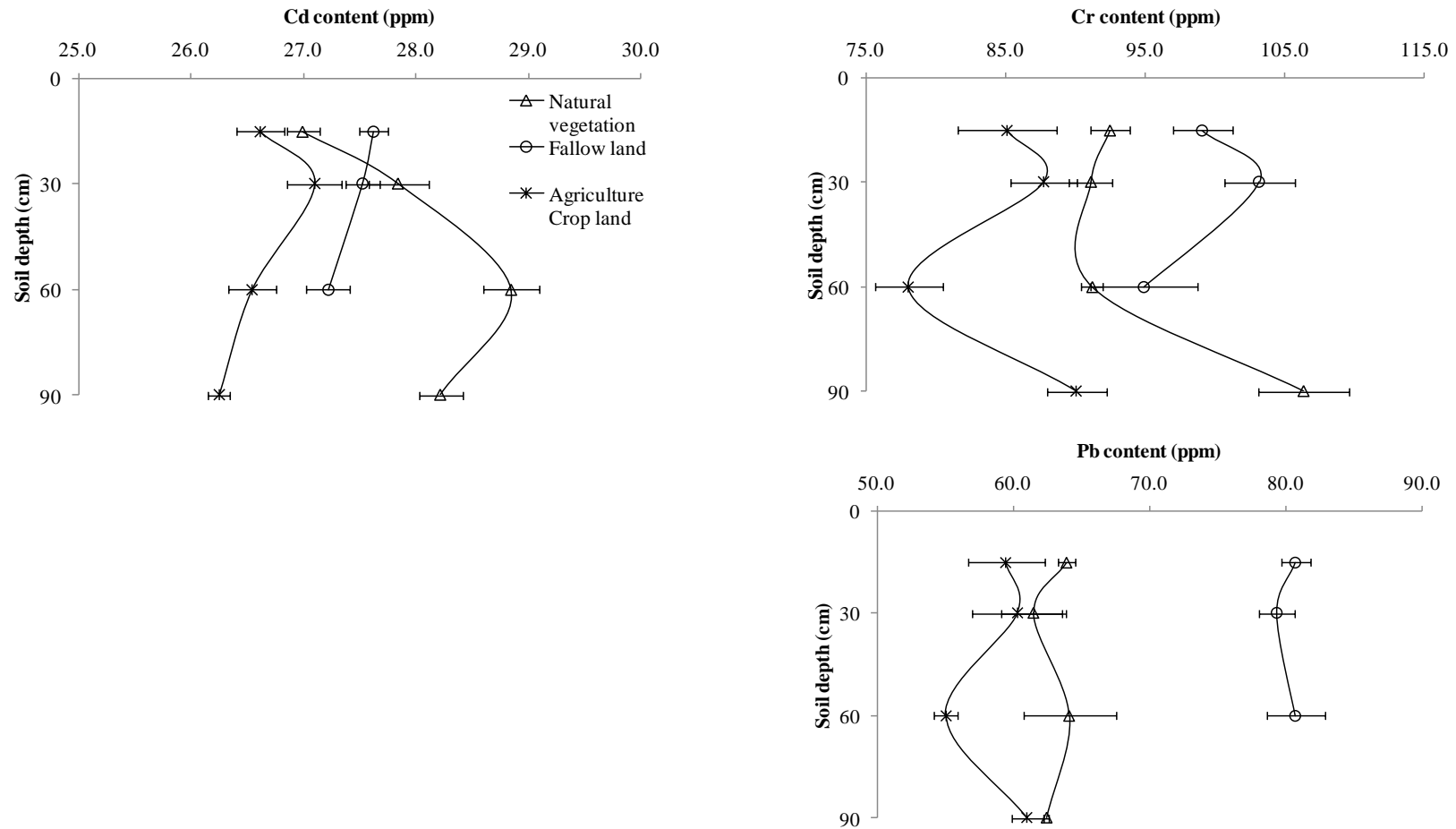


Fig. 4. Distribution patterns of mean heavy metals in soil profiles under different land use types (n = 3, natural vegetation; n = 2, fallow land; n = 3, crop land)

#### 4. CONCLUSION

The total metal content of the study area soil exceeded the background concentrations. The characteristic of the soils of the study area with lower pH, higher soil OC content and fine texture are influencing heavy metal mobility as indicated by more residual as compared to weak acid soluble fraction. The residual fraction generally does not pose immediate threat to the ecosystem nevertheless with passage of time along with other environmental factors this equation may change. Cd, Cr and Pb were found to be associated with mining activity and thus contributed more towards anthropogenic metal pool. Fallow land showed more anthropogenic metal deposition in plough layer as compared to other land uses. This may be the reason behind clogging of pores as evidenced by waterlogged fallow land [65]. The mean total anthropogenic metal accumulation in rice grain was found to be much lower as compared to the soil. However, the non-carcinogenic hazard index suggested potential health risk to local residents due to this rice grain consumption. Moreover, the carcinogenic hazard index through inhalation mode suggested no potential risk. Higher OC and fine textured soil of the region may be responsible for diminishing both metal mobility and plant uptake thus shielding the ecosystem from the toxic effect of the metals. The site specific management of this area is requisite of the time to restore ecosystem sustainability of the region.

#### DATA AVAILABILITY

The data used to support the findings of this study are available from the corresponding author upon request.

#### ACKNOWLEDGEMENT

The authors thank Indian Council of Agricultural Research (ICAR) - National Bureau of Soil Survey and Land Use Planning for providing necessary research assistance and funding for this study. The authors are also gratified to the support of Ms. Heena Kene and other laboratory colleagues during sample collection, preparation and analysis.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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