Metal contamination of agricultural soils in the copper mining areas of Singhbhum shear zone in India

SOMA GIRI^{1,*}, ABHAY KUMAR SINGH¹ and MUKESH KUMAR MAHATO²

¹Natural Resources and Environmental Management Group, CSIR-Central Institute of Mining and Fuel Research, Barua Road, Dhanbad 826 015, India.

²Department of Chemistry, Vinoba Bhave University, Hazaribag 825 301, India.

*Corresponding author. e-mail: soma0307@gmail.com

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The study was intended to investigate the heavy metal contamination in the agricultural soils of the copper mining areas in Singhbhum shear zone, India. The total concentrations of the metals were determined by inductively coupled plasma-mass spectrometer (ICPMS). Pollution levels were assessed by calculating enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factors (CF), pollution load index (PLI), Nemerow index and ecological risk index (R_I). The metal concentrations in the soil samples exceeded the average shale values for almost all the metals. Principal component analysis resulted in extraction of three factors explaining 82.6% of the data variability and indicated anthropogenic contribution of Cu, Ni, Co, Cr, Mn and Pb. The EF and I_{geo} values indicated very high contamination with respect to Cu followed by As and Zn in the agricultural soils. The values of PLI, R_I and Nemerow index, which considered the overall effect of all the studied metals on the soils, revealed that 50% of the locations were highly polluted with respect to metals. The pollution levels varied with the proximity to the copper mining and processing units. Consequently, the results advocate the necessity of periodic monitoring of the agricultural soils of the area and development of proper management strategies to reduce the metal pollution.

Keywords. Agricultural soil; heavy metals; copper mining areas; multivariate analysis; geo-accumulation index; Nemerow index.

1. Introduction

The contamination of agricultural soils by heavy metals has aroused considerable apprehension worldwide due to their toxicity and persistence (Cao *et al.* 2010; Ma *et al.* 2015). The sources of heavy metals in the soil can be of both natural and anthropogenic origins. Of the other anthropogenic sources, mining has emerged as one of the most important sources of heavy metals in the surrounding environment. Mining and milling operation together with grinding, concentrating

ores and disposal of tailings, along with mine and mill waste water, provide obvious sources of contamination (Adriano 2001; Li *et al.* 2014). Heavy metal contamination of the soils in the vicinity of the mine sites are recognized as one of the serious environmental problems around the world. The heavy metal contaminated soils have a potential to contaminate the other constituents of the environment like surface and groundwater sources, air and the agricultural crops growing on them (Borgese *et al.* 2013; Ji *et al.* 2013; Li *et al.* 2014).

Some metals like Cu, Fe, Mn, Ni and Zn are important as micronutrients for life processes in living organisms for life and regulate many physiological function of the body. However, many other metals like As, Cd, Cr and Pb have no known physiological activity and may exhibit toxicity even at low concentrations (Bruins *et al.* 2000; Cohen *et al.* 2001). Long-term exposure to heavy metals may lead to many adverse health effects including a variety of cancers, mental retardation and neurological, cardiovascular, kidney and bone diseases (Adriano 2001; Prüss-Ustün *et al.* 2011).

The study area falls in the Singhbhum shear zone (SSZ) which is known for its rich mineral deposits and production of copper and uranium ores. Although, few studies were carried out on the heavy metal distribution in the sediments, surface and groundwater sources and fish samples of the Subarnarekha River basin of which the study area is a part (Upadhyay *et al.* 2006; Giri *et al.* 2013; Giri and Singh 2014a, b, 2015, 2016). The studies indicated the deleterious effects of the copper mining and milling activities on the environmental components.

However, practically no serious efforts has been made to study the heavy metal contents of agricultural soils in the vicinity of copper mining areas of Singhbhum shear zone. The present study aims (1) to determine the concentration of the heavy metals (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V and Zn) in the agricultural soils, (2) to ascertain whether there was contamination with respect to these metals using various indices, and (3) to identify the sources of the metals in the soils by multivariate statistical analysis.

2. Materials and methods

2.1 Site description

The study was carried out in the copper mining areas of Singhbhum Shear Zone of Jharkhand which is known to be rich in mineral resources like copper, iron, uranium, gold and kyanite. The present study area extends from 86°20' to 86°30'E longitudes and 22°30' to 22°42'N latitudes, covering an area of about 160 km² and falls in Mosabani, Dhalbhumgarh and Ghatsila blocks of East Singhbhum district of Jharkhand state. The climate of the study area is temperate. Annual rainfall is 1200–1400 mm. This area is subject to the southwest monsoon and receives heavy rain (about 80%) during June to September (monsoon season). The

major crops grown in the study area are paddy, maize, pulses and some seasonal vegetables and fruits.

The Singhbhum shear zone forms an arcuate highly deformed linear zone in the Singhbhum crustal province and is known as one of the most potential sulphide bearing stretch of India. Some of the copper mining and processing entities of the area are at Rakha, Kendadih, Surda, Badia, Mosabani, Ghatsila and Maubhandar. The main copper belt extends over a distance of 130 km and harbors 18% of the total copper reserves of India. The copper mineralization along Singhbhum copper belt is located along the Dhanjori group of rocks at south of shear zone and Singhbhum group of rocks at north of shear zone. The copper sulphide mineralization is associated mainly with the meta-volcanics and meta-tuff sequences of the Dhanjori and Singhbhum Groups. The sulphide minerals consist predominantly of chalcopyrite, followed by pyrite and pyrrhotite, accompanied by magnetite and minor pentlandite, millerite, violarite, sphalerite and molybdenite. The gangue minerals are quartz, biotite, chlorite and sericite in variable proportions. The major rock types of the region are soda granite, Dhanjori lavas and Epidiorite-schist (Dunn and Dey 1942; Mukherjee 1968).

2.2 Sampling and analysis

Random samples were collected from 16 locations in the vicinity of the mining affected areas. The sampling locations were between 0.5 and 2.5 km from the mining or processing industries. Some locations (sample nos. 2, 3 and 6) were selected to study the effect of vehicular and other anthropogenic activities. The sample no. 1 served as a control as it was located in the forest area far from any copper mining and processing activities. The samples were representative for the study area.

Each soil sample of about 1 kg was taken from the depths of 0–15 cm, which represented the plough layer. Then, the soil samples were packed and sealed in polyethylene bags and transported to the laboratory for sample preparation. The samples were air dried at room temperature (25–30°C). Representative sub-sampling of the dried soils was carried out by coning and quartering method for uniform mixing and reducing variability of the samples and reducing to a desired weight (Rubio and Ure 1993; Loska *et al.* 2004; Alloway 2013). Then about 100 g of the sample was taken in a porcelain dish and dried in an oven at 110°C for 24 hr. The

samples were powdered in a dry mortar–pestle and sieved through standard sieve of 200 mesh size (Giri *et al.* 2013). The samples were then subjected to digestion in microwave by the method 3052 as given by USEPA (1996). Aliquots were preserved for the analysis of metals. Concentrations of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn were determined in soil samples using inductively coupled plasma–mass spectrometry (ICP-MS, Perkin Elmer Elan DRC-e).

2.3 Quality assurance and quality control

For the validation of the analytical procedure, standard reference materials (SRM) of estuarine sediment (SRM 1646a) supplied by the National Institute of Standards and Technology (NIST), USA was used. The heavy metal concentrations analyzed in the SRMs were in good agreement with the certificate values, which confirmed the feasibility of the analytical protocols in the determination of heavy metals in soil. The percentage of recovery varied from 89.4 to 109.7.

2.4 Statistical analysis

Pearson's correlation is a bivariate correlation which gives some idea regarding the relationship between two sets of data, and its coefficient is a measure of the strength of the association between the two variables (Ma *et al.* 2015). For the present study, Pearson's correlation analysis was selected to determine the relationships among different heavy metals. Principal component analysis (PCA) is a variation reduction technique in which a number of measured parameters can be transformed into a small number of artificial variables known as principal components (PC). The number of extracted PC is equal to the number of variables included in the analysis; however, normally PCs having eigen values >1 are taken into consideration as they explain for the maximum variance in the observed parameter (Kolsi *et al.* 2013; Huang *et al.* 2014). Varimax rotation is applied to all the extracted principal components to reduce the contribution of the variables which are not significant (Closs and Nichol 1975). Each variable considered for PCA has a weight factor associated with it. This weight factor, also referred to as PC score, is the correlation between the original variable and a factor. A PC score close to ± 1 indicates a strong correlation between the given variable and the factor. To evaluate the validity of PCA, the Barlett's

test of sphericity and Kaiser–Meyer–Olkin (KMO) test as a measure of sampling adequacy were taken into consideration. Large KMO value (>0.5) and suitable significance of Barlett's test ($p < 0.05$) were necessary to ensure the validity of PCA (Chen *et al.* 2014; Fu *et al.* 2014; Ma *et al.* 2015).

2.5 Calculation of indices to assess anthropogenic influence

2.5.1 Enrichment factor (EF)

In order to assess the degree of anthropogenic influence with respect to metals, the enrichment factor (EF) was calculated for each metal in the soil using the equation (1):

$$EF = \frac{(C_X/C_{Fe})_s}{(C_X/C_{Fe})_c} \quad (1)$$

where C_X and C_{Fe} refer to the concentration of element X and Fe in the soil (s) and earth's crust (c), respectively. Iron was used as reference element (Schiff and Weisberg 1999; Turner and Millward 2000) and the metal concentrations were normalized to the textural characteristic of soils with respect to Fe. A five-category ranking system is used in this paper to denote the degree of anthropogenic contamination (Sutherland 2000; Kartal *et al.* 2006; Giri *et al.* 2013). The categories are:

- $EF < 2$ states deficiency to minimal contamination
- $EF = 2\text{--}5$ moderate contamination
- $EF = 5\text{--}20$ significant contamination
- $EF = 20\text{--}40$ very high contamination
- $EF > 40$ extremely high contamination.

2.5.2 Geo-accumulation index (I_{geo})

Pollution levels of metal in soils can also be exemplified by the calculations of the geo-accumulation index values put forward by Muller (1979), which can be evaluated by equation (2). This is a way to assess the pollution levels in soils or sediments with respect to the toxic metals by comparing the present and past concentrations.

$$I_{geo} = \log_2(C_n/1.5B_n) \quad (2)$$

where C_n is the measured concentration of the heavy metal n in the soil and B_n is the geochemical background reference value. The reference value used for the study was average shale and control soil. The constant 1.5 is introduced in the equation

arbitrarily to account for the natural fluctuations that may have occurred throughout the years in the environment (Christophoridis *et al.* 2009).

2.5.3 Pollution load index (PLI)

Pollution load index (PLI) was introduced by Tomlison *et al.* (1980) to determine the extent of pollution due to the combined effect of metals in the soils (Giri *et al.* 2013). PLI is calculated as geometric mean of concentration factor (CF) value of n number of studied metals (equation 3). The index is based on the CF of each metal present in the soil or sediment which is expressed as equation (4) (Salomons and Forstner 1984).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (3)$$

where n is the number of metals and CF is the contamination factor.

$$CF = \frac{\text{Metal concentration in soil}}{\text{Metal concentration in average shale}} \quad (4)$$

Pollution load index (PLI) is a comparative means to evaluate the level of metal pollution and classified as follows:

- No pollution ($PLI < 1$)
- Moderate pollution ($1 < PLI < 2$)
- Heavy pollution ($2 < PLI < 3$)
- Extremely heavy pollution ($3 < PLI$).

2.5.4 Nemerow comprehensive index

For assessing the environmental quality of the agricultural soils around the copper mining areas, another index, i.e., the Nemerow comprehensive index (P_s) (Li *et al.* 2008) was used. The index is calculated using the following equations (5–7):

$$C_f^i = \frac{C_s^i}{C_n^i} \quad (5)$$

$$mC_d = \left(\sum_{i=1}^n C_f^i \right) / n. \quad (6)$$

$$P_s = \sqrt{\frac{(mC_d)^2 + (C_{f_{\max}}^i)^2}{2}}, \quad (7)$$

where C_s^i is the measured concentration of metal i in the soil sample (unit: mg/kg), C_n^i is the geochemical background value (average shale in this study) of metal i , (unit: mg/kg), C_f^i is the single pollution index of metal i , $C_{f_{\max}}^i$ is the maximum value of single pollution index of all metals, n is the number of

metals measured in the soil sample (i.e., $n = 11$ in this study), mC_d is Hakanson's modified degree of contamination index which summates all the single pollution indices (C_f^i) to estimate the overall contamination of metals at a location (Hakanson 1980).

The mC_d value is classified into seven classes by Brady *et al.* (2015) as:

- $mC_d < 1.5$ as unpolluted;
- $1.5 \leq mC_d < 2$ as slightly polluted;
- $2 \leq mC_d < 4$ as moderately polluted;
- $4 \leq mC_d < 8$ as considerably polluted;
- $8 \leq mC_d < 16$ as highly polluted;
- $16 \leq mC_d < 32$ as strongly polluted;
- $mC_d \geq 32$ as extremely polluted.

The Nemerow index is classified into five groups by Wu *et al.* (2015) as:

- uncontaminated if $P_s < 1$;
- slightly contaminated if $1 \leq P_s < 2$;

Figure 1. Map of the study area with sampling locations.

- moderately contaminated if $2 \leq P_s < 3$;
- strongly contaminated if $3 \leq P_s < 5$; and
- seriously contaminated if $P_s \geq 5$ (Ma *et al.* 2015).

3. Assessment of potential ecological risk

Potential ecological risk assessment was proposed by Hakanson (1980) to assess the degree of heavy metal pollution in soil or sediments, according to the toxicity of heavy metals and the response of the environment. Risk index (R_I) is introduced to evaluate the contamination degree of the soils considering the effect of multiple metals. R_I is defined according to equation (8) as summation of E_r^i of heavy metals where E_r^i is the monomial potential ecological risk factor defined by equation (9).

$$R_I = \sum E_r^i \quad (8)$$

$$E_r^i = T_i \frac{C_i}{C_0} \quad (9)$$

T_i is the toxic response factor for the metals and the values for As, Cd, Cu, Pb, Ni, Zn and Cr are

10, 30, 5, 5, 5, 1 and 2, respectively (Hilton *et al.* 1985; Wang *et al.* 2011). C_i is the concentration of metals in the soil, and C_0 is a reference value for metals. In the present study, the concentrations of the metals of the control site are taken as reference values.

The degree of E_r^i is classified as follows: $E_r^i < 40$, low risk; $40 \leq E_r^i < 80$, moderate risk; $80 \leq E_r^i < 160$, considerable risk; $160 \leq E_r^i < 320$, high risk; and $E_r^i \geq 320$, very high risk. The potential ecological R_I can be grouped into four categories with slight modification according to the recommended values by Wu *et al.* (2015): $R_I < 100$, low risk; $100 \leq R_I < 200$, moderate risk; $200 \leq R_I < 400$, considerable risk; and $R_I \geq 400$, very high risk.

4. Results and discussion

4.1 Distribution of metals in soil

Large variations were observed in the concentration of the metals collected from the 16 locations around the copper mining areas of SSZ (figure 1).

Table 1. Descriptive data of metals (mg kg^{-1}) in agricultural soils from the copper mining areas of Singhbhum shear zone.

	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Minimum	9.6	0.08	12.1	65.2	54.3	20,147	111.7	35.2	21.3	65.3	52.9
Maximum	121.1	0.84	63.8	751.0	3314.4	64,695	1045.0	303.4	102.6	200.8	621.4
Geomean	29.7	0.34	32.3	149.6	218.0	38,215	520.8	94.2	47.0	113.6	210.6
World average ^a	6.0	0.350	8.0	70.0	30.0	40,000	1000	50.0	35.0	90.0	90.0
Shale average ^b	13.0	0.3	19.0	90.0	45.0	47,200	850	68.0	20.0	130.0	95.0

^a Bowen (1979), ^b Turekian and Wedepohl (1961).

Figure 2. Concentrations of Zn, Ni, Cu, Cr, Co and As (mg kg^{-1}) in the agricultural soils of the study area.

Table 2. Comparison of metals (mg kg^{-1}) in agricultural soils with other studies.

Location	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn	References
Zhangjiakou (China)	8.51	0.138		56.7	30.9			24.5	20.5		68.1	Liang <i>et al.</i> (2015)
Larissa (Greece)	17.1	0.5		245.6	94.0			165.3	15.2		97.6	Skordas <i>et al.</i> (2013)
Manisa (Turkey)	22.3	0.14			38.7			98.2	12.9		54.4	Çolak (2012)
Chenzhou (China)	231	2.14		70.1	36.0			45.7	204		244	Ma <i>et al.</i> (2015)
Qingdao (China)		0.29		82.2	62.1			83.7	250.2		208.8	Xu <i>et al.</i> (2016)
Zhejiang (China)	15.5	0.72		47.7					68.6			Liu <i>et al.</i> (2013)
Zhangjiagang (China)	8.74	0.17		64.3	33.3				27.3			Hu <i>et al.</i> (2016)
Sukinda (India)				11336	6.2						84.6	Kumar <i>et al.</i> (2014)
Kombat (Namibia)			5.1	20	108	13,873	760	9.4	119		45	Mileusnić <i>et al.</i> (2014)
Miedzianka (Poland)	46	1.4		34.1	209		1334	19.4	46		82	Galuszka <i>et al.</i> (2015)
Shahrud (Iran)		0.3		83.7	24.3			33.3	18.1		80.4	Mirzaei <i>et al.</i> (2015)
Zaheerabad (India)	3.3		58.6	203.1	118.4			31.5	14.5	482.6	99.3	Sakram <i>et al.</i> (2015)
Bogra (Bangladesh)	36	6.3		54	57			83	97			Islam <i>et al.</i> (2015)
East Singbhum (India)	29.7	0.34	32.3	149.6	218.0	38,215	520.8	94.2	47.0	113.6	210.6	Present study

The minimum, maximum and geometric mean concentrations of the metals in the study area are provided in table 1. As frequently observed in the environmental samples, the concentrations of metals in the soil were better elucidated by the log normal distribution and thus, the central tendency was represented by geometric mean. The geometric mean concentration of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn was 29.7, 0.34, 32.3, 149.6, 218, 38215, 520.8, 94.2, 47, 113.6 and 210.6 mg kg^{-1} , respectively. The sequence of the metal concentration was generally as $\text{Fe} > \text{Mn} > \text{Cu} > \text{Zn} > \text{Cr} > \text{V} > \text{Ni} > \text{As} > \text{Pb} > \text{Co} > \text{Cd}$. The metal concentrations in the soil of the study area exceeded the values of the average concentration of metals in the shale (Turekian and Wedepohl 1961) and world average (Bowen 1979) for almost all the metals. As the study area is characterized by the presence of metal bearing formations accompanied with mining and industrial operations, it is obvious to have elevated levels of metals in the soils (Forstner and Wiltman 1983; Preston and Chester 1996). However, the amplification was more prominent for As, Co, Cr, Cu, Ni and Zn. The concentrations of these metals in the soils are given in figure 2. The concentrations of metals were observed to be generally higher at the locations which were near to existing or abandoned copper mining and processing units, e.g., Badia, Sohada, Terenga, Kendadih and Bodamdera.

Table 2 provides comparison of the metals in the agricultural soils of the study area with the other agricultural soils worldwide. The concentrations of the metals are in accordance with the other studies except for Cu which may be attributed to the copper mineralization and mining in the study area.

4.2 Statistical analysis

Pearson's correlation coefficients of the metals in the agricultural soils from the study area are depicted in table 3. Significant positive associations were seen ($p < 0.01$) for Fe with Mn, As and V; V with As and Cd; Cd with Zn; Cu with Ni and Co; Zn with Pb; Pb with Mn. A strong positive correlation necessarily do not point towards an identical source (Hani and Pazira 2011), however, inter-elemental relationships can provide remarkable suggestions on the pathways and even sources of the metals (Chen *et al.* 2014), for example, positive correlations between Cu and Ni and Cu and Co indicated a possibility of a common source which

Table 3. Pearson correlation matrix between different metals in the soils of copper mining areas of Singhbhum shear zone ($n = 16$).

	Mn	Cu	Pb	Zn	Ni	Co	As	Cd	Cr	V	Fe
Mn	1.000	0.019	0.706*	0.584*	0.244	0.332	0.591*	0.482*	0.454*	0.688*	0.754*
Cu		1.000	-0.006	0.222	0.667*	0.511*	0.234	0.387**	0.004	0.263	0.234
Pb			1.000	0.844*	0.199	0.255	0.461*	0.697*	0.665*	0.741*	0.685*
Zn				1.000	0.209	0.166	0.561*	0.856*	0.356**	0.732*	0.629*
Ni					1.000	0.832*	0.108	0.237	0.446*	0.257	0.275
Co						1.000	0.251	0.195	0.429**	0.369**	0.421**
As							1.000	0.580	0.270	0.771*	0.770*
Cd								1.000	0.200	0.808*	0.696*
Cr									1.000	0.398**	0.458*
V										1.000	0.932*
Fe											1.000

* Correlation significant at the 0.01 level (two tailed).

** Correlation significant at the 0.05 level (two tailed).

Figure 3. Loading plots of principal component analysis for the three rotated components.

may be derived from mining and processing of copper ores. Principal component analysis (PCA) was carried out on the heavy metal data of the agricultural soil samples in order to get a better view of their interrelationships and to reduce the dimensionality of the dataset, since a few of the new components explain the major part of data variance. It also helps in assigning source identity to each one of the PCs (Miller and Miller 2000). The KMO (0.615) and Barlett's test ($p < 0.001$) validated the approach of PCA. In the present set of data, three principal components were extracted explaining 82.6% of total variance (figure 3). The loading factors indicate that the first principal component (PC1) was associated with As, Cd, Fe, Mn, Pb, V and Zn explaining 43.5% of variance and seemed to be related to earth's crust and geological

formation of the area. The second component elucidated 22.1% of variation in the data and is underlined by significant factor loading for Cu, Ni and Co. This factor can be associated to the extensive copper mining in the study area. Ni and Co are exposed during copper mining and smelting as they are associated with copper deposits. The study area is rich in copper mineralization, so it is obvious to have high concentration of the Cu along with Ni and Co. But the concentrations of these metals are even higher than the background rock formations thus pointing towards the effect of mining and allied activities of the study area. The concentration of Cu, Ni and Co in the background rocks have been reported to be 46–52, 65–78 and 22–30 mg kg⁻¹, respectively (Mukherjee 1968).

The third factor having high loadings for Cr, Mn and Pb explicated 17.0% of the variance. This factor appeared to have arisen from other anthropogenic activities like waste incineration, coal combustion and vehicular pollution.

4.3 Contamination and toxicity assessment of metals in soil

Enrichment factor analysis indicated moderate to extremely high contamination of metals in the agricultural soils of the study area (table 4). The EF ranged from 1.4 to 8.9 for As, 0.59 to 2.48 for Cd, 1.01 to 5.62 for Co, 0.97 to 8.58 for Cr, 1.7 to 80.7 for Cu, 0.29 to 1.58 for Mn, 0.78 to 7.05 for Ni, 1.54 to 4.42 for Pb, 0.87 to 1.56 for V and 0.68 to 5.64 for Zn. Of all the studied metals, enrichment factor indicated highest contamination with respect to Cu which depicted significant contamination to extremely high contamination in half of the

Table 4. *Enrichment factor of metals in soil with respect to different locations of the copper mining areas of Singhbhum shear zone.*

Code	Location	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
1	Bhatin	2.35	0.62	1.59	1.84	3.53	1.00	0.29	1.16	2.68	1.56	1.33
2	Kuldiha	1.85	0.59	1.32	1.73	1.70	1.00	1.17	0.82	2.64	0.87	0.68
3	Darisai	2.76	2.18	1.01	1.78	2.95	1.00	0.86	0.85	3.60	1.08	4.83
4	Bodamdera	1.43	0.64	3.49	8.58	5.35	1.00	0.94	4.49	3.56	0.97	1.58
5	Rakha	1.61	1.94	1.20	1.84	5.46	1.00	0.75	1.15	1.98	0.93	2.43
6	Jagganathpur	1.72	1.66	5.62	2.89	2.98	1.00	1.58	7.05	4.15	1.34	4.79
7	Kendadih	7.01	0.96	1.77	1.94	9.52	1.00	0.70	1.16	1.54	0.99	1.97
8	Terenga	5.96	2.13	1.80	7.20	19.07	1.00	0.81	2.39	4.42	1.10	5.64
9	Benasol	2.84	2.48	1.76	1.89	5.20	1.00	0.70	1.15	4.15	1.27	5.08
10	Kutludih	1.71	1.13	2.38	1.05	11.00	1.00	0.81	0.96	3.71	0.96	4.75
11	Ghatsila	8.89	1.90	1.84	1.65	3.48	1.00	1.02	1.03	3.32	1.14	4.01
12	Chirugoda	3.39	2.05	1.37	1.88	2.43	1.00	0.90	1.29	3.16	1.13	4.02
13	Sohada	3.79	1.75	2.89	1.63	46.98	1.00	0.91	4.75	2.72	1.03	4.82
14	Pathergoda	1.71	1.02	3.32	2.06	1.81	1.00	0.78	0.78	2.96	1.03	1.72
15	Badia	4.31	2.35	3.31	0.97	80.72	1.00	0.56	4.58	1.94	1.17	2.57
16	Latia	2.03	1.43	2.63	1.36	2.90	1.00	0.30	2.61	1.96	0.90	1.34

Table 5. *Geo-accumulation index of metals in soil with respect to different locations of the copper mining areas of Singhbhum shear zone.*

I_{geo} value	I_{geo} class	Soil quality (Muller 1969)	Metals
>5	6 (>64-fold increase)	Extremely polluted	Cu
4–5	5	Highly polluted to very highly polluted	Cu
3–4	4 (25-fold increase)	Highly polluted	Cu
2–3	3	Moderately polluted to highly polluted	Cu, Zn, As, Cr
1–2	2 (five-fold increase)	Moderately polluted	Cu, Pb, Zn, Ni, Co, As
0–1	1 (double the background value)	Unpolluted to moderately polluted	Cu, Pb, Zn, Ni, Co, As, Cd, Cr, V
<0	0	Background concentration	Mn, Cu, Pb, Zn, Ni, Co, Cd, Cr, V, Fe

locations. The EF showed no pollution with respect to Mn and V in the study area. At most of the locations, As, Pb, Zn, Co, Ni and Cr were found to be at moderate contaminated stage; however, there were few locations where significant contamination were encountered with respect to these metals which can be attributed to mining, industries and other anthropogenic causes.

The geo-accumulation index proposed by Muller (1969) for the quantification of metal accumulation in sediments or soil consisted of seven classes (0–6) indicating various degrees of enrichment above the background values ranging from unpolluted (class 0) to extremely polluted (class 6) soil quality (table 5). Variations in the calculated I_{geo} values of the agricultural soils in the study area are

presented as boxplots in figure 4. Large variations were observed in the I_{geo} values for the metals in the study area as metals widely varied from class 0 to class 6 indicating large spatial variations; representing the background status for some metals to extremely polluted status for others. Largest variation was observed for Cu for which the I_{geo} values ranged from -0.31 to 5.62 ; thus falling under the I_{geo} class of 0–6, i.e., unpolluted to extremely polluted status. A moderate-to-high pollution (class 3) was indicated by the I_{geo} values for the metals Zn, As and Cr at some locations. The I_{geo} values were calculated for the soils using the control soil also, i.e., soil from the location 1 (figure 4). Except for V, the average I_{geo} values of all the metals were greater than zero when calculated with respect to

Figure 4. Boxplots of I_{geo} values (using average shale and control soil) of each metal in the agricultural soils of the study area.

Table 6. Contamination factor of metals in soil with respect to different locations of the copper mining areas of Singhbhum shear zone.

Code	Location	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn	PLI
1	Bhatin	1.06	0.28	0.72	0.83	1.58	0.45	0.13	0.52	1.21	0.70	0.60	0.61
2	Kuldiha	1.51	0.48	1.08	1.42	1.39	0.82	0.96	0.67	2.16	0.71	0.56	0.97
3	Darisai	1.74	1.38	0.64	1.13	1.86	0.63	0.55	0.54	2.28	0.68	3.05	1.10
4	Bodamdera	1.38	0.61	3.36	8.24	5.14	0.96	0.91	4.31	3.42	0.93	1.52	2.01
5	Rakha	0.87	1.05	0.65	0.99	2.94	0.54	0.41	0.62	1.07	0.50	1.31	0.85
6	Jagganathpur	0.74	0.71	2.40	1.24	1.27	0.43	0.67	3.01	1.77	0.57	2.04	1.12
7	Kendadih	9.31	1.28	2.35	2.58	12.65	1.33	0.93	1.54	2.04	1.32	2.62	2.35
8	Terenga	6.92	2.47	2.08	8.34	22.12	1.16	0.94	2.77	5.13	1.27	6.54	3.46
9	Benasol	2.77	2.41	1.72	1.85	5.07	0.97	0.68	1.12	4.04	1.24	4.95	1.99
10	Kutludih	1.18	0.78	1.64	0.72	7.58	0.69	0.56	0.66	2.56	0.66	3.28	1.25
11	Ghatsila	9.08	1.95	1.88	1.69	3.56	1.02	1.04	1.05	3.39	1.17	4.10	2.11
12	Chirugoda	4.65	2.81	1.87	2.57	3.33	1.37	1.23	1.77	4.33	1.54	5.52	2.49
13	Sohada	3.56	1.65	2.72	1.53	44.14	0.94	0.86	4.46	2.56	0.97	4.52	2.64
14	Pathergoda	1.14	0.68	2.22	1.37	1.21	0.67	0.52	0.52	1.97	0.69	1.15	0.98
15	Badia	3.93	2.15	3.02	0.88	73.65	0.91	0.51	4.18	1.77	1.06	2.34	2.38
16	Latia	1.63	1.15	2.11	1.09	2.32	0.80	0.24	2.09	1.58	0.72	1.08	1.16

the control soil. In this case also, the highest variability was observed for Cu (-0.98 to 4.95); thus indicating augmentation of the Cu concentrations in the study area with respect to background values also.

The degree of pollution by different metals as expressed by contamination factor (CF), suggested that the highest contamination was for Cu in the soils of the study area. The contamination factors for the different metals generally followed the sequence (table 6): Cu < As < Zn < Pb < Cr < Co < Ni < Cd < V < Fe < Mn.

PLI was calculated to evaluate the combined pollution effect by different metals at different sampling locations and is depicted in figure 5. A calculated PLI value < 1 for a location strongly advocates metal pollution (Cabrera *et al.* 1999). In the study area, the average PLI value was calculated to be 1.72, with minimum value of 0.61 and maximum value of 3.46 (for the location Badia). Almost 50% of the locations of the study area fall in the category of heavy pollution with respect to PLI .

The mC_d values for the different sampling locations of the study area varied from 0.73 to 8.58. The

Figure 5. Pollution load index (PLI) at different locations of the study area.

Figure 6. Nemerow index at different locations of the study area.

Table 7. Potential ecological risk indices of the agricultural soils of Singhbhum copper belt.

Code	Locations	E_r^i							R_I
		As	Cd	Cr	Cu	Ni	Pb	Zn	
2	Kuldiha	14.2	30.9	3.43	4.40	6.43	8.96	0.93	69.2
3	Darisai	16.4	88.7	2.73	5.88	5.16	9.45	5.11	133.5
4	Bodamdera	13.0	39.4	20.0	16.2	41.2	14.2	2.55	146.4
5	Rakha	8.19	67.3	2.40	9.28	5.91	4.42	2.20	99.7
6	Jagganathpur	6.93	45.4	2.99	4.01	28.7	7.34	3.43	98.9
7	Kendadih	87.7	82.3	6.24	39.9	14.7	8.46	4.39	243.8
8	Terenga	65.1	158.8	20.2	69.8	26.5	21.3	10.96	372.6
9	Benasol	26.1	155.1	4.47	16.0	10.7	16.8	8.30	237.5
10	Kutludih	11.1	50.1	1.75	23.9	6.35	10.6	5.49	109.4
11	Ghatsila	85.6	125.1	4.08	11.2	10.0	14.1	6.87	257.0
12	Chirugoda	43.8	180.9	6.23	10.5	16.9	18.0	9.24	285.5
13	Sohada	33.6	105.9	3.71	139.3	42.6	10.6	7.58	343.2
14	Pathergoda	10.7	43.7	3.32	3.81	4.94	8.17	1.92	76.6
15	Badia	37.1	138.0	2.14	232.4	39.9	7.36	3.92	460.8
16	Latia	15.4	73.9	2.64	7.33	20.0	6.54	1.80	127.6
Geometric mean		21.6	73.0	5.52	15.3	13.2	9.7	3.7	158.8

locations were placed in the classes of ‘unpolluted’ ($mC_d < 1.5$) to ‘highly polluted’ ($8 \leq mC_d \leq 16$) as per the classification of mC_d . The average impact of all the measured metals is considered in the calculation of mC_d and thus the contribution of one metal is diminished. As a consequence, the skewness will be meager for the mC_d values even if the soils are highly contaminated with one of the metals. The same is depicted in the present study where the soils are highly contaminated with Cu. But in Nemerow index, the impact of one single metal is quantified in a much more considerate way as it considers both the average and maximum contamination factors as per equation (7) (Brady *et al.* 2015). The Nemerow index values for the various locations of the study area ranged from 1.23 to 52.4 (figure 6) indicating seriously contaminated status ($P_s \geq 5$) at nearly 50% of the locations. Thus, the findings, taking into account of EF, I_{geo} , CF, PLI and Nemerow index, confirm that metal pollution in the study area is moderately to extremely serious varying between the locations and Cu being the most concerned metal. The highest degree of contamination was encountered at the locations near Cu mining and processing units.

The geometric mean E_i^i values for As, Cd, Cr, Cu, Ni, Pb and Zn were 22.7, 80.1, 4.2, 16.5, 14.1, 10.2 and 4.1, respectively, suggesting considerable risk for Cd. All the other metals were in the low risk category (table 7). The R_I ranged from 69.2 to 460.8 (geomean 172.5) representing moderate risk in the study area. Referring to the R_I category mentioned before, one sampling site was classified into very high risk and six sampling sites were classified into considerable risk. The potential ecological risks of other sites were low to moderate.

5. Conclusions

The levels of the metals in the agricultural soils of the copper mining areas of the Singhbhum shear zone were higher than the average shale and world average values for most of the cases. The high concentration of metals in the soils can be attributed to both natural and anthropogenic factors which are three clearly illustrated by the multivariate analysis. PCA resulted in extraction of three factors explaining 82.6% of the data variability out of which two indicated human activities and one factor indicated geogenic sources. The enrichment

factor and I_{geo} values indicated very high contamination with respect to Cu followed by As and Zn in the agricultural soils of the study area. The EF depicted least pollution with respect to Mn and V. The combined pollution effect of different metals was evaluated using PLI , R_I and Nemerow index, which revealed that 50% of the locations were in extremely polluted status with respect to metals. Only 25% of the locations could qualify to be placed in the uncontaminated category. The locations which were in close proximity to the existing or abandoned copper mining and processing units showed higher levels of metal pollution as compared to other locations and out of all the studied metals, Cu was the main metal of concern.

From the estimation of metal concentration in the agricultural soil samples collected from this study, we obtained a better knowledge regarding the impact of the copper mining and processing operations on the environment. Consequently, heavy metal concentrations in the soils should be periodically monitored and improved soil management practices are required to minimize possible impacts.

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