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Risk-based assessment of heavy metals in waste dump after 5 years of restoration using fruit orchard

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Abstract

Soil pollution due to accumulation of heavy metals is noteworthy in India through advance urbanisation and industrialisation, hence, soil pollution has become imperative hindrance for regional development and human health in recent periods. Sponge iron (also known as direct reduced iron or DRI, porous iron) industries are such a significant example for socio-economic development, responsible for generating large quantities of loose and fine textured wastes (dolochar, slag, fly ash) that are devoid of nutrients and having elevated concentration of toxic heavy metals. In the present study, restored waste dump (RWD) of an integrated sponge iron unit, Chhattisgarh was selected to assess the chronological variation in spatial distribution of heavy metals in RWD soil and their potential risk on human health and ecosystem. Characterisation of waste materials (dolochar, slag, flyash) infers high electrical conductivity and alkaline pH with high concentration of trace elements. Multiple indices (Nemerov pollution index, Ecological risk index) analysed to determine ecosystem pollution, exhibited lesser ecological risk in older RWD than younger RWD. The potential carcinogenic human health risks in the RWD 5 soil exhibited values within the acceptable range i.e., $1\times10^{-6} – 1\times10^{-4}$. The study concluded that a good quality of topsoil could generate proper substratum for reclamation of waste dump and application of fruit orchard as means of phytorestoration is efficient to reduce health risk to surroundings. Therefore, fruit orchard (guava) could be an optimum land use of sponge iron waste dump blanketed with good quality topsoil.

Keywords: Solid waste dump, heavy metals, health risk, ecological risk, restoration.

Introduction

Soil, a natural sink of contaminants and nutrients, plays a dynamic role in socio-economic stability and ecological safety[1,2]. Soil pollution due to accumulation of heavy metals is noteworthy in India through advance urbanisation and industrialisation such as mining, smelters, thermal power plants, application of fertilizers, atmospheric deposition[3]. Hence, soil contamination has become imperative hindrance for provincial growth and human wellness in recent periods[1,4]. Hazardous toxic metals such as copper (Cu), manganese (Mn), zinc (Zn), chromium (Cr) and nickel (Ni), have specific densities greater than $5 gcm^{-3}$ and usually non-biodegradable in natural environments with less concentration[1,5], have become a global threat as an important soil pollutant[6,7]. Elevated concentration of heavy metals can have adverse impact on the environmental, threatening not only soil, air, and water ecosystem, but also food chain via bioaccumulation and subsequent biomagnification via several biogeochemical cycles[8,9].

Therefore, the restoration of contaminated sites is mandatory with vegetation cover that can stabilize the ecosystem, control pollution, improve visual aesthetics and remove threats to human. Recently, India practises eco-restoration of degraded land through plantation of the native fruit tree species to get some economic return[10].

Heavy metals, emerged from both anthropogenic and natural sources, create potential risk to human wellness and the entire ecosystem owing to their toxicity, long-term ecosystem persistence, and bioaccumulation[11,12]. Therefore, in recent decades researchers are mainly focused on ecological and health risks along with distribution and environmental pollution of heavy metal[7,13-15]. Several methods like "geo-accumulation index (I_{geo})", "pollution load index (PLI)", "enrichment factor (EF)", "contamination factor (CF)", "Nemerov pollution index (NPI)", "potential ecological risk index (PERI)" are extensively employed to evaluate metal pollution[1,3,16]. For instance, the concentration (mg/kg) of Cr, Ni, Cu, and Zn were found 42.55, 15.26, 27.15, and 47.14 respectively in soil of Anka Artisanal gold mining area, Northwest Nigeria[17]. In degraded mine soil of Legacy mine site, Australia, Abraham et al.[18] reported the toxic metal concentration (mg/kg) in the order "Mn > Zn > Cr > Cu > Ni". In another study, in urban soil adjacent electronics manufacturing sector, Wu et al.[1] found 'moderate to high' levels of pollution along with high non-carcinogenic and carcinogenic risk to population. Sponge iron (also known as direct reduced iron or DRI, porous iron) industries are important for socio-economic advancement and have generated molten iron at integrated steel plant, essential for urbanisation (i.e., electric steel production, blast furnace feed) of country. Despite having the significance of such industrialization, it is obvious that considerable volume of wastes (dolochar, slag, fly ash) are generated in an integrated sponge iron plant as steel making factories or sponge iron industries generally use poor quality F grade coal (low calorific value: 2400-3360kcal/kg, ash content >40% by weight) due to non-availability of good grade coal. Maiti and Maiti[19] reported that 154 tonnes of iron ore (65 wt. % Fe) and 120 tonnes of non-coking coal (B grade) are required for production of 100 tonnes of sponge iron that generates 45 tonnes solid wastes including 25 tonnes of dolochar. Large variety of solid waste materials and pollutants including heavy metals are usually dumped over the area influenced by industries, agriculture or other economic activity. It becomes a challenging task for reclamations to stabilise waste dumps as these wastes are fine, loose and devoid of nutrients.

The study was conducted mainly based on the hypothesis that with increasing reclamation age, the intensity of environmental as well as human risk due to heavy metal exposure will be less. Taking this into consideration, the objectives of present study are as follows: (1) to assess the chronological variation in spatio-temporal variation of toxic metals in waste dump (RWD0, RWD5); (2) to evaluate the potential ecological and health risk (non-carcinogenic and carcinogenic) associated with heavy metal exposure via various pathways.

Methodology

Study site: Solid waste dumps of an integrated sponge iron unit (Chhattishgarh, India) were selected for the present study which lies between latitudes 22°00'-22°02' N and longitudes 83°22'-83°23'E, and covers an area of around 7ha (Figure-1). The study site comprised of dry tropical climate with three distinctive seasons i.e., winter (Dec–Feb), summer (Apr–Jun) and monsoon (July–Sep). The range of temperature is 30–49°C and 8–25°C in summer and winter respectively.

Soil sampling: During winter season (January, 2018), the following sampling design was employed to collect soil samples: Ten 10m*10m quadrates were laid in restored waste dump. Five sub-samples were collected (four from corners and one from centre) from each quadrate, mixed thoroughly and reduced to 0.5kg using the coning quartering method to obtain one composite sample; hence, 10 composite samples were collected[10] from of 0-10cm depth near rhizosphere of fruit orchard. The samples were sealed in plastic zipper bags, and brought to the laboratory.

Analysis of samples: For the assessment of toxic metal concentration in RWD soil, all soil samples were air-dried at laboratory room temperature (20-25^{o}C), then gently crushed by using a porcelain made mortar - pestle (500cc capacity), and sieved (mesh size 8; < 2 mm).Analysis protocols for total metal concentration in soil sample of restored waste dump are as follows: The dried samples were placed in a desiccators before being analysed for metals. For the analysis, oven-dried soil samples (0.2g) were digested in a microwave digestion system ("ETHOS 1, Milestone SrL, Sorisole, BG, Italy") for 90 minutes at 120 psi pressure with 10ml of aqua regia mixture. The digested extracts were diluted with 1% HNO_3, filtered through a Whatman # 42 filter paper, and the sample volume was made up to 50ml. Prepared samples were kept in 4°C prior to metal analysis (Cu, Mn, Ni, Cr, Zn, Fe, Pb) using FAAS ("FAAS-GBC Avanta PM, Melbourne, Australia"). Cu, Mn, Ni, Cr, and Zn have detection limits of 0.001, 0.0015, 0.009, 0.003, and 0.008ppm, respectively.

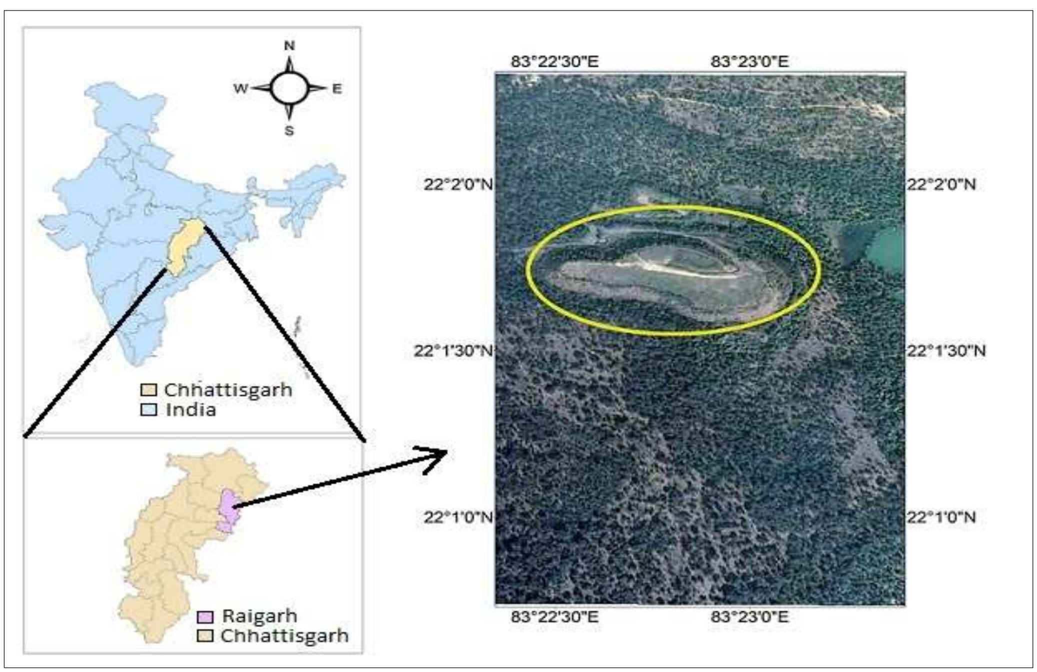


Figure-1: Location map of the study area.

Analytical quality assurance and quality control analysis: Soil environments are known to have heterogeneous characteristics with different degrees of variability as a fundamental feature that cannot be anthropogenically controlled. To quantify the variability, during the sampling, soil samples were collected in a replicate manner. The analytical quality and accuracy were assured through proper standardization by using procedural blanks, reagent blank, duplicate samples, and certified reference materials (NRC-CNRC MESS-4) for determining the presence of any interference. Throughout the experiment, analytical grade chemical reagent and double distilled deionized water were employed. The FAAS was calibrated using blank and drift reagent after every five measurements to get a high calibration coefficient. The recovery percentage of metals ranged between 91.13% and 98.48% (Table-1).

Table-1: The recovery percentage of analysed metals.

Elements	Certified quantity values for trace metals in MESS-4	Experimental value for trace metals in MESS-4	Recovery percentage
Cu	32.9 ± 1.8	30.94 ± 2.1	94.04 %
Mn	298 ± 14	271.57±15.69	91.13 %
Ni	42.8 ± 1.6	41.69 ± 2.07	97.40 %
Cr	94.3 ± 1.8	92.87 ± 2.78	98.48 %
Zn	147 ± 6	142.8 ± 5.63	97.14 %
Fe	37.9 ± 1.6	35.8 ± 1.46	94.45 %
Pb	21.5 ± 1.2	20.7 ± 2.31	96.27 %

Environmental risk assessment: Nemerov pollution index: The Nemerov Pollution Index can be employed to evaluate metal contamination by using the following formula[20,21]:

$$NPI = \sqrt{[(\frac{1}{m}\sum_{i=1}^{m} Pi)^2 + Pi^2 max]/2}$$

Where, Pi = (C/B) = pollution index for specific metal, in which “C” signifies the soil HM content and “B” signifies the geochemical background value; m = number of heavy metals studied; Pi^2max = highest value of pollution index of all metals;

The pollution classes according to NPI are presented by Zhong et al.[22] as follows: “≤0.7 = excellent; 0.7-1 = clean; 1-2 = slight pollution; 2-3 = moderate pollution; ≥3 = heavy pollution”.

Potential Ecological risk index (PERI): The PERI can be employed to evaluate metal contamination by using the following formula:

$$PERI = \sum_{i=1}^{m} ER$$

$$ER = Trf^i \times Pi$$

Where, ER = ecological risk; m = number of HM studied; Tr^i = toxicity response coefficient for HM [23]; Pi = (C/B) = pollution index for specific metals.

The ERI classes used were those of Hakanson[23]: “≤90 = low; 90-180 = moderate; 180-360 = strong; 360-720 = very strong; ≥720 = highly strong”.

Human Health risk assessment: The human health risk assessment from heavy metal exposure in soil is commonly used to evaluate both carcinogenic and non-carcinogenic risks to people who are in exposure to toxic metals via inhalation, ingestion, or skin contact.

Exposure assessment: People are mostly exposed to toxic heavy metals found in the soil through three various routes: oral consumption, inhalation, and skin contact. The risk assessment methodologies in this study strictly followed the standards from the USEPA's Exposure Factors Handbook[24]. The following equations were used to compute the average daily doses (ADDs) ($mg\ kg^{-1}\ day^{-1}$) for both children and adults:

$$ADD_{ing} = \frac{Csoil \times IngR \times EF \times ED}{BW \times AT} \times 10^{-6}$$

$$ADD_{inh} = \frac{Csoil \times InhR \times EF \times ED}{PEF \times BW \times AT}$$

$$ADD_{derm} = \frac{Csoil \times SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6}$$

$$ADD_{total} = ADD_{ing} + ADD_{inh} + ADD_{derm}$$

Where, C_{soil}= the metal concentration in soil. The definition of exposure factor and recommended reference values of all indices applied to evaluate the ADDs values for children and adult are given in Table-2.

Non-carcinogenic health risk assessment: Non-carcinogenic risk from toxic metals is generally estimated as the hazard quotient (HQ). It can be defined as the quotient of the average daily dose of each exposure route, divided by the reference exposure dose which is referred as toxicity threshold value for a specified metal. The hazard quotient of individual metal was determined with the following equation:

$$HQ_i = \frac{ADD}{RfD}$$

Where, ADD = the “average daily dose” of each exposure pathways, R*f*D is the “reference exposure dose” ($mg\ kg^{-1} day^{-1}$) estimated for daily exposure through each pathway to the population.

Table-2: Recommended value for exposure risk assessment.

Parameter	Description	Adult	Children	Reference
IngR	Ingestion rate	100 mg day^{-1}	200 mg day^{-1}	25
EF	Exposure frequency	350-day $year^{-1}$	350-day $year^{-1}$	26
ED	Exposed duration	26 years	6 years	26
BW	Body weight	68 kg	15 kg	25
AT	Average time	ED × 365 (Non-carcinogen) 70 × 365 (Carcinogen)	ED × 365 (Non-carcinogen) 70 × 365 (Carcinogen)	26
InhR	Inhalation rate	20 m^3day^{-1}	7.6 m^3day^{-1}	26
PEF	Particle emission factor	1.36×10^9 m^3kg^{-1}	1.36×10^9 m^3kg^{-1}	25; 27
SA	Exposed skin area	5700 cm^2	2800 cm^2	25; 27
SL	Skin adherence factor	0.07 mg $cm^{-2}h^{-1}$	0.2 mg $cm^{-2}h^{-1}$	27
ABS	Dermal absorption factor	0.001	0.001	27

According to USEPA[28], hazardous index (HI) was quantified to assess the overall influence of all heavy metals and estimated as follows:

$$HI = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{derm}$$

According to the USEPA[25] study, if HI<1, there is no danger of non-carcinogenic consequences, but if HI > 1, there is a risk of non-carcinogenic health impacts [1].

Carcinogenic health risk assessment: Carcinogenic health risk (CR), as defined by USEPA[28], the probability of occurrence of any sort of cancer owing to the individual's exposure via different pathways. The CR of Cr, Pb, and Ni were quantified using following equation:

$$CR = ADD \times SF$$
$$TCR = \sum CR = CR_{ing} + CR_{inh} + CR_{derm}$$

Where, SF, TCR are carcinogenic slope factor (mg $kg^{-1}day^{-1}$) and total carcinogenic risk (unitless) respectively. Previous studies evaluated the permissible range of TCR in range between 1×10^{-6} and 1×10^{-4} that suggests the TCR value below 1×10^{-6} possess no significant health risk to human[1,3,29,30].

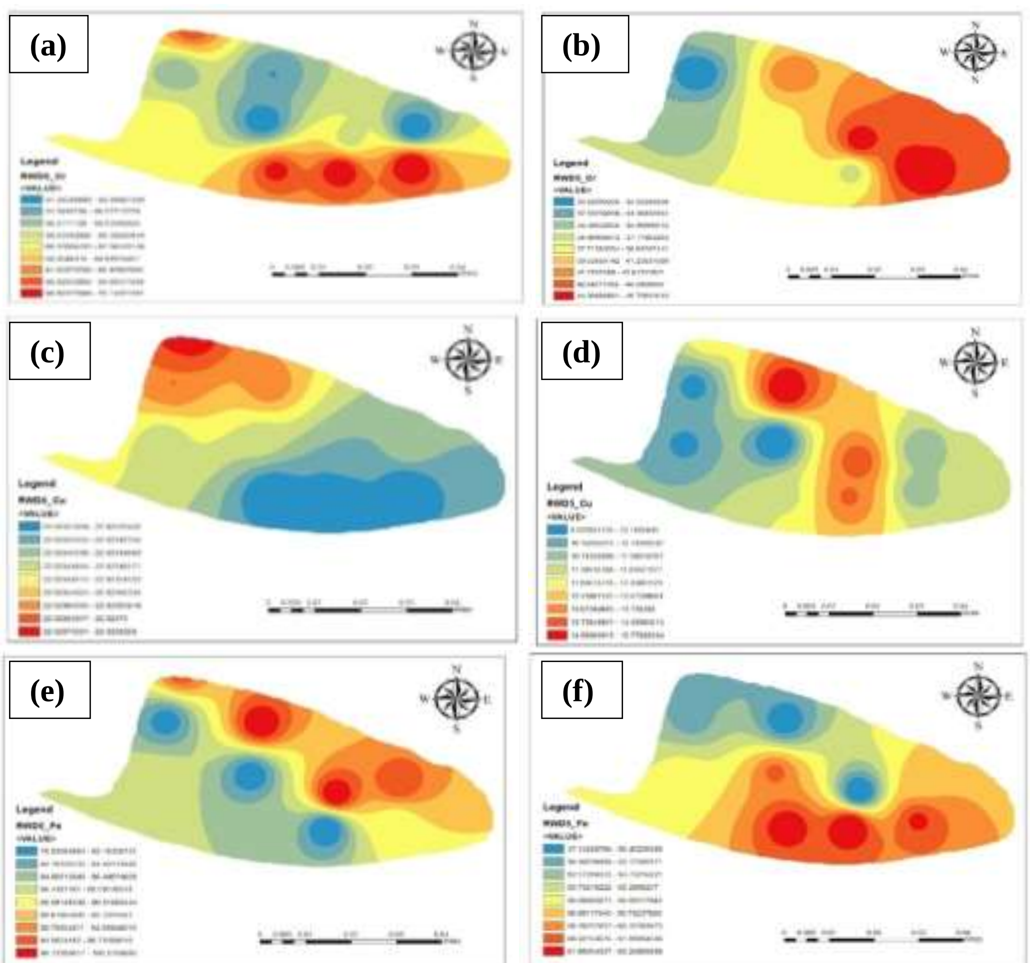
Statistical analysis: Multivariate statistical analysis was employed in metal concentration of soil. Data was examined for homoscedasticity and normality with Levene's test and Shapiro-Wilk test respectively. Pearson correlation matrix (PCM) and principal component analysis (PCA) were employed to find out relationships among metals and their source identification respectively. All the statistical analysis was done by using SPSS 21.0 (IBM SPSS Inc., Chicago, USA). Spatio-temporalvariation of heavy metals was performed by geostatistical analysis i.e., Inverse Distance Weighted (IDW) interpolation method with ArcGIS software (ArcGIS, version 10.5).

Results and discussion

Spatio-temporalvariation of HM concentration in soil: As a consequence of industrial activities such as steel processing, mining, waste dumps usually have higher concentration of potential toxic elements. Total metal concentration (mg/kg) in RWD5 was in sequence of Mn > Zn >Fe >Cr >Pb >Cu > Ni. The higher concentration of Mn and Zn in soil could be attributed to the composition of parent rocks or the application of the macronutrient fertilisers or combustion of fuels in industry or incineration of waste[31]. The total metal concentration of Cu, Ni, Cr, Fe and Pb in RWD5 was 2.23, 2.94, 1.57, 1.58 and 1.92 times lower than RWD0 while 1.35- and 2.05-times higher Mn and Zn in RWD5 implies successful restoration of the area. The increased concentration of Cr, Fe and Pb in solid waste dump at initial phase of restoration could be due to industrial activities, metal dust deposition.

Figure-2 depicts the spatio-temporal variation of toxic metal concentrations in soil samples taken from a fruit orchard in RWD0 and RWD5. When the spatial distribution of the seven toxic metal concentrations in soil is concerned, it is clear that the distribution is generally heterogeneous and derived from several sources. In initial phase of reclamation Mn was the most abundant heavy metal followed by Fe, Pb and Cr. These findings are consistent with the research reported in mine degraded land of legacy mine site in Victoria, Australia [18]. So, it is obvious that the Mn and the total concentration of seven congeners (summation of all metals) have a similar trend which directs that Mn could be a reliable predictor for total heavy metal concentration of study area. In this study, the mean concentration of Cu, Mn, Ni, Cr, Zn, Fe and Pb after restoration were 11.89, 609.08, 10.38, 39.37, 64.78, 56.32 and 36.84 mg kg^{-1}, respectively. Compared these values to global soil average [32] and critical soil concentration[33], it can be seen that the mean concentration of all metals in RWD5 (after 5 years of restoration) is within limits.

Multivariate analysis of HM in soil: In this study Pearson correlation matrix and principal component analysis (PCA) were employed to examine the relationship and probable potential metal contamination sources in study area. The positive correlation indicates high significant ($p<0.05$) correlation between most of the examined metal which represents their similar source of origin, interdependence and similar behavior during transport[34]. High communalities of about 80% of the variables, indicating high degree of variable correlation. In initial phase of reclamation (RWD0), significant ($p < 0.05$) correlation between Cu-Pb ($r = 0.514$), Mn-Cr ($r = 0.753$), Ni-Fe ($r = 0.510$) and Fe-Zn ($r = 0.593$) further indicates the possible similar source of these metals. Similarly, after 5 years of restoration (RWD5), significant ($p < 0.05$) correlation between Cu-Ni ($r = 0.574$) and Mn-Cr ($r = 0.729$) indicates positive effect of restoration and probable source apportionment of metals. Simultaneously, PCA showed Ni, Zn and Fe; Mn and Cr; Cu and Pb; and Cu and Ni; Mn and Cr; Fe and Pb were closely related to each other in RWD0 and RWD5 respectively. Furthermore, these elements were highly correlated, indicating that they were most likely derived from the same anthropogenic source (industries, dump sites) such as electroplating and galvanization, steel manufacturing, metal alloys industries of investigated area. Zn showed strong negative loading indicating unique anthropogenic sources than other metals such as metal processing industries, burning of fuel and local solid waste of study area. The high positive loading of Cu in PCA indicates anthropogenic inputs of industrial application (copper wire, electrodes, vehicle parts), dumping of solid waste and atmospheric deposition. The strong positive loading of Ni may indicate its origin from emission of metal processing industries of investigated region.



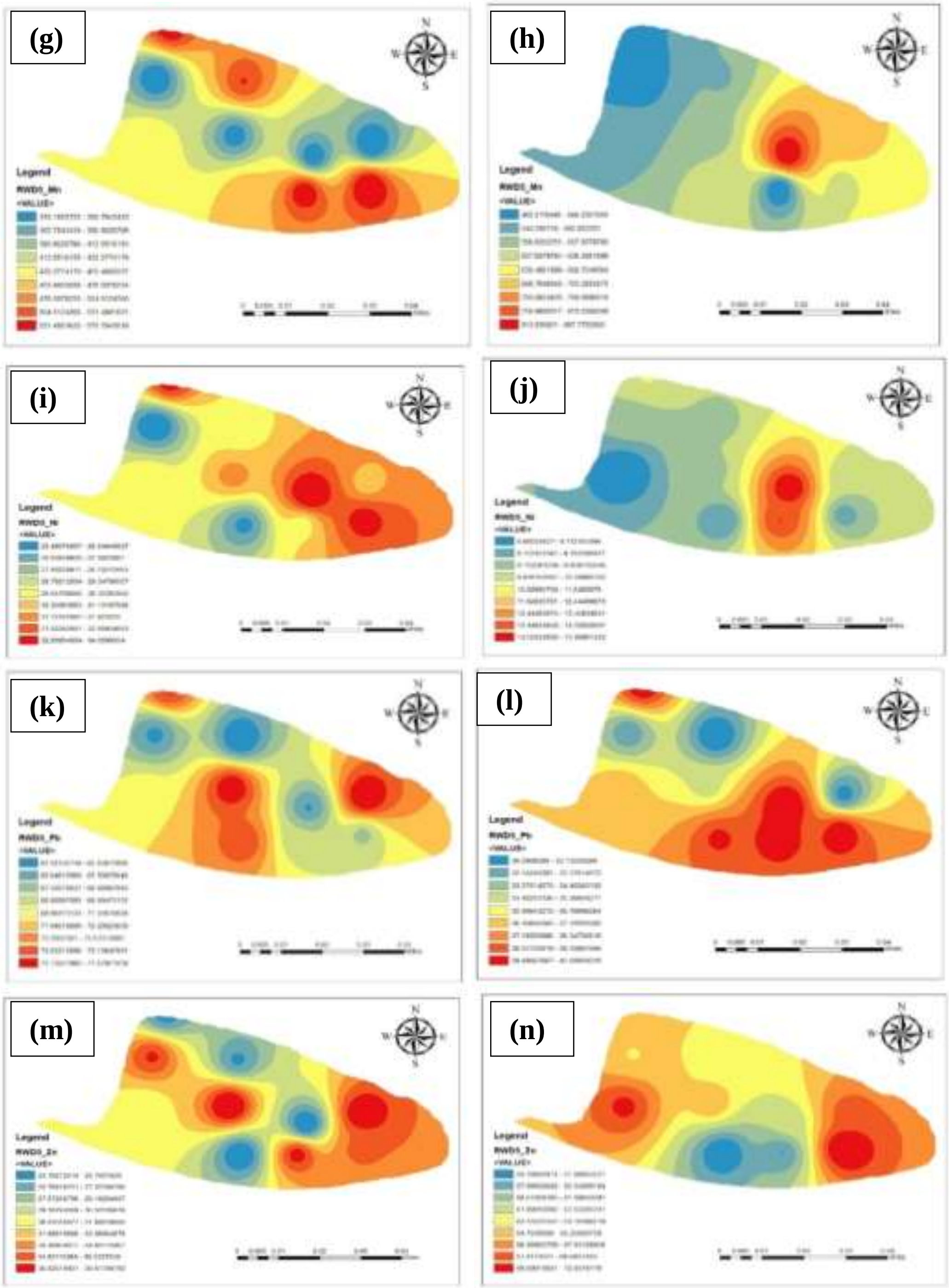


Figure-2: Spatial distribution of HM (a,b) Cr, (c,d) Cu, (e,f) Fe, (g,h) Mn, (i,j) Ni, (k,l) Pb, and (m,n) Zn in RWD0 and RWD5, respectively.

Environmental risk assessment: The soil HM contamination in present study area occurs mainly owing to the presence of highly industrialised area, large pollutants emitting sector like iron ore mining areas in Dantewada district (Bailadila deposit) and steel manufacturing industry. Due to lack of ecological awareness, sometimes industry generated wastes are dumped in former fertile and arable land, hence, significant amount of toxic metals accumulated mostly in the adjacent soils, with concentrations that will be decreased with increasing of restoration age. Such metal dispersions, resulting from such other anthropogenic or metallurgical operations, have been reported in various studies[35,36]. As previously mentioned, in initial phase of restoration, the concentration of Cr, Fe and Pb exceeded the recommended world soil average [32] and critical soil concentration[33] values in present study. So, the assessment of environmental risk due to toxic metal exposure in study area (before and after restoration) is highly required to understand the restoration efficiency. The investigated area after 5 years of restoration, exhibits relatively less ecological risk than RWD0 according to pollution indices such as, Nemerov pollution index (NPI) and potential ecological risk index (PERI). But it doesn't appear in "low pollution" or "low ecological risk" classes even after 5 years of restoration that indicates the importance of long-term strategic restoration approach for sustainable, risk-free restored ecosystem.

Potential human health risk assessment: Cao et al.[37] suggested soil as one of the most substantial toxic metal exposure mechanisms to human. There are various ways through which chemical substances can access the human body upon environmental or occupational exposure; specially it could be inhaled, ingested and absorbed through the dermal contact. In present study, all 3 major routes, i.e., oral intake, inhalation, skin absorption of toxic elements through soil for children and adults are demonstrated in Table-3a and 3b; Table-4a and 4b.

Non-carcinogenic risk: The following are the distributions of ADD_{total} for metals in soils in the study area: Mn > Zn > Fe > Cr > Pb > Cu > Ni for RWD 5 and Mn > Fe > Pb > Cr > Zn > Ni > Cu for RWD0 for both adult and children, respectively. Table-3a shows the total non-carcinogenic daily dose (ADD_{total}) for adults and children. ADD_{total} of metals were found to be lower for adults than children. In present study, the importance of three different exposure routes for both adults and children increased in the following manner: inhalation > dermal >ingestion, which was coherent with the reports of Shi et al.[38], Wei et al.[39], Wu et al.[1], Kumar et al.[16], Baltas et al.[3].

Table-3a: Non – carcinogenic risk due to HM exposure in RWD 0.

Elements RWD 0	ADD_{ing}		ADD_{inh}		ADD_{derm}		ADD_{total}	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Cu	3.75E-05	3.40E-04	5.51E-09	9.49E-09	1.49E-07	9.51E-07	3.76E-05	3.41E-04
Mn	6.36E-04	5.77E-03	9.35E-08	1.61E-07	2.54E-06	1.61E-05	6.39E-04	5.78E-03
Cr	8.70E-05	7.89E-04	1.28E-08	2.20E-08	3.47E-07	2.21E-06	8.74E-05	7.92E-04
Ni	4.30E-05	3.91E-04	6.33E-09	1.09E-08	1.71E-07	1.09E-06	4.32E-05	3.92E-04
Zn	4.45E-05	4.03E-04	6.54E-09	1.13E-08	1.77E-07	1.13E-06	4.47E-05	4.04E-04
Fe	1.26E-04	1.14E-03	1.85E-08	3.19E-08	5.02E-07	3.20E-06	1.26E-04	1.14E-03
Pb	9.98E-05	9.05E-04	1.47E-08	2.53E-08	3.98E-07	2.53E-06	1.00E-04	9.08E-04
Elements RWD 0	HQ_{ing}		HQ_{inh}		HQ_{derm}		HQ_{total}	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Cu	9.37E-04	8.49E-03	1.37E-07	2.36E-07	1.25E-05	7.93E-05	9.50E-04	8.57E-03
Mn	1.38E-02	1.25E-01	6.54E-03	1.13E-02	1.38E-03	8.77E-03	2.17E-02	1.45E-01
Cr	2.90E-02	2.63E-01	4.57E-04	7.88E-04	4.63E-03	2.95E-02	3.41E-02	2.93E-01
Ni	2.15E-03	1.95E-02	3.07E-07	5.30E-07	3.18E-05	2.02E-04	2.18E-03	1.97E-02
Zn	1.48E-04	1.34E-03	2.18E-08	3.76E-08	2.96E-06	1.88E-05	1.51E-04	1.36E-03
Fe	1.50E-05	1.36E-04	8.42E-05	1.45E-04	7.18E-06	4.57E-05	1.06E-04	3.27E-04
Pb	2.85E-02	2.59E-01	4.17E-05	7.18E-05	7.59E-04	4.83E-03	2.93E-02	2.64E-01
HI	Adults				Children			
	0.088				0.732			

The HQ values for non-carcinogenic risk, children were more prone to risk than adult. The HQ for children ranged between 2.93E-01–3.27E-04 and 1.96E-01– 2.06E-04 in RWD0 and RWD5, respectively; while HQ_s for adults were ranged between 3.41E-02 – 1.06E-04 and 2.94E-02 – 6.71E-05 in RWD0 and RWD5, respectively. For both children and adults, HQ of HM_s were in sequence of Cr > Pb > Mn > Ni > Cu > Zn > Fe and Mn > Cr > Pb > Ni > Cu > Zn > Fe in RWD0 and RWD5, respectively. The findings reveal that ingestion is the principal route via which heavy metals can detriment both adults and children. The study also discovered that the non-carcinogenic risk for Cr and Pb in RWD0 were 3.41E-02 and 2.93E-01; 2.93E-02 and 2.64E-01 for adult and children, respectively, which are higher than the values obtained for the other HM_s. The HI for adults and children were 0.088 and 0.732; 0.068 and 0.534 in RWD0 and RWD5, respectively. Since HI < 1, the non-carcinogenic risks of metals in the study area are not significant[40]. Overall, the findings demonstrate that the children are more delicate to the negative health impacts of metals, as they are more prone to oral consumption through hand and mouth[3].

Carcinogenic risk: According to the IARC (“International Agency for Research on Cancer”), Cu, Mn and Zn could be stated as non-cancer inducing elements[1]; therefore, only the carcinogenic risks for Cr, Pb and Ni were determined in this study. Though Fe has carcinogenic effect to human health, but due to unidentified cancer slope factor (CSF) value, carcinogenic risk for Fe has not been calculated. The average ADD for Cr, Pb, Ni were estimated based on three exposure routes (ingestion, inhalation and dermal) for both children and adults, given in Table-4a and 4b. The carcinogenic ADD_{total} of Cr was found to be higher than Pb and Ni. The ADD_{total} of Cr and Pb estimated for children was found to be significantly higher that of adults whereas reverse was found for Ni.

Table-3b: Non – carcinogenic risk due to HM exposure in RWD 5.

Elements RWD 5	ADD_{ing}		ADD_{inh}		ADD_{derm}		ADD_{total}	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Cu	1.68E-05	1.52E-04	2.47E-09	4.25E-09	6.69E-08	4.26E-07	1.68E-05	1.52E-04
Mn	8.59E-04	7.79E-03	1.26E-07	2.18E-07	3.43E-06	2.18E-05	8.62E-04	7.81E-03
Cr	5.55E-05	5.03E-04	8.16E-09	1.40E-08	2.21E-07	1.40E-06	5.58E-05	5.05E-04
Ni	1.46E-05	1.33E-04	2.15E-09	3.70E-09	5.83E-08	3.71E-07	1.46E-05	1.33E-04
Zn	9.13E-05	8.28E-04	1.34E-08	2.31E-08	3.64E-07	2.32E-06	9.17E-05	8.31E-04
Fe	7.94E-05	7.20E-04	1.17E-08	2.01E-08	3.17E-07	2.02E-06	7.97E-05	7.22E-04
Pb	5.20E-05	4.71E-04	7.64E-09	1.32E-08	2.07E-07	1.32E-06	5.22E-05	4.72E-04
Elements RWD 5	HQ_{ing}		HQ_{inh}		HQ_{derm}		HQ_{total}	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Cu	4.19E-04	3.80E-03	6.13E-08	1.06E-07	5.57E-06	3.55E-05	4.25E-04	3.84E-03
Mn	1.87E-02	1.69E-01	8.83E-03	1.52E-02	1.86E-03	1.19E-02	2.94E-02	1.96E-01
Cr	1.85E-02	1.68E-01	2.92E-04	5.02E-04	2.95E-03	1.88E-02	2.17E-02	1.87E-01
Ni	7.32E-04	6.63E-03	1.04E-07	1.80E-07	1.08E-05	6.88E-05	7.43E-04	6.70E-03
Zn	3.04E-04	2.76E-03	4.48E-08	7.71E-08	6.07E-06	3.86E-05	3.10E-04	2.80E-03
Fe	9.45E-06	8.57E-05	5.31E-05	9.14E-05	4.53E-06	2.88E-05	6.71E-05	2.06E-04
Pb	1.48E-02	1.35E-01	2.17E-05	3.74E-05	3.95E-04	2.51E-03	1.52E-02	1.38E-01
HI	Adults				Children			
	0.068				0.534			

Moreover, the carcinogenic risks (CR) and the total carcinogenic risk (TCR) of the toxic metals (Cr, Pb and Ni) as depicted in Table 4a and4b. As shown in Table 4a and 4b, the CR ranged between 3.64E-05–7.85E-10; 2.32E-05–2.66E-10 for children and between 1.80E-05–1.97E-09; 1.15E-05 – 6.71E-10 for adults in RWD0 and RWD5, respectively. The estimated CR values were in sequence Cr > Pb > Ni. The findings highlighted that Cr has a significantly higher CR value than other metals, implying that it poses a major carcinogenic risk. In RWD0 and RWD5, the TCR for adults and children was 1.83E-05 and 3.70E-05; 1.16E-05 and 2.36E-05, respectively. Overall, the findings showed that the probable carcinogenic health hazards of toxic metals in soils at the restored waste dump for adults and children were within an acceptable range, i.e., $1\times10^{-6} – 1\times10^{-4}$[3]

Table-4a: Carcinogenic risk due to HM exposure in RWD 0.

Elements RWD 0	ADD_{ing}		ADD_{inh}		ADD_{derm}		ADD_{total}	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Cr	3.23E-05	6.77E-05	4.75E-09	1.89E-09	1.29E-07	1.89E-07	3.24E-05	6.79E-05
Ni	-	-	2.35E-09	9.35E-10	-	-	2.35E-09	9.35E-10
Pb	3.70E-05	7.76E-05	5.45E-09	2.16E-09	-	-	3.70E-05	7.76E-05
Elements RWD 0	CR_{ing}		CR_{inh}		CR_{derm}		CR_{total}	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Cr	1.61E-05	3.38E-05	1.99E-07	7.94E-08	1.69E-06	2.49E-06	1.80E-05	3.64E-05
Ni	-	-	1.97E-09	7.85E-10	-	-	1.97E-09	7.85E-10
Pb	3.15E-07	6.59E-07	2.29E-10	9.10E-11	-	-	3.15E-07	6.59E-07
TCR	Adult				Children			
	1.83E-05				3.70E-05			

Table-4b: Carcinogenic risk due to HM exposure in RWD 5.

Elements RWD 5	ADD_{ing}		ADD_{inh}		ADD_{derm}		ADD_{total}	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Cr	2.06E-05	4.31E-05	3.03E-09	1.20E-09	8.22E-08	1.20E-07	2.07E-05	4.33E-05
Ni	-	-	7.99E-10	3.17E-10	-	-	7.99E-10	3.17E-10
Pb	1.92E-05	4.04E-05	2.83E-09	1.12E-09	-	-	1.92E-05	4.04E-05
Elements RWD 5	CR_{ing}		CR_{inh}		CR_{derm}		CR_{total}	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Cr	1.03E-05	2.16E-05	1.27E-07	5.06E-08	1.08E-06	1.58E-06	1.15E-05	2.32E-05
Ni	-	-	6.71E-10	2.66E-10	-	-	6.71E-10	2.66E-10
Pb	1.64E-07	3.43E-07	1.19E-10	4.73E-11	-	-	1.64E-07	3.43E-07
TCR	Adult				Children			
	1.16E-05				2.36E-05			

Conclusion

This research insights significant description of the chronological variation (before and after 5-years of restoration) in overall pollution level and health risks posed by toxic metals in solid waste dump of an integrated sponge iron unit in Central India. Compared with the permissible limits of Indian standard [41] and the average crustal value[42] of heavy metals in soil, RWD5 soils showed relatively lower metal concentration as a whole. According to the pollution index such as NPI and PERI for Cu, Mn, Ni, Zn, Cr, Fe and Pb the values were indicative of relatively low ecological risk and low contamination of pollution for all metals in RWD5 compared to RWD0. Multivariate statistics suggested that in initial phase of reclamation (RWD0), significant ($p < 0.05$) correlation between Cu-Pb ($r = 0.514$), Mn-Cr ($r = 0.753$), Ni-Fe ($r = 0.510$) and Fe-Zn ($r = 0.593$) further indicates the possible similar source of these metals. Similarly, after 5 years of restoration (RWD5), significant ($p < 0.05$) correlation between Cu-Ni ($r = 0.574$) and Mn-Cr ($r = 0.729$) indicates positive effect of restoration and probable source apportionment of metals. The risk model due to exposure in heavy metals developed by USEPA[40] was employed to assess probable health risk to humans. The non-carcinogenic risk for adults were lower than children though it was insignificant for the present study (HI<1). The probable carcinogenic health risks for children and adults due to heavy metals exposure in soils of the 5- years old restored waste dump was in an acceptable range i.e., 1×10^{-6}–1×10^{-4}. Therefore, application of fruit orchard could be a restoration strategy of sponge iron waste dump blanketed with good quality topsoil.

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