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Full Length Research Paper

Spatial Evaluation of the Heavy Metals in Abandoned Gold Ore Tailings in Kolar Gold Fields

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The current study was carried out to assess the concentration of selected heavy metals in the abandoned gold mining site in Kolar Gold Fields, Karnataka, India. The BGML (Bharat Gold Mines Limited) company was technically involved in the gold extraction process for over two centuries. The wastewater and soil after the extraction of gold, which contained several heavy metals, were dumped in and around the mining sites in KGF, resulting in pollution of the immediate surroundings like soil, water, and air. The distribution of elements was assessed and statistically analyzed to understand the levels of contamination in soil using Thermo Scientific's ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) with Iteva software. Four sampling sites (A, B, C, and D) were selected based on their proximity to the residential areas and analyzed between July to December 2014. Analysis of soil samples collected from four mine dumps in the study area indicates high levels of heavy metals at the mean concentration of 1512 mg/kg, 40.25 mg/kg, 29384 mg/kg, 72.15 mg/kg, 108 mg/kg, 63.75 mg/kg, 58.2 mg/kg, 97.3 mg/kg, of Arsenic (As), Cadmium (Cd), Iron (Fe), Nickel (Ni), Copper (Cu), Lead (Pb), and Chromium (Cr), far above the threshold values in soil except for Manganese (Mn) with 97.3 mg/kg under safe limits as per the regulatory bodies (WHO 2004). The results of this study would facilitate in identifying the extent of surface soil pollution, and the prognosis of entry of pollutants into biotic components.

Introduction

Kolar Gold Fields, or K.G.F., is a town in Karnataka's Kolar district's Bangarpet taluk. The KGF gold mines lie at latitude 12°53'12" N, longitude 78° 15'03" E, on a short schist strip. It comprises KGF, a township populated by gold mine workers' families. KGF has mined gold underground for almost 120 years. Gold has been mined 3 km below the surface using 65 km of tunnels, and 40 million tons of mill tailings generated is spread across 4 square Km. After the valuable gold ore is extracted, the processing water and finely powdered rock are mixed to make tailings having a characteristic chemical and physical makeup. Factors such as ore type, local geochemistry, extraction method, pulverized material size, and chemical process all play a role in determining the final product (Franks *et al.*, 2011). Determining acceptable metal ions in soil (Oblotke *et al.*, 2016) and water is critical (Bortey-Sam *et al.*, 2015). Trace metals can enter the water system by leaching rocks, and forest fires, due to the high sulfide content, groundwater around tailings is acidic and contains several non-essential metals (Mitleni *et al.*, 2011) and (Harish *et al.*, 2015) recorded pH values of 3.25–6.28 and 3.48–8.12, respectively. Vegetables grown in contaminated soil and water can be harmful to people and other higher organisms because they absorb and store non-essential heavy metals including arsenic, cadmium, and nickel. Most Essential heavy metals like iron, cobalt, and copper are needed for plant, human, and microbial metabolism. Components of enzymes and electron transport routes, also control osmotic pressure. Non-essential heavy metals such as arsenic (As), cadmium (Cd), nickel (Ni), chromium (Cr), and lead (Pb) are poisonous in ecosystems but serve no biological function. Plants absorbing these metals may cause them to enter the food chain (Ndeddy *et al.*, 2016), (Miyazawa *et al.*, 2011 2009) and also it may impact agricultural lands (Roy *et al.*, 2012) the physical and socio-economic wellness of people residing in the affected region (Verma *et al.* 2012; Harish and David 2015; Mustak *et al.* 2015). There are reports suggesting that these heavy metals present in soil can percolate into ground water and pond water, thus reaching higher order organisms like fishes (Varma *et al.*, 2015 and Voigt *et al.*, 2012) and causing an

imbalance to its metabolism (Shajahan *et al.*, 2022) and neurological toxicity in fishes (Green *et al.*, 2018) and (Jia *et al.*, 2018).

Materials and Methods

Study area

During this research, a general methodology was devised based on spatiotemporal factors like place and time. So the four places selected based on the minimal distance from the abandoned gold mining sites were Oorgaum, Tenants, Champion, and Balghat and named A, B, C, and D, which are located 50, 100, 200, and 300 meters from the mining sites, respectively.

The four sampling seasons were

Season 1- January -March

Season 2- April-June

Season 3- July-September

Season 4- October-December

Methodology for Objective 1: Within the time frame of July-December 2014, a total of 24 soil samples were examined (12 per season) to determine the quantity of certain heavy metals. The results of soil contaminants in the form of heavy metals in mg/Kg were compared against the maximum permissible limits devised by USEPA (U.S. Environmental Protection Agency 2002) and WHO (World Health Organization 2004).

Collection of soil samples

The sampling was done between July to December 2014 from four sampling sites (gold ore tailings). Soil samples (n=4) were collected from each site per month, so 16 samples were analyzed every month. Sampling was done from the site during the two seasons to find the presence of individual heavy metals As, Cd, Fe, Ni, Cr, Cu, Pb, and Mn. 0.5 kg of soil samples were collected from the outer surface, i.e. 10-20 cm in depth in self-locking polythene bags after removing surface contamination. Sample preparation procedures for spectrochemical determination of total recoverable elements were carried out as per U.S Environmental Protection Agency (2005).

Sample preparation

For the determination of total recoverable analytes in solid samples, a sample was mixed thoroughly and a portion of it was transferred to a tared weighing dish, sample was weighed and weight recorded. To achieve homogeneity, the dried sample was sieved using a 5-mesh propylene sieve and ground in a mortar and pestle. High-purity reagents were used whenever possible. All acids used for this method were of ultra-purity grade, all chemicals for quantification were purchased from Rankem chemicals. To analyze the samples Thermo Scientific make ICP-OES (Inductively Coupled Plasma- Optical Emission Spectroscopy) was used with Iteva software.

Digestion and analysis

A 32% HCl and 70% HNO₃ acids (Rankem chemicals- Pure analytical grade) were used as reagents. Aqua-regia was prepared by mixing concentrated HNO₃ and HCl acids at a ratio of 1:3, respectively. About one gram of every reference material or dry powdered soil was mixed with 28 mL of aqua-regia in a 250 mL conical glass flask. The flask was gently swirled to mix the reactants and heated to a temperature of 120°C for 5 hours on a hot plate. The dissolved samples were filtered after cooling down using a filter paper washed through with 3% HNO₃ acid into 100 mL HDPE (High-Density Polyethylene) bottles and analyzed using ICP-OES. All glassware used in sample preparation was cleaned before use by immersing in a 10% v/v HNO₃ acid for 24 hours followed by rinsing with deionized distilled water. Chemical analyses were carried out at the ARML, Bangalore, India using ICP-OES, iCAP 6300, Thermo Fischer and analyzed using ITEVA software.

Table 1. Operating conditions of the ICP-OES used for the analysis of soil samples.

ICP-OES working specifications:

ICP-OES Model	iCAP 6300, Thermo Fischer
Nebulizer flow	0.65 L/min
Plasma flow	15 L/min
Auxiliary flow	1.5 L/min
Replicate read time	3 Sec
Sample uptake delay	35 Sec
Stabilization delay	15 Sec
Rinse time	30 Sec
Pump rate	15 rpm
Power	1 KW

Statistical analysis : The statistical analysis was conducted using paired sample t-test at p<0.05 level using Statistical Package for the Social Sciences (SPSS) software version 23.0

Results and Discussion

Table 2: Showing descriptive statistics for various assessed heavy metals in sampling sites with significance level at $P>0.005$

	Oorgaum			Tenants			Champion			Balghat		
	Significance P>0.005	Mean \pm SE	SD	Significance P>0.005	Mean \pm SE	SD	Significance P>0.005	Mean \pm SE	SD	Significance P>0.005	Mean \pm SE	SD
As	0.364	3652.33 \pm 73.83	255.937	0.364	704.08 \pm 26.47	91.696	0.364	645.58 \pm 16.388	56.738	0.859	783.17 \pm 35.62	123.81
Cd	0.285	77.33 \pm 2.911	10.084	0.285	18.50 \pm 1.329	4.602	0.708	21.67 \pm 1.549	5.365	0.708	30.92 \pm 1.869	6.473
Fe	0.213	41915.17 \pm 520.114	1801.27	0.363	24280.67 \pm 581.995	2015.951	0.363	24572.08 \pm 327.688	1134.935	0.285	35979.25 \pm 1389.949	4814.924
Ni	0.101	11.75 \pm 1.5617	5.429	0.285	85.50 \pm 1.5357	5.317	0.793	93.17 \pm 1.808	6.264	0.151	89.17 \pm 3.104	10.752
Cr	0.708	32.17 \pm 2.849	9.870	0.285	126.33 \pm 6.267	21.71	0.285	131.75 \pm 3.635	12.952	0.285	119.25 \pm 4.449	15.410
Cu	0.364	74.58 \pm 2.42	8.382	0.708	66.92 \pm 1.406	4.870	0.793	88.08 \pm 4.441	15.3813	0.213	77.617 \pm 4.428	15.341
Pb	0.151	36.08 \pm 1.545	5.351	0.213	28 \pm 1.446	5.009	0.364	120.83 \pm 4.855	16.819	0.364	32.17 \pm 1.942	6.726
Mn	0.101	82.33 \pm 1.94	6.719	0.151	91.92 \pm 1.52	5.265	0.285	103.92 \pm 4.13	14.92	0.605	95.92 \pm 2.973	10.30

Arsenic (As):

Was observed beyond permissible limits in all four sampling sites. The highest concentration was seen in sample site A (Oorgaum) at 4100 mg/Kg, which is 330 times more than the permissible limit of 12mg/kg, whereas (Chakraborti *et al.*, 2013) found 9136 mg/kg in Jainapur village soil of Karnataka. The lowest concentration was observed at sample site C at 640 mg/kg as shown in Fig.1. The average mean concentration of all four sampling sites was around 1512 mg/kg from July-December 2014.

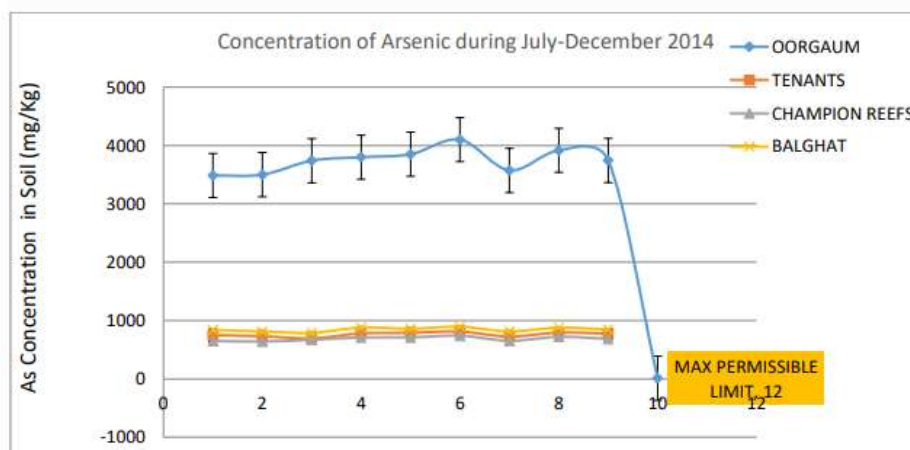


Fig 1: Concentration of Arsenic (As) in soil during July-December 2014 in mg/kg

Cadmium (Cd):

The maximum permissible limit for cadmium in soil according to USEPA 2002 is 1.5 mg/kg. All four sampling sites showed in excess, whereas the highest concentration of 92mg/kg and the lowest at 14 mg/kg was observed in sample sites A and B respectively as shown in Fig.2. The average mean concentration of all four sampling sites was 40.25 mg/kg, which was 26 times more than the permissible limits. 1.24 mg/kg of cadmium was reported by (Zeng *et al.*, 2022) in the coal mining fields of Xinjiang, China.

Iron (Fe):

Iron being an essential heavy metal, but still present in excess in the soil is detrimental to the higher organism. All four sampling sites showed higher concentrations and the average mean concentration was around 29384 mg/kg. The highest concentration was found in sample site A at 44680 mg/kg against the permissible limit of 21000 mg/kg laid down by WHO 2004. The lowest concentration was still beyond permissible limits with 22765 mg/kg at sample site B as shown in Fig.3. Whereas (Chakraborti *et al.*, 2013) found 50383 mg/kg of iron in Jainapur village soil of Karnataka

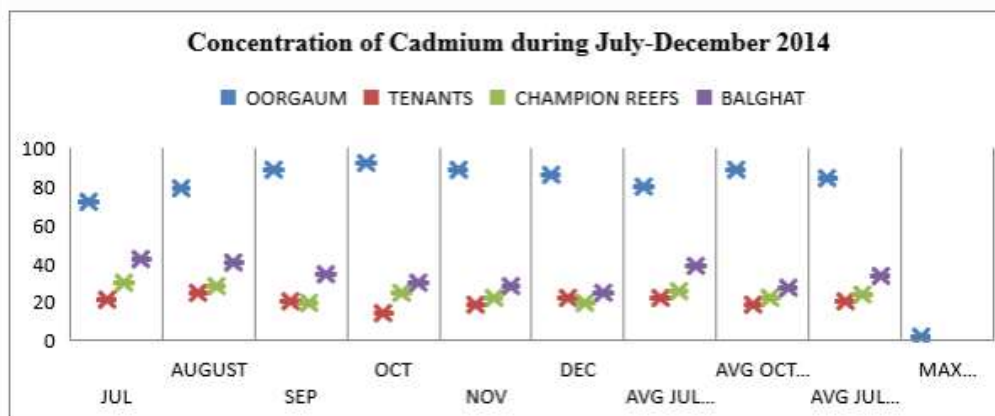


Fig. 2. Concentration of Cadmium (Cd) in soil during July-December 2014 in mg/kg

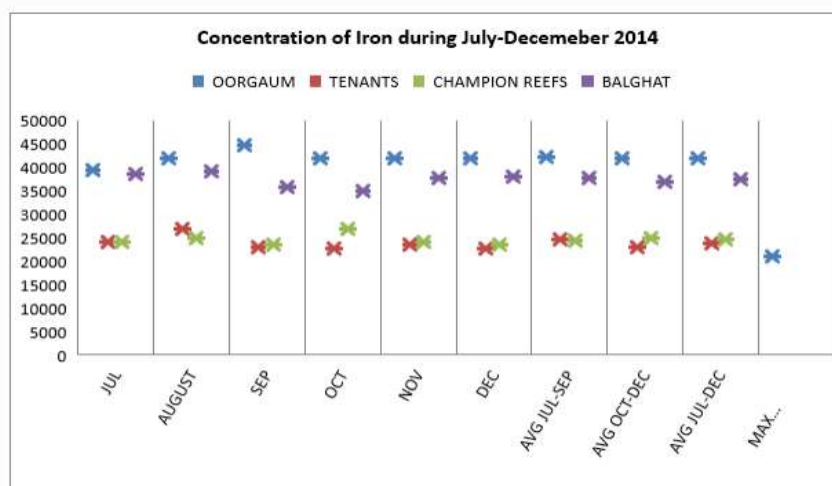


Fig 3: Concentration of Iron (Fe) in soil during July-December 2014 in mg/kg

Nickel (Ni):

The maximum permissible limit for nickel in soil according to WHO 2004 is 50 mg/kg. Three sampling sites B, C, and D showed in excess, whereas the highest concentration of 102 mg/kg and the lowest at 5 mg/kg was observed in sample sites C and D respectively. The average mean concentration of all four sampling sites was 72 mg/kg, which was 1.4 times more than the permissible limits. Sampling site A had shown signs of having safe limits of 11.5 mg/kg across the July-December 2014 campaign as shown in Fig.4. Whereas (Chakraborti *et al.*, 2013) found 91 mg/kg of nickel in Jainapur village soil of Karnataka.

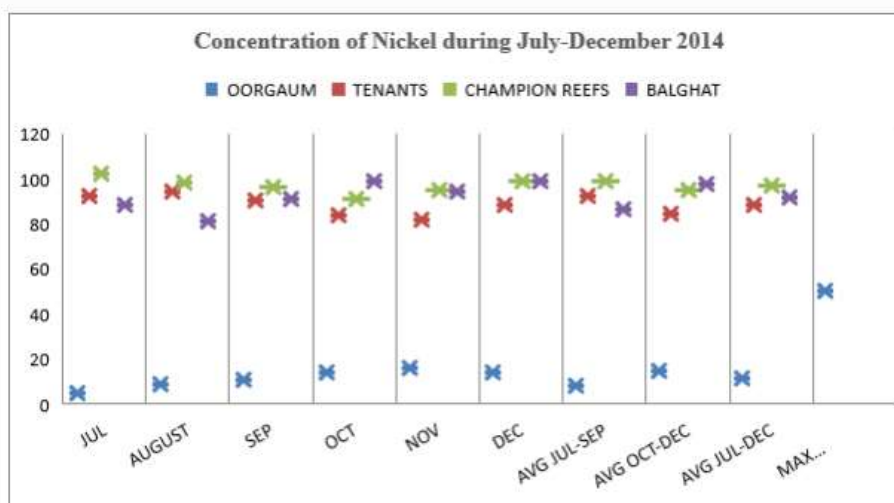


Fig 4: Concentration of Nickel (Ni) in soil during July-December 2014 in mg/kg

Chromium:

During July-December 2014 soil analysis, the average mean concentration of all four sampling sites was 108 mg/kg, which was 1.7 times more than the permissible limits. The maximum permissible limit for chromium in soil according to WHO 2004 is 64 mg/kg. All four sampling sites showed more than permissible limits, whereas the highest concentration

of 151 mg/kg and the lowest at 24 mg/kg was observed in sample sites C and A respectively as shown in Fig.5. Whereas (Chakraborti *et al.*, 2013) had found 112 mg/kg of chromium in Jainapur village soil of Karnataka.

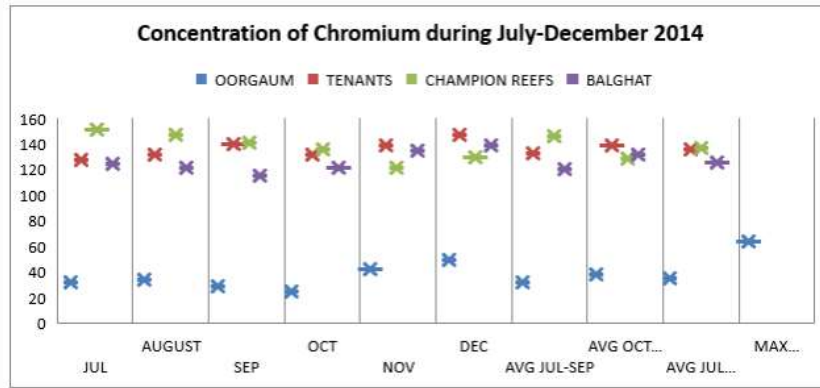


Fig 5: Concentration of Chromium (Cr) in soil during July-December 2014 in mg/kg

Copper:

The maximum permissible limit for copper in soil according to USEPA 2002 is 63 mg/kg. All four sampling sites showed in excess, whereas the highest concentration of 110 mg/kg and the lowest at 60 mg/kg was observed in sample sites C and B respectively as shown in Fig.6. The average mean concentration of all four sampling sites was 63.75 mg/kg, which was almost in lines of permissible limits. Whereas (Chakraborti *et al.*, 2013) found 93 mg/kg of iron in the Jainapur village soil of Karnataka. 162.36 mg/kg of copper was reported by (Zeng *et al.*, 2022) in the coal mining fields of Xinjiang, China.

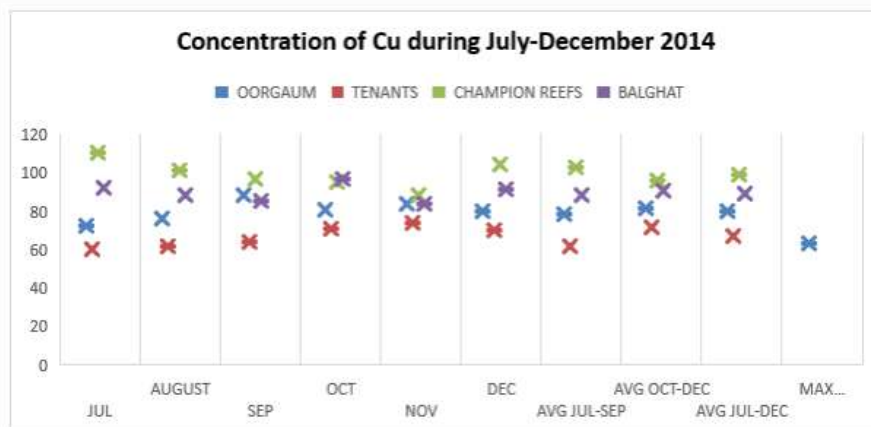


Fig 6: Concentration of Copper (Cu) in soil during July-December 2014 in mg/kg

Lead:

During July-December 2014 soil analysis, the average mean concentration of all four sampling sites was 58.2 mg/kg, which was comparatively less than the permissible limits. The maximum permissible limit for lead in soil according to WHO 2004 is 98 mg/kg. Except for sample site C, all other sampling sites showed less than the set permissible limits, whereas the highest concentration of 140 mg/kg and the lowest at 19 mg/kg was observed in sample sites C and B respectively as shown in Fig.7. Whereas (Chakraborti *et al.*, 2013) had found 34 mg/kg of lead in Jainapur village soil of Karnataka.

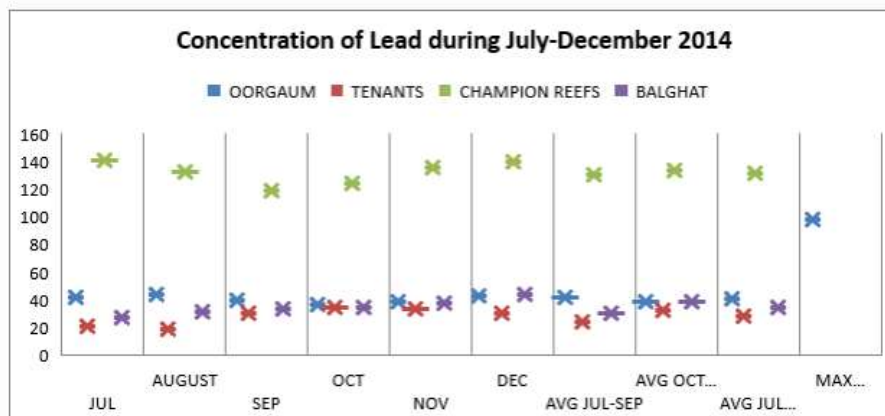


Fig 7: Concentration of Lead (Pb) in soil during July-December 2014 in mg/kg

Manganese:

The only heavy metal that was observed within the permissible limit in all four sampling sites is manganese (Mn). The maximum permissible limit for the manganese in soil according to WHO 2004 is 210 mg/kg as shown in Fig.8. All four sampling sites showed that the values were within permissible limits. The highest concentration of 124 mg/kg and the lowest at 78 mg/kg were observed in sample sites C and A respectively. The average mean concentration of all four sampling sites was 97.3 mg/kg, which was almost in the line with permissible limits. Whereas (Chakraborti *et al.*, 2013) found 6039 mg/kg of manganese in the Heggandoddi village soil of Karnataka.

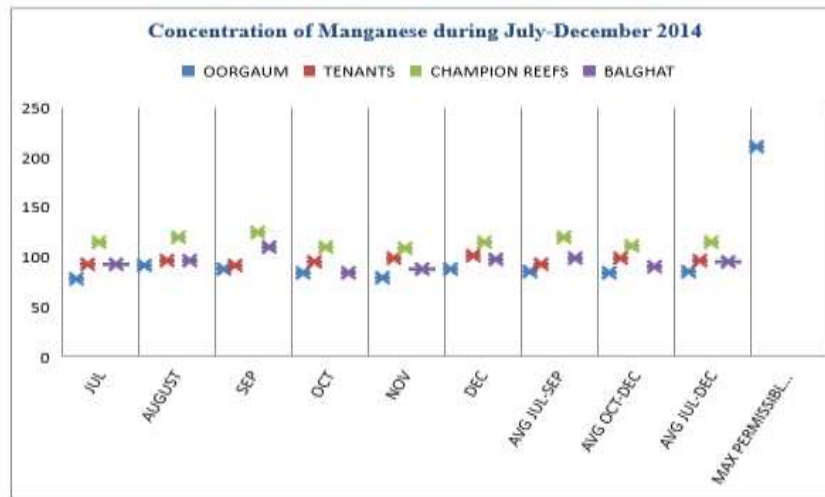


Fig 8: Concentration of Manganese (Mn) in soil during July-December 2014 in mg/kg

Conclusion

Analysis of heavy metals in soil samples indicated alarming levels of heavy metals like As, Cd, Fe, Cr, Cu, and Pb beyond the permissible limits set by WHO(2004) and USEPA (2002). As (Arsenic) was found 330% more than the permissible limit in site A and 125% more in sites B, C, and D. Only manganese was found to be present within the permissible limits in all four study areas. Statistical analysis using One-way ANOVA was used followed by SPSS software showed an insignificant correlation between various seasons of the year to that concentration of heavy metals, thereby we infer that these metals are not dependent on seasons and are present throughout the year in soil due to the past gold mining activities.

The current study exemplifies that 7 out of 8 heavy metals assessed were beyond the maximum permissible limits set by WHO 2004. Manganese was the sole heavy metal that was found to be present within permissible limits of WHO 2004. The present study accomplishes that further study is required to minimize the levels of contamination caused due to gold mining activities and the measures to be conceived to curb the entry of HM into both abiotic and biotic components of the study area, thereby reducing the effects caused by HM on higher order plants, animals and humans. This study also emphasizes measures to be taken to attain reclamation and remediation of the immediate environment in which the people of Kolar Gold Fields live.

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