Assessment of heavy metal contamination in soils around chromite mining areas, Nuggihalli, Karnataka, India

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Abstract Toxic heavy metals represent one of the possible environmental hazards from mine lands, which affect many countries having historic mining industries. The primary aim of the study was to investigate the degree of soil pollution occurring near chromite mines, and make a systematic evaluation of soil contamination based on geoaccumulation index, enrichment factor and pollution index. This paper presents the pollution load of toxic heavy metals (As, Ba, Co, Cr, Cu, Mo, Ni, Pb, Sr, V, Zn and Zr) in 57 soil samples collected around three different active (Tagdur), abandoned (Jambur) chromite mining sites as well residential zone around Chikkonda-nahalli of the Nuggihalli Schist Belt, Karnataka, India. Soil samples were analyzed for heavy metals by using Wavelength dispersive X-ray fluorescence spectrometry. Results indicated that elevated concentrations of Cr, Ni and Co in soils of the study area exceed the Soil Quality Guideline limits (SQGL). The high enrichment factor for Cr, Ni Co obtained in the soil samples show that there is a steady increase of toxic heavy metals risk in this area, which could be correlated with the past mining activity and post abandoned mining in the area. The data was also treated to study the geoaccumulation index, pollution index and spatial distribution of toxic elements. Emphasis need to be put on control measures of pollution and remediation techniques in the study area.

Introduction

Heavy metals in soil may come from agriculture activities, urbanization, industrialization and mining activities. Among these mine activity is considered as one of the most dangerous anthropogenic activities in the world. Mining operation, grinding, concentrating ores and disposal of tailings, provide obvious sources of contamination in the environment, along with mine and mill waste water (Adriano 1986). Even after the cessation of the mining works, huge tailing ponds, as a result of the accumulation of the wastes in pyramidal structures remain in the area with the consequent environment risk. As a result, elevated levels of heavy metals can be found in and around metalliferous mines due to discharge and dispersion of mine wastes into nearby agricultural soils, food crops and stream systems. Eventually, they may pose a potential health risk to residents in the vicinity of mining areas. Many studies have been conducted on heavy metal contamination in soils, plants, waters and sediments from metalliferous mines throughout the world (e.g., Thornton 1980; Fuge et al. 1989; Merrington and Alloway 1994). The extent and degree of heavy metal contamination around the mines vary depending upon geochemical characteristics and mineralization of tailings. Specifically, opencast mining activities have a serious environmental impact on soils and water streams, having generated millions of tones of sulphide-rich tailings (Bhattacharya et al. 2006; Rodríguez et al. 2009). The adverse effects of mining activities in the environment have been addressed by many authors in many parts of

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the world (Chopin and Alloway 2007; Gomes and Favas 2006; Lee 2003; Moreno et al. 2007; Navarro et al. 2004; Sun et al. 2006).

Trace elements contained in the residues from mining and metallurgical operations are often dispersed, included in particulate material or in aqueous solution by wind and/or water after their disposal (Lottermoser 2007). According to transport process, pollution could be established due to primary contamination, formed by residues placed close to the contamination sources, secondary contamination, produced as a result of trace element dispersion out of its production areas, through water and wind, whereas tertiary contamination, which involves trace element mobilization (Martínez-Sánchez et al. 2008).

The aim of the study was to evaluate the levels of toxic metals and to determine the associations between the different toxic elements with respect to their spatial distribution that can explain the spatial patterns of soil pollution in the area. Degree of pollution in soil, was also assessed using geoaccumulation index (I_{geo}) enrichment factor (EF) and pollution index. By this study it would provide baseline data regarding the distribution, accumulation of toxic metals in soils and would help in designing the pollution abatement strategy to control the spread of pollutants in the environment surrounded by mining activity.

Materials and methods

Study area

The Nuggihalli schist belt (NSB) is located in Karnataka state with coordination between 12°54′58″–13°1′48N″ latitude to 76°29′50′–76°22′45″E longitude. The present study area covers an area of 200 km^2 in southern part of the Nuggihalli schist belt which is situated in the western part of the Dharwar Craton in Karnataka, India. Geologically the Dharwar Craton is subdivided into the Western Dharwar Craton and the Eastern Dharwar Craton by a 500 km long lineament of alkali feldspar-rich granite known as the Closepet granite (Gupta et al. 2003; Naqvi 2005). The chromitite mineralization usually occurs as lenses, tabular or irregular bodies in the NSB. The chromite deposit were reported from the Jambur, Tagadur, Bhaktarhalli, Rangenbetta, and Byrapura areas (Radhakrishnan 1957). There are four important mining sites namely Bairapura, Bhaktarhalli, Tagadur and Jambur, of which only Bhaktarahalli and Tagadur mining is active.

Sampling method

The total numbers of 57 soil samples were collected from the top surface, i.e., 15 cm depth. The samples were collected using plastic spatula in self locking polythene bags and were sealed in double bags. The location of soil samples were noted using hand held Garmin GPS in the study area and it is shown in Fig. 1. Soil samples were dried for two days at 60 °C. The dry soil samples was finely powdered to 250 mesh size (US Standard) using swing-grind and then pellets were prepared for X-ray fluorescence spectrometry (XRF) analysis using a backing of boric acid and pressing it at 25 tons of pressure. A hydraulic press was used to prepare pellets to determine the trace elements. During the course of analysis to monitor the quality of chemical analysis and examine the accuracy of the data, soil reference materials, SO-1 and SO-4 issued by Canadian reference materials were analyzed with soil samples.

Instrumentation

A Philips PW2440 model MagiX PRO, wavelength dispersive fully automatic, microprocessor controlled with 168 position automatic PW 2540 vrc sample changer X-ray Spectrometer was used along with 4 kW X-ray generator for the determination of heavy metals like Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, V, Y, Zn and Zr in soil samples. The MagiX PRO XRF is a sequential instrument with a single goniometer measuring channel covering the entire elemental range. A rhodium (Rh) anode X-ray tube was used, which may be operated at a 60 kV and current up to 125 mA, at a maximum power level of 4 kW. Philips software "Super Q" was used to take care of dead time correction and interelement matrix effects. International soil reference materials from US Geological Survey, Canadian Geological Survey, International working group, France and NGRI, India were used to prepare calibration curves for trace metals (Krishna et al. 2007). Statistical parameters are given in Table 1.

Index of geoaccumulation (I_{geo})

The index of geoaccumulation enables the assessment of contamination by comparing the current and pre-industrial concentrations originally used with bottom sediments (Muller 1969), it can also be applied to the assessment of soil contamination. It is computed using the following equation:

$$I_{geo} = \text{Log}(C_n / 1.5 B_n)$$

where C_n is the measured concentration of element in the samples and B_n is either directly measured in texturally equivalent uncontaminated soils or taken from the literature. The constant 1.5 allow us to analyze natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences.
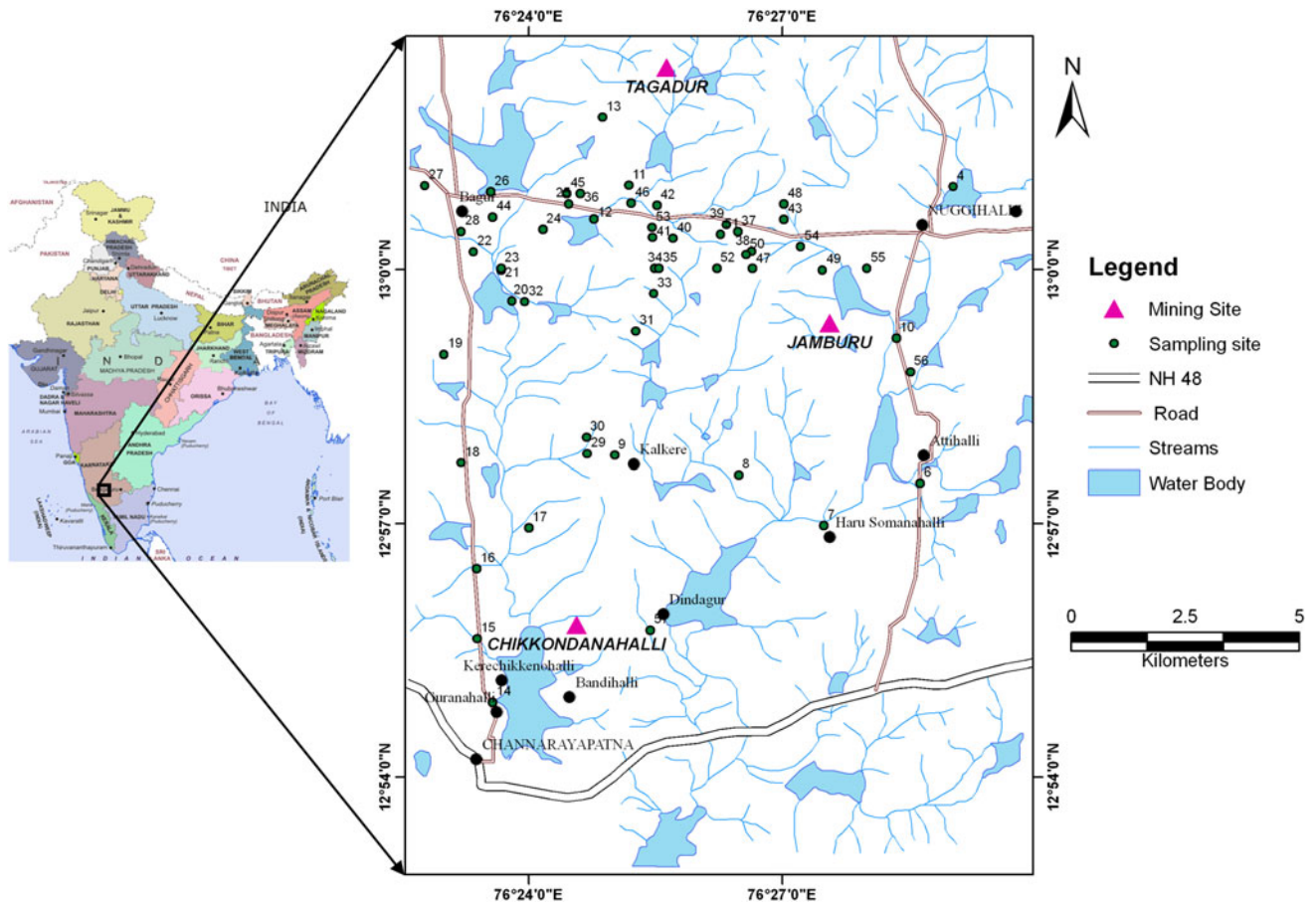
Fig. 1 Study area map with sampling locations

Table 1 Statistical parameters of metal content in Soil of Nuggihalli and reference value (Taylor and McLennan 1995) mg/kg

Parameters	Min	Max	Average	Standard deviation	Median	Kurtosis	Skewness	Reference value
As	0.00	11.20	2.47	1.38	2.30	29.09	4.50	1.5
Ba	168.30	602.30	488.79	78.15	506.20	4.24	−1.54	550
Co	2.10	74.20	21.54	14.92	19.10	4.06	1.79	10
Cr	64.10	4863	499.96	916.81	205.80	16.39	3.94	35
Cu	1.50	153.60	24.00	21.99	18.75	23.78	4.25	25
Mo	0.00	6.90	3.29	1.60	3.45	−0.48	−0.02	1.5
Ni	0.80	1,398.20	168.49	286.02	61.45	8.33	2.89	20
Pb	0.60	84.10	11.28	11.17	9.90	35.10	5.39	20
Sr	14.40	470.70	195.36	97.65	192.15	0.14	0.55	350
V	4.60	141.50	78.00	31.43	74.30	−0.41	0.04	60
Zn	57.00	655.20	98.54	86.53	80.60	33.33	5.59	71
Zr	14.60	945.50	395.35	162.82	378.40	1.68	0.65	190

Here, modified calculations based on the equation given by Krzysztof et al. 2003, was applied in the present studies where C_n denotes the concentration of a given element in the soil tested, and B_n denotes the concentration of element in the earth's crust (Taylor and McLennan 1995). For some elements like As, Hg and Sb the average concentration in the earth's crust is much higher than the average concentration in the shale accepted by Muller (1969) as a reference value. Here, the focus is between the concentration obtained and the concentration of elements in the earth's crust because soil is a part of the layer of earth's crust and its chemical composition is related to the one of the crust. The

Table 2 Index of geoaccumulation (I_{geo}) and contamination level

I_{geo}	I_{geo}	Contamination level
<0	0	Uncontaminated
0–1	1	Uncontaminated to moderately contaminated
1–2	2	Moderately contaminated
2–3	3	Moderately to strongly contaminated
3–4	4	Strongly contaminated
4–5	5	Strongly to extremely contaminated
>5	6	Extremely contaminated

Table 3 Enrichment factor (Sutherland 2000)

Level	Enrichment factor
<2	Depletion to minimal enrichment suggestive for or minimal pollution
2–5	Moderate enrichment, suggestive of moderate pollution
5–20	Significant enrichment, suggestive of a significant pollution signal
20–40	Very highly enriched, indicating a very strong pollution signal
>40	Extremely enriched, indicating an extreme pollution signal

Müller index of geoaccumulation, I_{geo}, indicating the level of contamination found in various sediments and soils. I_{geo} consists of seven grades ranging from unpolluted to very seriously polluted (Table 2) (Muller 1969).

Enrichment factor (EF)

The value of EF was calculated using the modified formula given by Krzysztof et al. (2003) based on the equation suggested by Buat-Menard and Cherselet (1979). The EF was based on the standardization of a tested element against a reference one. A reference element is one characterized by low occurrence variability (Saur and Juste 1994; Sutherland 2000; Reimann and De Caritat 2000).

In this study Zirconium (Zr) was used as reference since it occurs as an oxide or a silicate and belongs to the lithophile elements, it has a high chemical stability during weathering. Most of Zr minerals accumulate in placer deposits, small quantity takes part in sedimentation circulation and absorbed by clay minerals (Wang et al. 2008). Zr has been used widely in geochemical studies of mineral weathering as a stable lithogenic element or for assessment of depletion of more reactive heavy metals in sediments (Rubio et al. 2000; Zhang et al. 2006; Cobela-Garcia and Prego 2003) and to reduce the scatter data and allow a precise definition to background value as normalizer. So, in this study Zr was chosen as the reference element.

$$EF = \{C_n(\text{sample}) / C_{ref}(\text{sample})\} / \{B_n(\text{background}) / B_{ref}(\text{background})\}$$

where C_n (sample) is the concentration of element in soil, C_{ref} (sample) is the content of the reference element in the examined environment, B_n(background) is the content of examined element in the reference environment and B_{ref}(background) is the content of the reference element in the reference environment. The crystal zircon (Zr) value used is 190 mg/kg (Taylor and McLennan 1995). EF consists of five grades ranging from depletion to extremely enriched (Table 3) (Sutherland 2000).

Pollution index

It is generally agreed that most heavy metal contamination in the surface environment is associated with a mixture of contaminants rather than one metal. Thus, many workers have used pollution index (PI) of soils to identify multi-element contamination resulting in increased overall metal toxicity (Nimick and Moor 1991; Chon et al. 1998). Generally, pollution index is defined as the ratio of heavy metal concentration of the corresponding metal to its geochemical background concentration. In this study, the geochemical background concentration levels for soils suggested by Canadian soil quality guidelines of the Canadian Council of Ministers of the Environment (CCME 1991) were adopted for the assumed permissible levels and the PI was calculated by the equation;

$$\text{Pollution Index} = C_i / S_i$$

where PI is the evaluation score corresponding to each sample, C_i is the measured concentration of the examined metals in the soils, and S_i is the geochemical background concentration of the metals. The PI values of each metal contamination can be classified as either low contamination (PI ≤ 1.0); moderate contamination (1.0 < PI ≤ 3.0); high contamination (PI > 3.0).

Results and discussions

Spatial distribution of trace elements as environmental contaminants

During the last couple of decades, trace element studies appears to have been dominated with their role as environmental contaminants; and infers that perhaps metals are the most important group of contaminants. Both organic and inorganic environmental contamination and pollution is of equal significance. The prioritization of pollutants or contaminants largely depends upon their potency to cause harm to the environment and the availability of the
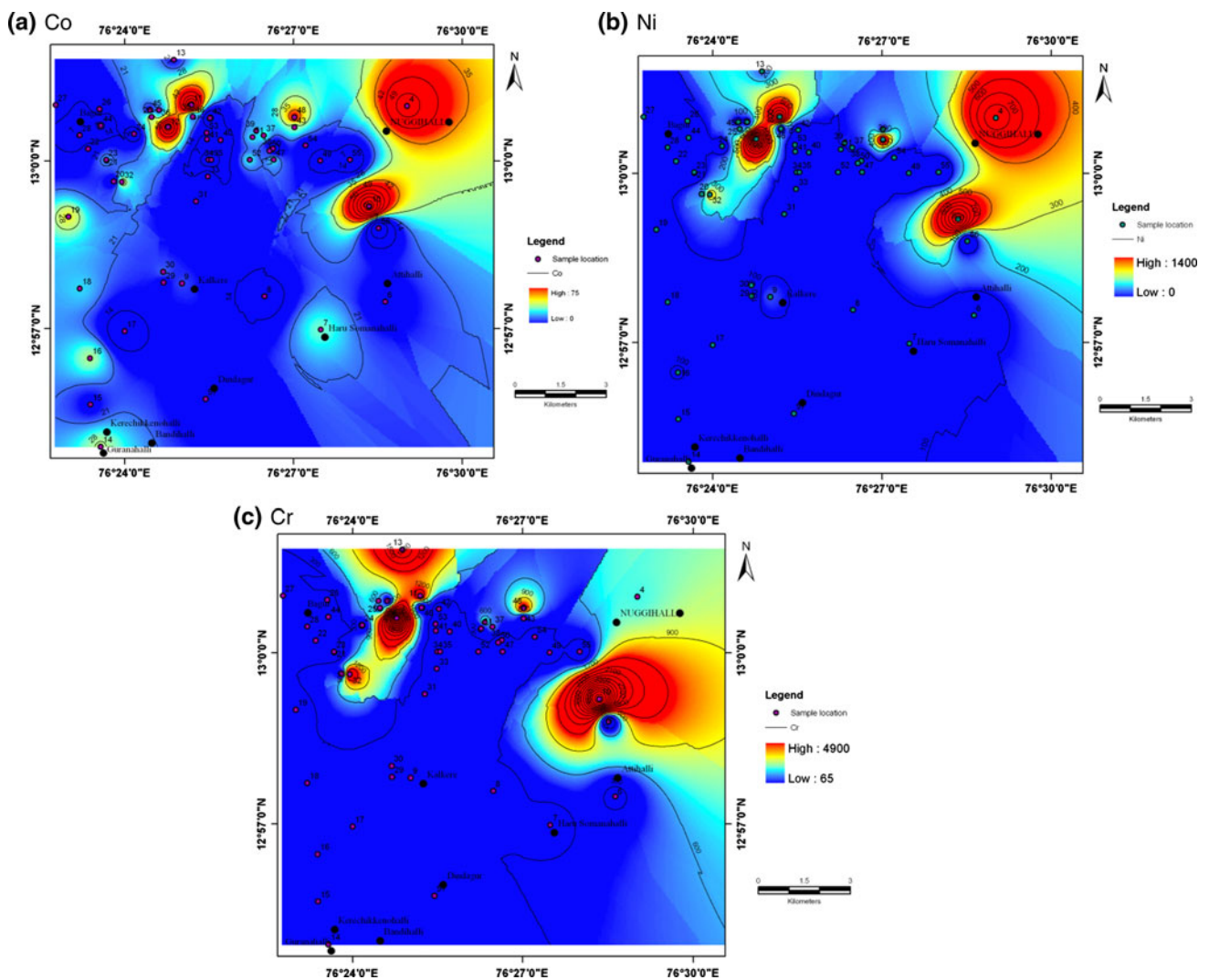
Fig. 2 Spatial distribution maps for Co, Ni and Cr

methods used to assess them. Indeed, most toxic inorganic contaminants like Pb, As, Cr, Cd, Ni and Zn are reported in their decreasing order of frequency of occurrence in US National Priority list sites.

Chemical analysis of soils collected from mine workings and mine dumps in the study area indicated high levels of As, Ba, Cr, Co, Cu, Mo, Pb, Sr, V, Zn and Zr. Table 1 represent the relevant statistical data of the elements), far above the threshold values in soil. Because of the location of residential area amidst the dumps, there is high probability that these high concentrations may cause health hazards. Spatial distributions of selected heavy metals such as Co, Ni and Cr are exhibited (Fig. 2) with the help of ArcGIS 9.3.1 Version. The maps were generated by ordinary interpolation method in spatial analysis tool of GIS then contour was generated and revealed. Therefore, the concentration spatial distribution map of

heavy metals was an indicator of the heavy metal contamination in soils.

Arsenic

The mean arsenic content in the soil was 2.5 mg/kg ranging from 0.00 to 11.20 mg/kg, which is identified below the permissible levels of 12 mg/kg (CCME (Canadian Council of Ministers of the Environment) 1991). The I_{geo} calculated for As changes from -1.17 to -2.29 (Fig. 3). The mean I_{geo} for arsenic was 0.04 mg/kg, which indicated practically uncontaminated soil, while maximum values classify soil as heavy to heavily contaminated. The results obtained for EF ranged from 0 to 4.09 (Fig. 4). The maximum and minimum values implied deficiently in minimal soil enrichment as per five categories recognized on the basis of EF (Sutherland 2000) with arsenic.

Fig. 3 Indexes of geoaccumulation for metals in soils of Nuggihalli

Legend
- Max
- 75 percentile
- Median
- 25 percentile
- Min
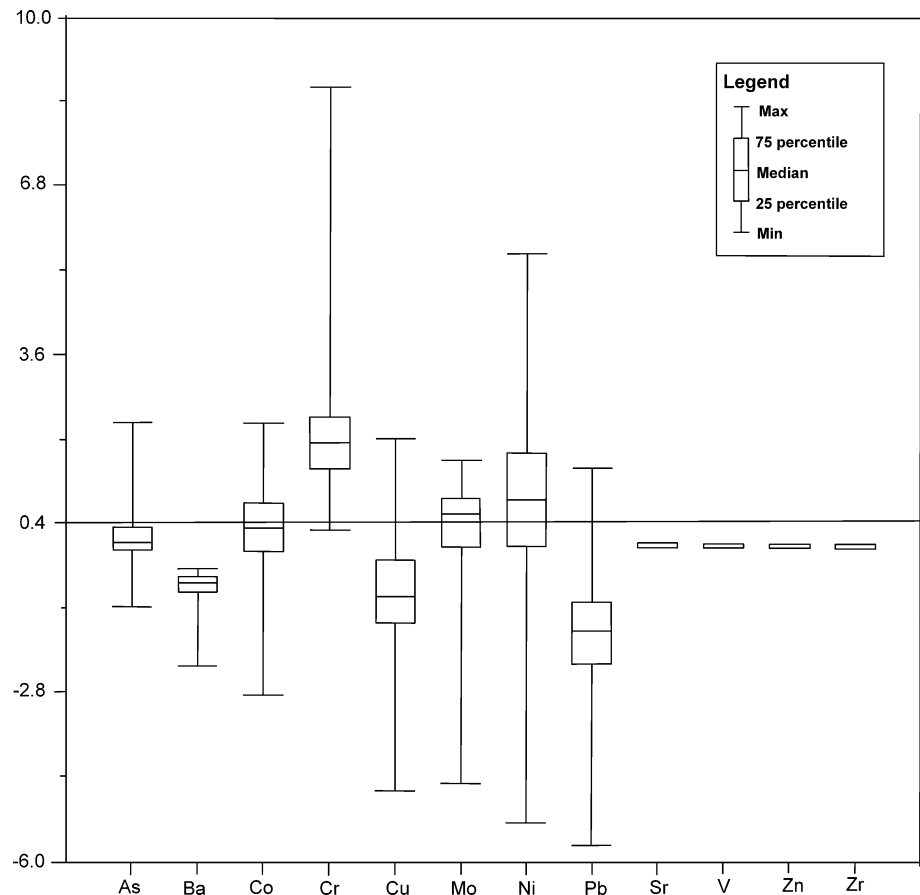
Barium

The average barium content is 488.8 mg/kg and ranges from 168.3 to 602.3 mg/kg showed less than mean content indicating the polluted soil. The I_{geo} obtained ranges from −2.29 to −0.45 revealed that nearly all the samples examined fell into class 0 practically uncontaminated with barium as per Muller's six classes of the geoaccumulation index (Fig. 3). The EF was also low and ranged from 0.21 to 3.98, confirming a moderate enrichment with barium (Fig. 4).

Cobalt

The cobalt ranged from 2.1 to 74.2 mg/kg and the mean concentration is 21.5 mg/kg. The I_{geo} calculated ranges from −2.84 to 2.31 mg/kg (Fig. 3) and the mean value of 0.18 which denoted less soil contamination and maximum values classified the soil is moderately contaminated. Similarly the EF ranges from 0 to 90.0 and its mean 3.11, confirming a moderate enrichment of cobalt in soil (Fig. 4).

Chromium

The average concentration of chromium is 790.98 mg/kg and much higher values were reported in the study area ranges

from 64.1 to 4,863 mg/kg in the soil samples collected in the study area. The I_{geo} revealed that most of the samples examined fell into classes five and seven, strongly to very strongly contaminated ranging from 0.29 to 8.67 (Fig. 3). The EF obtained for chromium ranges from 0.78 to 859.91 (Fig. 4) which again falls under the class of very high enrichment. There are about five Chromium mining sites in the study area, due to this mining activity the soil of the study area enriched with chromium. The source of chromium appears to be anthropogenic from the mining activity, in the study area.

Copper

The average copper content in the soil examined was 24 mg/kg. The I_{geo} obtained for copper ranges from −4.64 to 2.03 mg/kg (Fig. 3) and the mean value is −0.93 confirmed practically unpolluted soil. The EF for copper ranges from 0 to 3.37 (Fig. 4) indicate moderate enrichment, suggestive of moderate pollution of copper in the soil.

Molybdenum

The Molybdenum content ranged from 0 to 6.9 mg/kg and its average value is 3.3 mg/kg. The I_{geo} indicated that the soils of Nuggihalli area falls under class I and II ranging

Fig. 4 Enrichment factors (EFs) for metals in soils of Nuggihalli
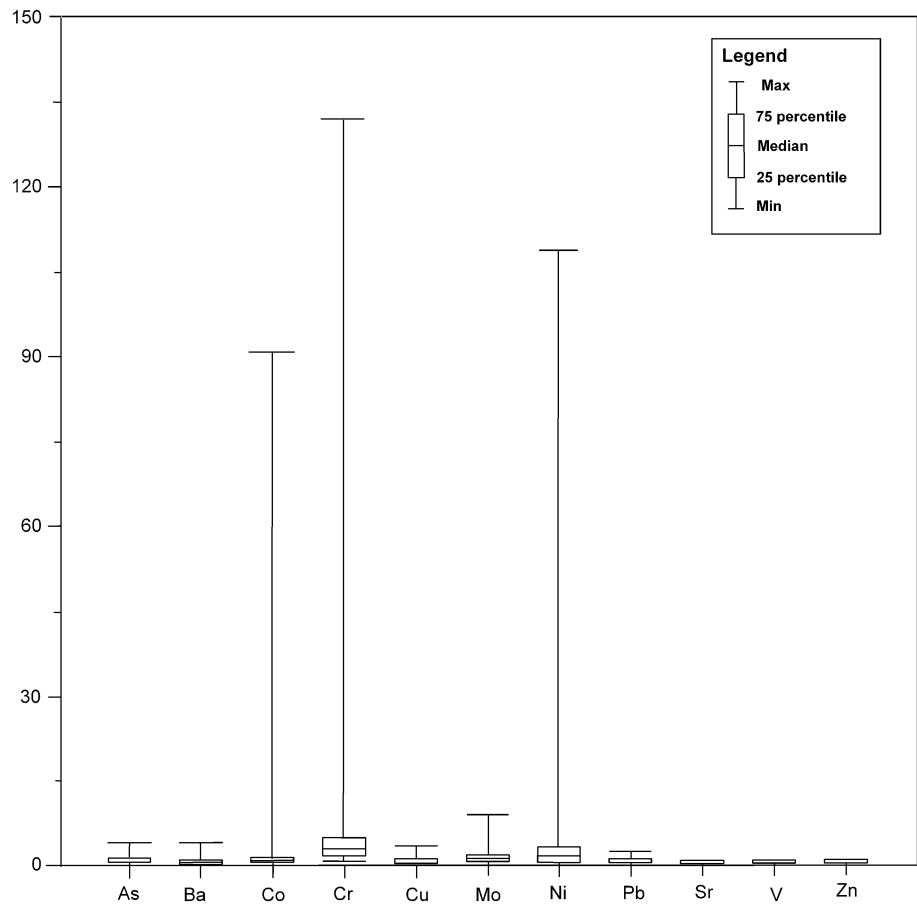
from −4.49 to 1.62 showing practically unpolluted to moderately polluted. Similarly in the case of EF it showed moderate enrichment suggestive of moderate pollution with the mean content of 2.10.

Nickel

The average of Nickel content 168.5 mg/kg in soils ranges from 0.8 to 1,398.2 mg/kg. Nickel in soil is usually present in the organically bound form, which under acidic and neutral conditions increases its mobility and bioavailability (Kabata-Pendias and Pendias 1999). The I_{geo} values ranges from −5.23 to 5.54 mg/kg (Fig. 3) with the mean value of 1.7 fell under classes three, moderately contaminated (Muller 1969). The EF for nickel ranges from 0 to 595.7 with a mean of 17.29 (Fig. 4), significant enrichment of Nickel in the soil.

Lead

With the mean value of 11.3 mg/kg and ranges from 0.6 to 84.1 mg/kg shows all the soil samples were not contaminated with Pb, the Pb value for surface soil on the global scale has been estimated to be 25 mg/kg levels above this suggest an anthropogenic influence (Kabata-Pendias and Pendias 1999). The I_{geo} obtained for Pb ranges from −5.64 to 1.49 mg/kg

(Fig. 3) indicate practically unpolluted with mean value of −1.67. Similarly, the EF ranges from 0 to 2.3 also show the soils in the study area are depletion to minimal enrichment (Fig. 4).

Strontium

Strontium is easily mobilized during weathering, especially in oxidizing acid environments, and is incorporated in clay minerals and strongly fixed by organic matter (Gowd et al. 2010). The average strontium concentration in the study area is 195.4 mg/kg and ranges from 14.4 to 470.7 mg/kg (Fig. 3). Moreover, the concentration of Sr in soil is within permissible levels, which indicate its normal concentration and reflect the background value in soil. However, in the study area Sr content in soil was falling in class 0 showing uncontaminated with I_{geo} ranging from −5.19 to 0. The EF ranges from 0 to 0.67 indicating the depletion to minimal enrichment of Sr in the soil (Fig. 4).

Vanadium

The V in the soils is estimated to be the average of 78.0 mg/kg ranging from 4.6 to 141.5 mg/kg. The I_{geo} indicated that the soils in Nuggihalli area falls under class 1 ranging from −0.99 to 0.5 and mean value of 0.19 showing unpolluted

Table 4 Pearson correlation coefficient matrix for elements in the soil samples

	As	Ba	Co	Cr	Cu	Mo	Ni	Pb	Sr	V	Zn	Zr
As	1.00	0.38	−0.11	−0.09	**0.74**	0.00	−0.17	**0.98**	0.03	0.06	**0.70**	−0.11
Ba		1.00	−0.47	−0.56	0.29	−0.39	−0.70	0.30	0.21	0.55	0.13	0.43
Co			1.00	**0.74**	0.22	−0.20	**0.86**	−0.09	−0.57	0.08	−0.05	−0.60
Cr				1.00	−0.03	0.08	**0.83**	−0.05	−0.37	−0.20	0.01	−0.45
Cu					1.00	−0.35	0.01	**0.77**	−0.21	0.40	**0.73**	−0.23
Mo						1.00	0.20	0.02	0.54	−0.96	−0.22	−0.06
Ni							1.00	−0.11	−0.37	−0.36	−0.01	−0.56
Pb								1.00	0.07	0.03	**0.72**	−0.12
Sr									1.00	−0.54	−0.12	0.37
V										1.00	0.18	0.12
Zn											1.00	0.01
Zr												1.00

Bold values indicate significant correlation matrix at $P \leq 0.01$
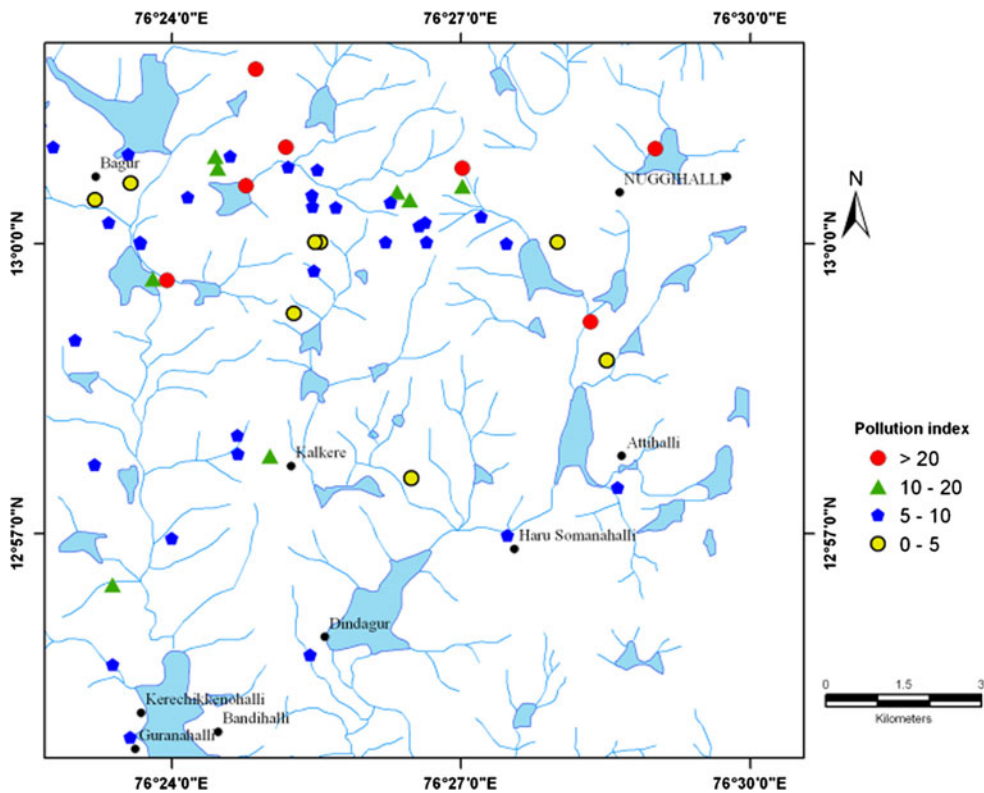
Fig. 5 Scatter diagram of pollution index (PI) for soils

and EF's indicated depletion to minimal enrichment with mean content of 0.73 ranging from 0.16 to 2.58.

Zinc

The average zinc concentration in the study area is 98.5 mg/kg, ranges from 57 to 655.2 mg/kg, which is moderate. The I_{geo} indicated that the soils in the study area fall under classes 0 to 1 ranging from minimum of 0.03 practically uncontaminated and 1.09 showing to moderately contaminated (Fig. 3). The EF ranging from 0.21 to 11.11 indicate minimal enrichment (Fig. 4) with mean value of 0.97. The normal threshold value prescribed in soil is 200 mg/kg.

Correlation of heavy metals and its contribution in the soil of Nuggihalli

Basic statistical parameters (Table 1) of the elements show that all elements are represented by high skewness and kurtosis coefficients except Ba and Mo. Heavy metals in soil usually have complicated relationships among them and numerous factors control their relative abundance e.g., original contents of heavy metals in parent materials, rocks and various processes of soil formation and anthropogenic factors such as contamination by mining activity and human activity. Pearson's correlation analysis was performed on the obtained data in which the strong positive correlation ($r^2 > 0.5$) was identified between As–Cu, Pb; Co–Cr, Ni; Cu–Pb, Zn; Pb–Zn (Table 4).

The highest correlation coefficients are found between As–Cu ($r = 0.74$); As–Pb ($r = 0.98$); As–Zn ($r = 0.70$); Co–Cr ($r = 0.74$); Co–Ni ($r = 0.86$); Cr–Ni ($r = 0.83$); Cu–Zn ($r = 0.73$); Pb–Zn (0.72); Mo–V ($r = 0.96$). Such high correlations between soil heavy metals may reflect that these heavy metals had similar pollution level and sources. The strong correlation between As–Pb indicates source of agriculture activity in the area and Cr–Ni show leaching of some of toxic metals like Ni, Zn from tailings of the chromite mines. Overall the elements As, Co, Cr, Cu, Mo, V, Pb, Ni and Zn are grouped together, indicating that the anthropogenic sources of these heavy metals are closely related in the soils of the study area. Further, using the pollution index equation, the scatter diagram for the PI in surface soil is shown in Fig. 5. A PI of >5.0 was found in the places in the study area, which are considered to be contaminated. With the exception of these two places, however, the PI in most soils sampled was <5.0.

Conclusion

The study area Nuggihalli and its surrounding areas are contaminated due to Chromium metalliferous mining in various places like Tagadur, Jambur, Bhaktarahalli and Bairapura. The detected levels of total metal contamination in many of samples were found to exceed international threshold values. Risk assessment based upon soil quality guidelines limits proves that the soil is a serious health risk to humans.

The application of the index of geoaccumulation, EF and pollution index enabled us to find elevated contents of some toxic metals in soils of Nuggihalli mining area As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn. It may be caused by leaching of the elements from the soil into water-bearing formations. These elevated amounts may enter into the food chain and thus pose a hazard to human and animal health. The high content of toxic metals in the environment

may also cause an increase in their content in groundwater as a result of leaching.

The analytical results of Cr, Co and Ni obtained in the soils of the study area also indicated that the pollution by these elements in the area originated mainly from past mining activity in the area, either from indiscriminate dumping of mining wastes or from release of untreated effluents on to the ground which contaminate the underground water table. The present study carried out in the mining area is first of its kind to assess the contribution of toxic metal contamination by knowing the total metal concentration of individual toxic metals. A detailed speciation studies by knowing different forms of toxic metals are to be carried out to know the exchangeable metal processes and organic bound metals based on the leaching and extraction studies. Further, according to the environmental quality criteria for soils, the site would require remediation.

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