

Spatial variability and temporal changes in the trace metal content of soils: implications for mine restoration plan

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Abstract Trace metals in soils may be inherited from the parent materials or added to the system due to anthropogenic activities. In proposed mining areas, trace metals become an integral part of the soil system. Usually, researchers undertake experiments on plant species selection (for the restoration plan) only after the termination of mining activities, i.e. without any pre-mining information about the soil-plant interactions. Though not shown in studies, it is clear that several recovery plans remain unsuccessful while carrying out restoration experiments. Therefore, we hypothesize that to restore the area effectively, it is imperative to consider the pre-mining scenario of metal levels in parent material as well as the vegetation ecology of the region. With these specifics, we examined the concentrations of trace metals in parent soils at three proposed bauxite locations in the Eastern Ghats, India, and compared them at a spatio-temporal scale. Vegetation quantification and

other basic soil parameters accounted for establishing the connection between soil and plants. The study recorded significant spatial heterogeneity in trace metal concentrations and the role of vegetation on metal availability. Oxidation reduction potential (ORP), pH and cation exchange capacity (CEC) directly influenced metal content, and Cu and Ni were lithogenic in origin. It implies that for effective restoration plant species varies for each geological location.

Keywords Mines · Nitrogen-fixing species · Soil monitoring · Surface soil · Trace metals

Introduction

Mining of minerals, inevitably, leads to the disruption of the soil system. Such destructions result in a permanent reduction of soil productivity and may significantly alter the hydrologic system (Chandra et al. 2011). Metals are present in soil in different chemical forms, which influence their reactivity and hence their mobility, bioavailability and subsequent toxicity. Often, because of mining, the mobility of trace metals changes. Movement of trace metals in soil layers is of major environmental concern as their transport in soil eventually leads to deterioration of other components in the environment (Abolude et al. 2009). Trace metal concentrations in soils remain associated with either biological or geochemical cycles and influenced by anthropogenic activities (Prusty 2008; Prusty and Azeez 2007). Issues related to metal contamination and management are

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common due to human activity and its subsequent impact on the environment (Fernandes and Henriques 1991; Kabata-Pendias and Pendias 1992). Other factors influencing trace metal content in soil are mineralogical and geochemical compositions of the parent rock, organic matter content, particle size distribution, soil horization, age, drainage, vegetation and aerosol input (Kabata-Pendias 1993; Prusty and Azeez 2007; Prusty et al. 2008).

Trace metals in the soil can cause phytotoxicity and exhibit impaired microbial activities in the rhizosphere region. Largely, metal toxicity does not arise in natural soils with their native vegetation. Ultramafic ecosystem, natural mineral deposits, comprises of metal-enriched soils and high concentrations of Ni, Cr and Co (Brooks 1987). Endemic metallophytes inhabiting this ecosystem thrive well in metal-enriched environments. After some time, the native plants often become adapted to these elevated levels (Brooks et al. 1992; Ouzounidou 1994). Nevertheless, in case of new growth regimes, e.g. agriculture, plants may not be suitable for such soils. Thus, this would lead to either toxicity or absence of colonization of the species (Fergus 1954).

The mining industry has several environmental implications and repercussions. Various mining processes release trace metals in unnaturally high amounts (Helmisaari et al. 1995). Thus, stern environmental legislations make reclamation and reforestation of mined areas quintessential for metal cleanup. The damage to the soil and vegetation due to mining, unless carefully prevented, is tremendous, as the original ecosystems by the mining process remain grossly disturbed or buried. Thus, fundamental restoration becomes essential. Literature review reveals that the majority of studies on the soil referring to the metals were undertaken in highly contaminated and industrial areas. There are very few studies on metal distribution in naturally occurring forest ecosystems. Soil properties play an important role in nutrient and trace metal dynamics in the system. Knowledge about plants that help in ameliorating contaminated soils (Chandra 2012) is essential. Thus, we assume that information on soil properties, related metal concentrations and vegetation pattern are obligatory to understand their distribution on a spatio-temporal scale. This will help in strengthening the recovery plan with naturally occurring plant species. Studies on the temporal variation are also important in view of the annual vegetation cycles and their role in the soil nutrient cycling (Prusty et al. 2008). With these specifics, the present study

examined the soil characteristics and assessed levels of select trace metals (Cu, Ni and Zn) on a spatio-temporal scale in proposed bauxite mining locations. The study also focused on the basic soil properties, which tend to affect metal concentrations, and involved changes in vegetation patterns as select plant species may influence soil pH, which in turn affects the metal concentrations. In the present study, we assessed and discussed metal variability in the investigated areas in relation to pH, ORP, organic matter, TAP (total available phosphorous), K and vegetation ecology.

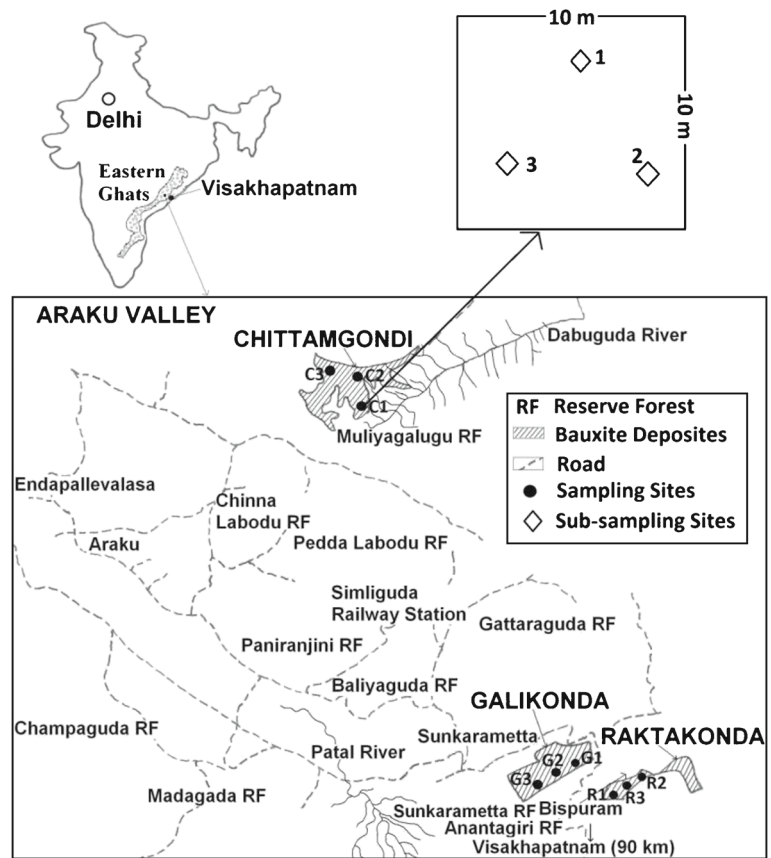
Materials and methods

Study area

We undertook the study in Araku, Eastern Ghats, India, and selected three bauxite locations (Raktakonda, Galikonda and Chittamgondi, Fig. 1) for examining metal variability in the natural soil system. Lateritic bauxite capping over khondalite covered the hilltops of these three locations. The soil type predominantly was lateritic in the plains and lateritic and rocky in the hilltops. Red ferruginous loam mixed with quartzite was on the higher slopes and sandy loam to clayey on the lower slopes and villages. The forest type, particularly along the slopes of the hillocks and valleys, was secondary in origin (SubbaRao and Kumari 2002). The indigenous tribal community followed the 'slash and burn' practice. The plant species common for bauxite-rich deposits were present in the area. The temperature variation was from 10 to 37.8 °C. The annual rainfall varied from 800 to 1,000 mm in the plains and 1,000 to 2,000 mm in the hills.

Geological Survey of India (GSI) and Mineral Exploration Corporation Ltd. (MECL) reported 10.8 million tonnes of mineable bauxite reserve in Raktakonda (GEL 2005a). A blanket of laterite bauxite in varying thickness occurred on Galikonda hilltop. Reddish- or brownish-coloured bauxite was present as moderately hard lenses and weathered patches. Occasionally, khondalites were present in the capping. Bauxite was residual in origin and of quaternary age. Galikonda had 13.60 million tonnes of mineable bauxite reserve (GEL 2005b). Outcrops of bauxite capping over khondalite covered the Chittamgondi hilltop. Chittamgondi had 24.57 million tonnes of mineable bauxite reserve (GEL 2005c). Gibbsite was the main aluminous mineral, haematite and goethite were iron ore minerals, and

Fig. 1 Study area map



kaolinite was the clay mineral, in all the three locations. In Raktakonda and Galikonda, alumina varied from 40 to 56 %, iron oxides varied from 7 to 28 %, silica was less than 4 %, titanium was 3 %, and alumina/silica module was less than 16. In Chittamgondi, alumina was between 40 and 58 %, iron oxides varied between 5 and 34 %, and silica was less than 4 %. Soil particle size was in the order sand>silt>clay. Mostly, the rocks of khondalite and charnockite groups of the Archean age, forming a part of the peninsular shield, represented the region (ICFRE 2007).

Soil sampling, processing and analyses

We undertook the study for two consecutive years and followed random soil sampling protocol for all the three locations, seasonally (February, May, August and November). For spatial variations, we selected three sites from each location, i.e. three sites each from Raktakonda, Galikonda and Chittamgondi. We collected samples in triplicate at each sampling site

(Raktakonda: R1, R2 and R3 sites; Galikonda G1, G2 and G3 sites; Chittamgondi: C1, C2 and C3 sites), from four successive layers, i.e. 0–5 cm, 5–10 cm, 10–15 cm and 15–20 cm in depth using a plastic scoop. In total, we collected 864 soil samples (3 locations×3 sites×3 replicates×4 layers×4 seasons×2 years) during the entire survey. The field sampling involved (1) packing of soil samples in pre-cleaned airtight plastic bags, (2) labelling with appropriate coded number and (3) subsequent transfer to the laboratory for further processing. In laboratory, the samples were (1) air-dried at normal room temperature (Jackson 1958), (2) homogenized using an agate mortar and pestle, (3) sieved through a standard sieve of 2-mm mesh (Tandon 2005) and (4) stored in pre-cleaned plastic containers for further analysis.

We processed one portion of the stored samples following standard protocols for soil characterization that included pH, ORP (oxidation reduction potential, millivolts), TOC (total organic carbon, percentage), CEC (cation exchange capacity, milliequivalents/kilogram), TAP (total available phosphorous, milligrams/kilogram)

and K (milligrams/kilogram) (Allen 1989; Tandon 2005). The pH and ORP were analyzed in soil-water extracts (1:5 w/v) using digital electrodes. TOC (percentage) was estimated following the modified chromic acid wet digestion method of Walkley and Black (1934), wherein the organic matter was oxidized with a mixture of potassium dichromate and concentrated sulphuric acid, utilizing the heat of dilution of the acid to speed up the process. The unspent potassium dichromate was back titrated against ferrous sulphate solution. We extracted soil samples with ammonium acetate at pH 7.0 for CEC estimation (Darmody and Marlin 2002). TAP (milligrams/kilogram) determination in soil was by ammonium fluoride extracting solution as per Bray and Kurtz (1945). Estimation of TAP (milligrams/kilogram) was done spectrophotometrically using Perkin Elmer Spectrophotometer (model Lambda 35). We determined the concentration of TAP in the samples using linear regressions (with zero intercept). Extraction of K was with 1 M neutral ammonium acetate solution (SubbaRao and SammiReddy 2005). The extraction of K was done by shaking 5-g samples of air-dried soil in 25 ml of extractant for 30 min, followed by filtration and subsequent analyses using a Flame Photometer (Systronics 126). We processed the other fraction for estimation of trace metals. Estimation of Cu, Ni and Zn was after digesting the samples following mixed acid digestion technique (Allen 1989). The acid digest was stored in acid-cleaned metal-free polypropylene bottles. Estimation of Cu, Ni and Zn in the digest was by using Atomic Absorption Spectrometer (AAS) (Perkin Elmer AAnalyst 200). We used calibration curves to calculate the concentration of the metals. A reagent blank helped in zeroing the instrument. Later, we aspirated different standard solutions and soil sample digest into the AAS. We verified the precision of the method and accuracy by running blanks and internal standards simultaneously. The precision and bias were usually <10 %. Standard addition technique reduced the matrix effects in the analyses. The estimated detection limit of the metal in the soil was 0.1 µg/g, and reanalysis of pre-analysed soil samples showed a recovery rate of 96.7 %. For quality assurance throughout the experiments and analyses, all extracting reagents were prepared using metal-free, AnalaR grade chemicals procured from the Qualigens Fine Chemicals Division of GlaxoSmithKline Pharmaceuticals Limited, Mumbai, India. Reagent preparation was by double-distilled water, which was prepared using quartz double distillation assembly. Standard cleaning procedures for polypropylene bottles and other

glassware used in the experimental work were as per Laxen and Harrison (1981).

Vegetation sampling

We followed line transect method for vegetation composition of the entire study area. Two transects were laid in each location. Along transects, quadrats of three sizes were laid at varying intervals. We studied trees, shrubs and herbs by laying quadrats of 20×20 m, 5×5 m, and 1×1 m, respectively. Tree category comprised individuals with >10-cm girth at breast height (GBH), as the species growth was not much. In total, we laid 15 quadrats for trees and 60 quadrats each for shrubs and herbs for vegetation composition study (Table 1). This helped in understanding the vegetation ecology and vegetation composition of the study area.

We laid additional quadrats of 10×10 m in each season at each soil sampling site (R1, R2, R3, G1, G2, G3, C1, C2 and C3) to relate soil parameters with plant species in the soil sampling stations. We collected soil subsamples (in triplicates) from quadrats of 10×10 m, and recorded the dominant plant species to assess the impact of dominant plant species on soil metal concentrations.

Data analyses

The Shannon-Wiener's index of diversity (H') for plants was calculated using the software Species Diversity and Richness (version 2.65, Colwell 1994–2004). We conducted univariate test, general linear model ANOVA (GLM-ANOVA), to assess the variations in the metal

Table 1 Dominant plant species observed at sampling locations in Araku

Location	Plant species
Raktakonda	<i>Ageratina adenophora</i> , <i>Chromolaena odorata</i> , <i>Cipadessa baccifera</i> , <i>Euphorbia hirta</i> , <i>Indigofera</i> sp., <i>Phoenix acaulis</i> , <i>Richardia scabra</i> , <i>Tridax procumbens</i>
Galikonda	<i>Chromolaena odorata</i> , <i>Eulalia wightii</i> , <i>Heteropogon contortus</i> , <i>Phoenix acaulis</i> , <i>Richardia scabra</i>
Chittamgondi	<i>Cipadessa baccifera</i> , <i>Crotalaria</i> sp., <i>Indigofera</i> sp., <i>Lantana camara</i> , <i>Mitracarpus villosus</i> , <i>Murraya koenigii</i> , <i>Phoenix acaulis</i> , <i>Tephrosia</i> sp., <i>Tridax procumbens</i>

levels among the months, locations, sites and layers. Least significant difference (LSD) test was a post hoc analysis for measuring the significant differences. A test of correlation (two-tailed) was also performed among Cu, Ni, Zn, pH, ORP, TOC, CEC, P and K using the software MegaStat (Orris 2000). Principal component analysis (PCA) was done to better quantify the relationships among the variables under study. The first three principal components (PCs), based on the Eigen values >1 , were chosen. All differences reported in the text are significant at the $\alpha=0.05$ level. We used SPSS 11.0 (Norusis 1990) for statistical analyses.

Results

Physicochemical characteristics

The soil pH ranged from 4.2 to 6.4, which is a characteristic of lateritic soil. The redox potential in soil solution of the studied samples was between +25 and +209 mV. TOC ranged from 0.66 to 4.19 %. TAP varied between 0.000004 and 0.0007 %, and CEC between 41 and 233 meq/kg. Potassium concentrations ranged from 15 to 746 mg/kg and varied among locations, sites and layers (GLM-ANOVA, $P<0.05$). TOC, pH, TAP and CEC varied significantly among months, locations, sites and layers (GLM-ANOVA, $P<0.05$).

Metal concentrations

Copper at Raktakonda ranged from 16.8 to 25.8 mg/kg and at Galikonda between 15.0 and 24.9 mg/kg. Chittamgondi recorded the highest (31.8 mg/kg) and the lowest (13.0 mg/kg) concentrations of Cu. GLM-ANOVA ($P<0.05$) and post hoc test (LSD, $P<0.05$, Table 2) revealed that all the months and locations differed significantly with respect to soil Cu. Among nine sampling sites, R1, G1, G2, G3, C2 and C3 differed significantly with each other and from the rest in terms of Cu level in soil.

Nickel at Raktakonda was between 38.1 and 79.9 mg/kg, at Galikonda between 28.9 and 66.9 mg/kg, and at Chittamgondi between 23.5 and 101.9 mg/kg. Nickel levels in soil varied among the months, locations, sites and layers (ANOVA, $P<0.05$). All months, except for May 2007 and November 2007, were distinct with respect to Ni in soil. Sites R1, R3, G2, C2 and C3 were distinct from each other and from other sites with respect

to Ni levels. Nickel distribution in upper two layers was significantly distinct from others (LSD, $P<0.05$, Table 2).

Zinc at Raktakonda ranged between 10.4 and 48.5 mg/kg, at Galikonda between 13.4 and 46 mg/kg, and at Chittamgondi between 11.0 to 52.1 mg/kg. Zinc levels in soil varied significantly in all the months (GLM-ANOVA and LSD, $P<0.05$, Table 2). Sites R2, G1, G2 and C2 were significantly distinct from each other. Among the soil layers, the upper layer (0–5 cm) was distinct from the rest with respect to Zn level. Both Ni and Zn were distinct among locations.

The C2 site at Chittamgondi had the highest concentrations of Cu, Ni and Zn. Nickel concentrations increased significantly down the layers. Contrary to Ni, Zn concentrations decreased down the soil layers. The maximum concentration of Cu was in the month of November each year, and for Ni, it was the month of May.

Vegetation

Three major forest types, viz. moist mixed deciduous, dry savannah and scrub forest were seen in the study area. The vegetation at three locations varied from small evergreen patches in valleys to moist deciduous and dry deciduous tracts towards the heights. The hilltop of all the three locations was a plateau area with scanty vegetation. *Phoenix acaulis*, a bioindicator of bauxite, dominated and almost covered the mine lease area irrespective of seasons. Shannon-Wiener's index (H') for species diversity of trees, shrubs and herbs was 1.15, 1.36 and 1.64 in Raktakonda and was 1.05, 1.44 and 1.58 in Galikonda, respectively. The H' values for shrubs and herbs in Chittamgondi were 1.78 and 2.25, respectively. Chittamgondi hilltop had no mature trees (GBH >10 cm). As compared to trees and shrubs, we recorded high herb density in all the locations. Apart from *P. acaulis*, species such as *Chromolaena odorata*, *Indigofera* sp., *Ageratina adenophora* and *Cipadessa baccifera* were also present at Raktakonda. *Tridax procumbens*, *Euphorbia hirta* and *Richardia scabra* were dominant herbs at Raktakonda (Table 1). At Galikonda, the dominant shrub after *P. acaulis* was *C. odorata*, and the dominant herbs were *R. scabra*, *Eulalia wightii* and *Heteropogon contortus*. At Chittamgondi, *C. baccifera*, *Lantana camara* and *Murraya koenigii* were present in addition to *P. acaulis*. *T. procumbens* and *Mitracarpus villosus* were

Table 2 Least significant difference (post hoc) tests for the variables studied in the soils of Araku

Parameters	Attributes	1	2	3	4	5	6	7	8	9
Cu	Month	23.2±3.0 a	19.6±3.1 b	21.1±3.3 c	22.5±3.6 d	23.6±2.8 e	22.8±3.4 f	21.6±2.2 ^g	18.9±1.8 ^h	
	Location	21.0±2.0 a	20.0±2.1 b	24.0±3.9 c						
Ni	Site	20.8±1.9 a	21.2±1.9 b	21.2±2.1 b	19.5±2.1 c	19.8±1.9 d	20.1±2.1 e	21.3±3.1 ^b	27.3±3.0 ^f	23.8±3.1 ^g
	Location	45.0±8.6 a	49.0±10.7 b	55.0±9.7 c	42.0±13.1 d	55.0±11.3 c	58.0±10.1 e	67.0±17.1 ^f	56.0±13.1 ^g	
Zn	Site	53.0±8.7 a	46.0±8.9 b	62.0±17.7 c						
	Location	57.0±8.5 a	48.0±8.3 b	55.0±6.9 c	46.0±8.1 b	44.0±9.0 d	48.0±9.3 b	46.0±14.7 ^b	70.0±12.8 ^e	69.0±13.8 ^f
pH	Layer	52.6±13.4 a	53.6±13.3 b	54.1±14.2 c	54.0±15.1 c					
	Location	43.0±4.9 a	40.0±4.0 b	15.0±2.2 c	14.0±1.0 d	16.0±2.4 e	18.0±1.4 f	19.0±1.7 ^g	18.0±1.1 ^f	s
ORP	Site	22.0±11.9 a	22.3±10.2 b	24.3±12.0 c						
	Location	23.0±12.7 a	20.1±10.5 b	22.9±12.1 a	21.6±9.7 c	22.3±10.0 d	23.0±11.0 a	23.7±12.0 ^a	25.3±12.7 ^e	23.8±11.3 ^a
TOC	Layer	23.4±11.9 a	22.9±11.4 b	22.5±11.3 b	22.6±11.1 b					
	Location	5.8±0.4 a	5.5±0.5 b	5.5±0.3 b	5.2±0.3 c	5.3±0.4 d	5.4±0.3 b	5.6±0.3 ^b	5.5±0.4 ^b	
CEC	Site	5.4±0.4 a	5.4±0.3 a	5.7±0.4 b						
	Location	5.4±0.4 a	5.5±0.4 a	5.3±0.4 a	5.3±0.3 a	5.404 a	5.5±0.3 a	6.1±0.2 ^b	5.5±0.3 ^a	5.5±0.3 ^a
TAP	Layer	5.6±0.3 a	5.5±0.4 b	5.5±0.4 b	5.4±0.4 c					
	Location	71±20 a	91±27 b	88±18 b	107±16 c	97±22 d	95±20 b	88±18 ^b	87±22 ^b	
K	Site	97±21 a	95±20 a	79±23 b						
	Location	95±21 a	92±22 a	103±18 b	102±18 b	96±21 c	88±20 a	57±14 ^d	90±16 ^a	91±18 ^a
K	Layer	84±19 a	91±24 b	91±23 b	95±23 c					
	Location	3.0±0.7 a	3.0±0.7 a	2.6±0.7 a	2.5±0.5 a	2.6±0.6 a	2.6±0.5 a	2.4±0.6 ^a	2.3±0.7 ^b	
K	Site	2.6±0.5 a	3.1±0.5 b	2.2±0.6 c						
	Location	2.8±0.5 a	2.3±0.5 b	2.7±0.5 c	3.1±0.6 c	3.0±0.6 c	3.1±0.5 c	1.6±0.5 ^d	2.6±0.4 ^c	2.4±0.4 ^c
K	Layer	2.6±0.5 a	2.5±0.5 a	2.5±0.7 a	2.9±0.5 b					
	Location	146±53 a	128±51 b	130±53 b	95±36 b	108±55 b	103±58 b	90±33 ^b	89±37 ^b	
K	Site	91±37 a	106±57 b	136±49 c						
	Location	92±38 a	86±27 a	96±43 a	99±58 a	100±54 a	120±57 a	165±40 ^b	123±40 ^a	120±53 ^a
K	Layer	141±51 a	118±51 b	96±45 c	89±44 c					
	Location	0.00019±0.0001 a	0.00017±0.0001 b	0.00015±0.0001 b	0.00014±0.0001 b	0.00014±0.0001 b	0.0001±0.0001 ^d	0.0001±0.0001 ^c	0.00012±0.0001 ^c	
K	Site	0.00013±0.0001 a	0.00011±0.0001 b	0.00015±0.0001 a						
	Location	0.00021±0.0001 a	0.00012±0.0001 b	0.0001±0.0001 c	0.0001±0.0001 c					
K	Layer	87±58 a	87±44 a	172±139 b						
	Location	75±29 a	98±73 a	87±61 a	75±29 a	86±44 a	101±51 a	256±175 ^b	166±91 ^c	95±76 ^a
K	Site	172 a	112 b	93 c	85 c					
	Location									

Source of variation: months (1, Nov 2006; 2, Feb 2007; 3, May 2007; 4, Aug 2007; 5, Nov 2007; 6, Feb 2008; 7, May 2008; 8, Aug 2008); location (1, Raktakonda; 2, Galikonda; 3, Chittamgondi); site (1, R1; 2, R2; 3, R3; 4, G1; 5, G2; 6, G3; 7, C1; 8, C2; 9, C3); and layer (1, 0–5 cm; 2, 5–10 cm; 3, 10–15 cm; 4, 15–20 cm). Within rows, means followed by the same letter are not significantly different at $P < 0.05$

the dominant herbs at this location. *Tephrosia* sp., *Crotalaria* sp. and *Indigofera* sp. were dominant during the months of October and November.

Correlation and PCA results

With regard to the concentrations of metals, the Cu showed a positive correlation with Ni, CEC and K (two-tailed test, $P < 0.05$). Nickel showed a negative correlation with Zn, TOC, CEC and TAP (Table 3). Zinc was positively correlated with pH, TOC, CEC, TAP and K and negatively with ORP. The PCA resulted in four PCs (Table 4) and explained 77.8 % of the total variance. PC1 accounted for 31.4 % of the total variance among soil metals, reflecting the influence of ORP, pH and CEC. PC2 accounted for 16.2 % of the total variance and reflected the influence of Cu and Ni. PC3 explained 16.1 % of the total variance and reflected the influence of TAP. Likewise, PC4 accounted for 14.1 % of the total variance and reflected the influence of TOC and Zn.

Discussion

The pH has a strong influence on metals’ solubility (McBride et al. 1997) because they are more mobile in soils with lower pH values. Several metal toxicities in substrates with low pH are due to anthropogenic processes (Fergus 1954; Kelly et al. 1990; Robinson et al. 1995). According to Gnandi and Tobschall (2002), redox potential and pH in the soil solution are the main agents for metal mobility in the soil layers. Heavy metal movement, with water in soil, requires the metal in

soluble phase or associated with mobile particulates (Waller and Pickering 1992). Biddappa and Rao (1973) reported that rainfall and pH have a negative correlation due to intensive washout of the bases from the soil. Further, Zhang and Shan (2000) reported that higher CEC and lower pH of soils stimulate release of trace metals. In the present case, Araku soils were acidic with soil redox potential between +25 and +209 mV. This, with higher rainfall at the Araku hillocks, would have resulted in the release of trace metals. Zinc becomes mobile at a pH <6, and Cu is more mobile at pH <2 (Tack et al. 1996). McLaren and Crawford (1973) also reported higher Cu adsorption with increased pH. Nitrogen-fixing plant species cause an accelerated decline in soil pH resulting in higher availability of metals (Mertens et al. 2004). The soils of Araku support good plant diversity. During the survey, we observed that plants such as *Crotalaria* sp., *Indigofera* sp., *Tephrosia* sp., members of the family Fabaceae and nitrogen-fixing species were dominant during certain months. Therefore, the seasonal variations (among months) in the concentrations of Cu, Ni and Zn in soils of Araku are attributable to the plant species growing in the area across the months. Soil analyses revealed that these nitrogen-fixing species reduced the pH and thus made the metals more mobile in the soil during the respective months. Chittamgondi location had almost no tree species on the hillock and had more shrubs and herbs. We recorded few individuals of *Crotalaria* sp. and *Indigofera* sp., apart from *Tephrosia* sp., which dominated the C2 site at Chittamgondi. These plant species would have resulted in lower pH and hence made the metal concentrations highest at C2 site

Table 3 Correlation matrix of metals and select physicochemical parameters in Araku soil

Variables	Cu	Ni	Zn	pH	ORP	TOC	CEC	TAP	K
Cu	1								
Ni	0.456	1							
Zn	NS	-0.131	1						
pH	NS	NS	0.293	1					
ORP	NS	NS	-0.299	-0.955	1				
TOC	NS	-0.118	0.273	-0.226	0.226	1			
CEC	0.13	-0.081	0.297	0.627	-0.638	-0.084	1		
TAP	NS	-0.217	0.187	0.133	-0.13	-0.101	0.195	1	
K	0.179	NS	0.148	0.403	-0.398	-0.263	0.454	0.169	1

Sample size=864; ±0.067 critical value for R at $P < 0.05$ (two-tailed)

NS not significant at $P < 0.05$

Table 4 PCA of soil metals and other variables from all the locations—factor loadings

Parameters	Principal components			
	PC1 (ORP, pH, CEC)	PC2 (Cu, Ni)	PC3 (TAP)	PC4 (TOC, Zn)
Cu	-0.002	0.894	0.198	0.027
Ni	0.021	0.758	-0.453	-0.060
Zn	0.373	0.022	0.184	0.749
pH	0.943	-0.038	0.014	-0.025
ORP	-0.949	0.072	-0.044	0.041
TOC	-0.305	-0.037	-0.121	0.830
CEC	0.738	0.137	0.346	0.098
TAP	0.070	-0.102	0.841	0.042
K	0.504	0.217	0.571	-0.065
Total loading ^a	2.826	1.459	1.449	1.272
% Variance explained	31.400	16.206	16.104	14.129

Extraction method: principal component analysis; rotation method: varimax with Kaiser normalization (rotation converged in six iterations)

^aSums of squared loadings

(Table 1). Additionally, manmade forest fire might have also caused variations in the metal concentrations in the soil samples (Paliwal and Sundaravalli 2002).

According to Kabata-Pendias and Pendias (1992), the total Cu content of uncontaminated surface soils worldwide ranges from 13 to 24 mg/kg. Thus, Cu levels in Araku soil are marginally higher, and probably, its origin is the geological substrate. Organic matter usually fixes Cu and hence prevents leaching of the metal; thus, available form of Cu deficiency often occurs in soils with high organic matter. Rajagopal et al. (1974) also reported negative relationship between Cu and organic carbon.

The determination of metal background concentration is chiefly according to local bedrock geochemistry and supplemented to differing degrees by anthropogenic inputs (Prusty et al. 2009). Regional differences in geology and anthropogenic sources give rise to spatial variations in total metal concentrations. Slash and burn practice of agriculture accounted for the only anthropogenic source in Araku. Thus, the geology of the area might have driven such location-specific significant variations for metals in soils of Araku. Nickel in soils occurs in more readily extractable forms when compared to Cu (Alloway 1990). Thus, the highest concentration of Ni in soils of Araku are attributable to the nature of solubility of this metal, which made it more bioavailable. Metal concentrations may redistribute into different parts of the soil profile due to geochemical and biogeochemical processes. Greater mobility of Ni is

strongly associated with organic matter. In Araku, Ni in soils was negatively related with TOC. This is indicative of the influence of geochemical and biogeochemical processes. Organic matter can interact with metals in two important ways. Firstly, the metals may mineralize from the soluble organic matter and change into bioavailable forms. Secondly, metal may bind into organic matter constituents that are immobile in the soil and form a fixation mechanism, by which metal does not release easily. Negative correlation between Ni and organic carbon in the present case is indicative of the presence of organic complexing agents in soils, thus affecting metal availability.

The smaller the ionic radius of any metal, the greater is its tendency to hydrolyze leading to reduced sorption (Horsfall and Spiff 2005). Evans (1989) and Alloway (1990), in reviewing the subject, stated that the adsorbing solid usually prefers one cation to another. This preference is proportional to the valency and inversely proportional to the hydrated radii (larger in cations with smaller ionic radii due to their increased polarizing power). In the present study, positive correlation between Cu and Ni and negative relationship between Ni and Zn are attributable to the isomorphic replacement between the two metal ions and relatively higher affinity of metals like Cu for the binding sites. PC2, which reveals interlinking of Cu and Ni, further confirmed this.

Alloway (1990) classified Zn concentration in soils as deficient if less than 10 mg/kg, normal if between 25

and 150 mg/kg, and excessive or toxic if more than 400 mg/kg. Kabata-Pendias and Pendias (1992) reported a worldwide Zn range of 17–125 mg/kg. Zinc in soils of Araku ranged between 10.4 to 52.1 mg/kg, which was normal. ORP, pH and rainfall pattern (resulting in leaching) might be the influencing factors for seasonal variations in Zn levels in soils. The differences in Zn concentrations among soil layers were attributable to pH variations. Lal and Biswas (1973) reported that calcareousness and high pH prevent the leaching loss of Zn. Thus, leaching results in lowering the Zn content. Zinc in the top layer was highest and distinct from the rest of the layers as in the case of pH (0–5 and 15–20-cm layers). Zinc is more mobile under acidic conditions (McGrath et al. 2004) than other heavy metals, and thus, a greater proportion of this metal would leach out over time from the acidic soils of the area. Since Zn is known to form phosphate salts (soluble) with the available phosphorous, lower pH values induce dissolution of phosphates and release of Zn into the soil.

The present investigation revealed positive correlation of Zn with TOC, CEC and TAP. The lower levels of Zn were attributable to the lower levels of TAP in soil layers. This indicates fixation of Zn (as zinc phosphate) in the solid phase of the soil that might have also reduced the availability of TAP in the soil. Gnanidi and Tobschall (2002) reported no relation of organic carbon with Zn. The mechanisms involved in the retention of metals by organic matter seem to include both complexation and adsorption, i.e. inner sphere reactions as well as ion exchange (Evans 1989; Rieuwerts et al. 2002). While many studies suggest a link between soil organic carbon content and fixation of metals in the soil solid phase, some authors (Sanchez-Camazano et al. 1994; Brallier et al. 1996) did not find such association. This clear difference is due to the tendency of metals to bind with organic components in both the solid and solution phases in soil. In the present study, ORP and pH were negatively correlated. The factor loading on the first PC (PC1) also suggests a negative relationship between ORP and pH. On the lower slopes of the Araku, mountain soils were high in organic matter and acidic in nature, which might have accounted for the strong negative correlation between ORP and pH. While reporting negative correlation of ORP with Zn, Chuan et al. (1996) verified that the solubility of Zn and other metals (Pb and Cd) in soils increased with decreased redox potential. Such mechanism is likely to be due to the dissolution of Fe-Mn oxyhydroxides under reducing

conditions resulting in the release of adsorbed metals. PC2 suggested a positive relationship between Cu and Ni reflecting their lithogenic origin.

Conclusion

The present investigation, on assessing the metal availability in soils of Araku, confirms that redox potential and pH in the soil solution are main agents for metal mobility in the soil layers in Araku. Organic carbon influenced Zn fixation in the soils. Copper was marginally high in the soil system of Araku. Concentrations of other metals examined were well within the safe limits. Seasonal variations in metal concentrations in soil were attributable to the nitrogen-fixing species, which were common in the study area. Elements are present in the soil in various forms that strongly affect their behaviour in terms of bioavailability, potential toxicity, chemical interactions and mobility across the layers. It is necessary to identify and quantify the forms in which the metal is present in the soil to gain a more precise understanding of the potential and real impact of higher levels of metals in soil. Thus, it is vital to examine the soil quality in areas with a post-mining scenario and plant species exposed to such situations. Hence, the present paper forms a base document on soil quality of the area, which is crucial and imperative for consideration before setting of a mine restoration plan. Researches done elsewhere have shown that many of the nitrogen-fixing plant species may be used during mine restoration. However, in the present case (acidic soil), after studying soil characterization and geological set up, we propose not to plant these (nitrogen-fixing) species, as they will further reduce the soil pH thus making the metal available to the system. Bayer's process in bauxite mining plants releases red mud as a product. The red mud (caustic and very alkaline in nature) may be used to bring the pH to near neutral in proper proportion with the over burden/mine tailing, while soil reclamation.

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