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A Comparative Study on Metal Accumulation in *E. indica, C. citratus* and *V. zizanioides* Grown on Copper Mine Waste

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Abstract: The concentrations of different forms of heavy metals (Cu, Ni and Mn) were determined in a mine dump material rich in chalcopyrite and compared with those of the natural vegetation colonizing in the dump. Dump materials are slightly acidic in nature, having low organic carbon and cation exchange capacity. Copper was the most abundant heavy metal, in both total (acid extractable) and bioavailable forms, and the relative abundance of metals was Cu>Ni>Mn. The Cu concentration in the $CaCl_2$ extracts varied between 0.2 and 0.5 $mgkg^{-1}$ and concentrations of average Ni and Mn were below detection limit. The heavy metal contents in the spontaneously occurring vegetation in the dump ranged between 5.4 and 217 mg Cu kg^{-1}, 10 and 81 mg Ni kg^{-1}, 8.5 and 264 mg Mn kg^{-1} when considering all the plant samples analysed. Naturally, colonized grass *Elusine indica* was found to accumulate highest concentrations of Cu, Ni and Mn followed by planted grass species *Cymbpopogon citratus* and *Vetiveria zizanioides*. However, *V. zizanioides* was found to uptake more Mn than *C. citratus.* The native plant species may contribute to decrease the heavy metal contents in the dump materials.

Key words: Cu-tailing, heavy metals, leaching.

Introduction

Mining activities such as crushing, grinding, washing, smelting and all the other processes used to extract and concentrate metals generate a large amount of waste rocks and tailings. These are often very unstable and make elements environmentally labile through normal biogeochemical pathways, to sink such as sediments, soils or biomass (Davies, 1980, 1983). The direct effect will be loss of cultivated land, forest or grazing land, and the overall loss of production (Wang et al., 2003). The indirect effects include air and water pollution and siltation of water body. This will eventually lead to the loss of biodiversity, amenity and economic wealth (Breadshaw, 1993). Establishment of vegetation cover can fulfil the objectives of stabilisation, pollution control, visual improvement and removal of threats to human beings (Freitas et al., 2004). Mine spoil or tailing dumps usually have barren surfaces, with rare plants that show signs of suffering such as stunted growth, chlorosis, nacrosis and anomalous development of roots with respect to shoots (Dinelli and Lombini, 1996).

Plant species found in metal-polluted/contaminated soils are expected to take up metals and eventually accumulate them (Baker, 1981). Some plants phytostabilise heavy metals in the rhizosphere through root exudates immobilisation (Blaylock and Huang, 2000) whilst other species incorporate them into root tissues (Khan, 2001). A number of plant species endemic to metalliferous soils have been found to accumulate metals at extraordinarily high levels (> 1% and up to 10%) in contrast to normal concentrations in plants. So far approximately 400 metal hyperaccumulators have been identified (Baker, 1981). Brooks et al. (1977) first used the term hyperaccumulator in relation to plants containing more than 1000-10,000 $mgkg^{-1}$ of Ni in dry tissue. The idea of using plant which hyperaccumulate heavy metals for remediation of metal-contaminated soil was first introduced in the 1980s (Chaney, 1983) and in recent years this has been developed as an effective technique (Salt et al., 1996).

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The aims of the present investigation were to (i) quantify the loss of metals due to natural leaching process, and (ii) phytoaccumulation of toxic metals in root and shoot portion of naturally colonized and planted grass species.

Materials and Methods

Study Area

The Mosaboni underground Cu-mine is located in the Eastern India in the state of Jharkhand (Figure 1). The deposit formed by a series of quartz veins was exploited by underground mining. Mineralisation is mainly in the form of sulphides. Chalcopyrite ($CuFeS_2$) and pyrites are two major sulphides associated with smaller quantities of sulphides of Ni, Co and Mo etc. Magnatite with minor amount of Ilmenite and rutile constitute the main oxide minerals. The veins are located between schist, migmatitites and granites. The Cu mining activity ceased in 1995, leaving huge heap of Cu-tailings.

About 14 tonnes (14,000 kg) of tailings was brought from Mosabani mines in December 2002 and spread in an experimental plot inside the Indian School of Mines, Dhanbad, Jharkhand. It is made up of concrete chamber having earthen ground with dimension of 5 m (L) × 5 m (B) × 0.5 m (D).

In both experimental plot as well as nearby natural soil, the growth of *Elusine indica* (naturally colonized), *Cymbpopogon citratus* and *Vetiveria zizanioides* (after 60 days of plantation) were studied.

Collection, Preparation and Analysis of Samples

Soil/Tailing analysis

The soil/tailings loosely adhered to roots were gently shaken off and the rhizosphere tailings adhering to roots

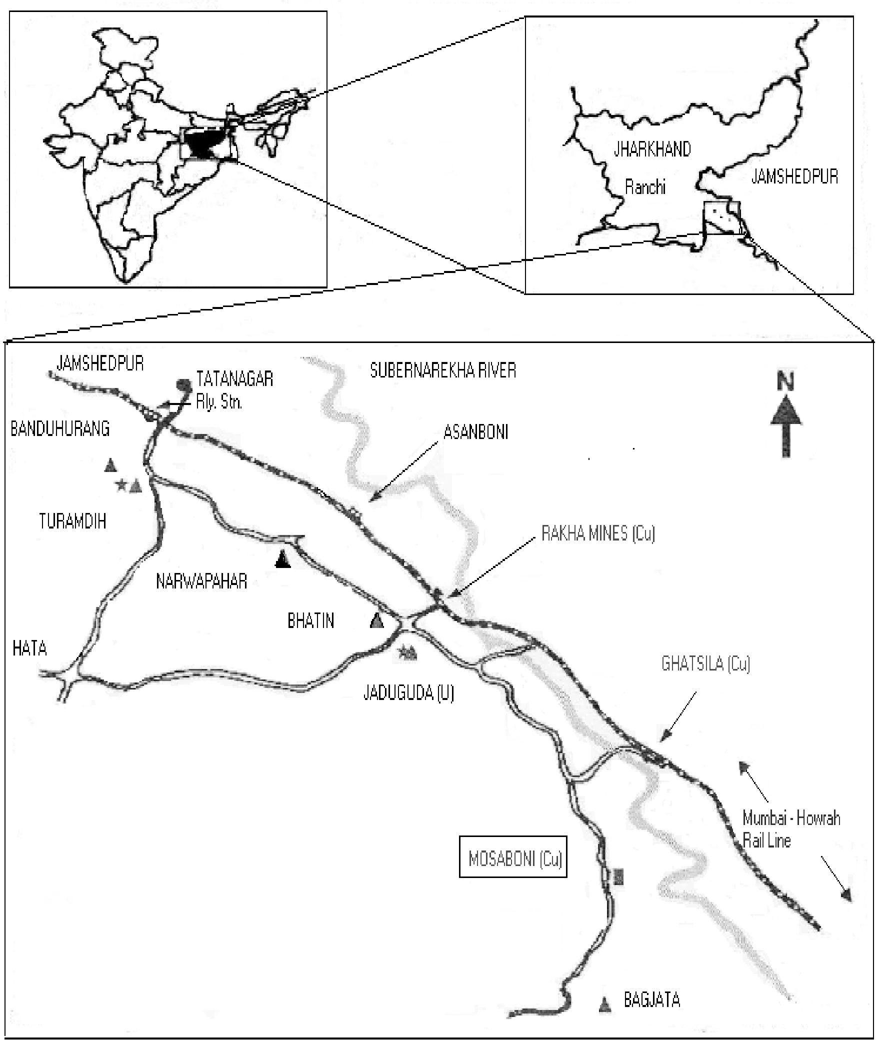

Figure 1: Location map of Mosaboni Cu-mine area.

were separated by hands. Rhizosphere tailings were then air-dried and sieved through 200-micron mesh. Samples were then analyzed for pH, electrical conductivity (EC), organic carbon (OC), and cation exchange capacity (CEC) (Gupta, 2000). For total metal contents, accurately 0.5 g oven-dried (80^oC for overnight) tailing was digested twice with 5 ml of 3:1:1 HCl:HNO_3:HF and once with 5 ml aqua-regia in a covered Teflon-beaker. Digested mass was then boiled with 1% HNO_3 solution, filtered in a volumetric flask followed by addition of 1% HNO_3 solution to make a final volume of 100 ml. For DTPA and $CaCl_2$ extractable fractions oven-dried tailings were extracted with 0.005 M DTPA (20 g tailings extracted by 40 ml solution) and 0.01005 M $CaCl_2$ (5 g tailings extracted by 50 ml solution) respectively (Lopez-Sanchez et al., 2002).

Plant analysis

Plant samples were thoroughly washed with running tap water and rinsed with demonized water to remove any tailing particles attached to the plant surfaces. The aboveground and underground tissues were then separated and oven dried overnight (80°C) to constant weight. The dried tissues were weighed and ground into powder for metal concentration analysis. A portion of 0.5 g of plant tissue was digested with 10 ml of conc. HNO_3 and conc. $HClO_4$ (5:1, v/v) as suggested by Yang et al., 2003 for total metal analysis.

Metals (Cu, Ni, Mn) in plant tissues and in rhizosphere tailings were measured by Flame Atomic Absorption with a GBC mod. Avanta Spectrometer. Accuracy was checked by means of duplicate analysis on selected samples (less than 10% relative variation). Inter-batch variations were monitored by repeated analysis of selected samples in the various analytical batches (less than 10% variation).

Statistical Analysis

The data were analyzed by one-way analysis of variance (ANOVA) to compare means of metal concentration in different substrate (tailing and soil). Duncan multiple range tests were carried out to compare differences between individual means.

Results and Discussion

General Properties of Tailings

The general characteristics of the tailings and natural soil are shown in Table 1. In tailings the pH ranged between 5.85 and 6.11. The slightly lower pH values were associated with the release of protons produced by oxidation of sulphide minerals present in the Cu tailings. The electrical conductivity was found 0.049 dSm^{-1}, which was less than natural soil (0.17 dSm^{-1}), found in the region. The average organic carbon contents were usually 0.18%, which was much below than the natural soil (1.52%). The CEC ranged between 3.58 and 3.87 cmol (+) kg^{-1}, which was lower than natural soil (12.8 cmol (+) kg^{-1}) in this region. The low cation exchange capacity can be explained by the small contribution made by the organic matter (low content and low negative charge due to the acidity of the samples), as well as lack of inorganic colloids (sandy and sandy loam textures).

Table 1: General characteristics of Mosaboni Cu-tailings in the experimental plot and natural soil

	Minimum	*Maximum*	*Average ± sd*
Cu-tailings			
pH H_2O (1: 2.5)	5.85	6.11	5.98 ± 0.13
EC (dSm^{-1})	0.047	0.052	0.049 ± 0.002
OC (%)	0.12	0.27	0.18 ± 0.08
CEC [c mol (+) kg^{-1}]	3.58	3.87	3.71 ± 0.15
Natural soil			
pH H_2O (1: 2.5)	7.38	8.29	7.80 ± 0.46
EC (dSm^{-1})	0.130	0.199	0.169 ± 0.035
OC (%)	1.12	2.05	1.52 ± 0.48
CEC [c mol (+) kg^{-1}]	11.60	14.02	12.81 ± 1.22

Heavy Metals in Tailings and Natural Soil

When comparing total concentrations, Cu was the most abundant heavy metal, followed by Ni and Mn (Table 2). The main Cu and Ni primary minerals were sulphides, mainly chalcopyrites, pyrites and nickel sulphides. Magnatite with minor amount of Ilmenite and rutile constitute the main oxide minerals. The release of heavy metals from the sulphides can occur by weathering of the mineralized due to generation of acid conditions during oxidation process (Pulford, 1991).

Even though total heavy metal concentrations have presumably low biological significance, various researchers (Kabata-Pandias and Pandias, 1984; Alloway, 1995; Alvarez et al., 2003) propose very similar toxicity threshold for these parameters. Concentration of the total heavy metal concentrations with the toxicity thresholds proposed by the above quoted authors indicates that the dump material present a high risk of phytotoxicity by Cu and Ni. However, both the environmental conditions,

Table 2: Metal concentration (mg/kg) in Mosaboni Cu-tailings in the experimental plot and control soil

Parameters	*Total*	*DTPA extractable*	*$CaCl_2$ extractable*
Cu-tailings			
Cu	240 ± 26 (215 – 266)	13.6 ± 1.1 (12- 15)	0.38 ± 0.12 (0.21- 0.51)
Ni	192 ± 2.7 (190-197)	0.68 ± 0.09 (0.55-0.88)	< 2
Mn	80 ± 4.6 (74-87)	0.55 ± 0.22 (0.35-0.83)	< 0.8
Natural soil			
Cu	39.4 ± 10 (30 – 49)	5.1 ± 0.9 (3.8 – 6.8)	< 1
Ni	17.6 ± 4.4 (11-22)	0.47 ± 0.056 (0.40-0.55)	< 2
Mn	229 ± 28 (202-264)	7.7 ± 0.7 (6.3-8.3)	< 0.8
	Cu	Ni	Mn
Toxicity threshold*	100	100	1500

* Kabata-Pendias and Pendias (1984).

which influence the mobility and availability of metals, and the plant species, may modify toxicity threshold (Alvarez et al., 2003).

The analysis of the potentially bioavailable metal fraction is probably more significant than the analysis of total content, because the former allows prediction of the risk of metal uptake by plants and its mobility in the system (Dinelli and Lombini, 1996; Freitas, et al., 2004). In the present study, Cu was most abundant metal in the bioavailable form followed by Ni and Mn, a sequence that is similar to that of total concentration. The bioavailable forms in tailings constituted 5.6% of the total Cu, 0.35% of the total Ni and 0.69% of the total Mn. However, in the natural soil both total and bioavailable Mn were much higher than Ni content. Except Cu, other elements in the exchangeable fractions of both tailings and natural soil were below the detection limit.

Heavy Metal Accumulation in Plants

The metal concentrations in *Elusine indica* were significantly higher than in *Cymbpopogon citratus* and *Vetiveria zizanioides* (Table 3). In the root of all the plant samples grown on tailings, Cu concentrations were higher than 20 mg kg^{-1}, considered by Kabata-Pendias and Pendias (1984) as the limit for toxicity. However, in the aboveground part of the plant samples, the same were within the normal range as suggested by Reeves and Baker (2000) for plants growing in metalliferous soils (5-25 mg kg^{-1}).

The concentration of Ni in plants generally reflects the concentration of the elements in the soils, although the relationship is more directly related to the soluble and exchangeable forms of Ni. The mobility of Ni in soil increases as the pH and CEC decreases (Alloway, 1995). Underground tissue of all the plant samples that had grown on tailings, had Ni concentration higher than 10 mg kg^{-1}, considered by Kabata-Pendias and Pendias (1984) as the limit for toxicity. Concentrations of Ni in all the studied plants, grown on non-contaminated soils were below detection limit. In all the species, the concentrations of Mn were within the range considered as toxic by Kabata-Pendias and Pendias (1984) (300-500 mg Mn kg^{-1}). In case of herbaceous species, the levels were within the ranges considered as normal by Alvarez et al. (2003) (20-300 mg Mn kg^{-1}). Reeves (2002) reported the range of 20-400 mg Mn kg^{-1} as normal in plants growing in metalliferous soils.

Table 3: Metal accumulation in shoot and root parts of plants (mg/kg) growing on Mosaboni Cu-tailings in the experimental plot and control soil

Plant species	*Cu*		*Ni*		*Mn*	
	Root	*Shoot*	*Root*	*Shoot*	*Root*	*Shoot*
Tailings						
E. indica	217^a	25^a	73^a	15	55^a	145^a
C. citratus	150^b	12^b	24^b	< 10	11^b	12^b
V. zizanioides	142^b	11^b	15^b	< 10	16^b	14^b
Natural soil						
E. indica	24^a	15^a	< 10	< 10	164^a	231^a
C. citratus	5^b	7^b	< 10	< 10	6^b	9^b
V. zizanioides	12^b	6^b	< 10	< 10	13^b	13^b

* Different letters in the same column and in the same substrate (soil or tailing) indicate a significant difference at $p<0.05$.

Conclusion

Chemical characterization of tailings of Mosaboni Cu mine revealed high concentration of heavy metals and low contents of organic carbon and CEC. The most abundant heavy metal in total as well as bioavailable fraction was Cu followed by Ni and Mn. Natural soil was found to contain much higher Mn in both total and bioavailable fraction than the Cu-tailings and the availability of metals was in the order Mn > Cu > Ni. In all the samples concentration of total Cu and Ni were found to exceed the toxicity threshold limit and the variability in the levels of heavy metals is likely due to the existence of distinct microhabitats within the experimental plot and the sampling plants at different stages in their growth cycle. Despite the chemical limitation and toxic environment of this material, various plant species were found to grow on it and accumulated much higher amount of metal than those growing on natural soil. *Elusine indica*, *Cymbpopogon citratus*, *Vetiveria zizanioides*, all of these plants were found to accumulate high concentration of Cu in their root tissue, when grown on tailings. *E. indica* accumulated significantly higher amount of Cu, Ni and Mn in their tissues compared to others. Thus, use of such plant species may reduce metal mobility in mine waste through absorption and accumulation by roots or precipitation within the rhizosphere.

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