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Research Article

METAL POLLUTION IN SOIL AND PLANTS NEAR COPPER MINING SITE

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ABSTRACT
Heavy metal concentrations were measured in the soil and plants at the vicinity of Khetri copper mining project (INDIA) to investigate the influence of metal mining on the surface environment. Elemental concentrations in soil and vegetation were determined by A.A. Spectrophotometer. Metal concentration in soil samples was found greater than the normal soil copper concentration. In the soil sample collected from region cropped with *Adhatoda* plants metal concentration ranges from 29.5 mg/kg to 885.54 mg/kg, whereas in the region of *Aerva* was cropped metal concentration ranges from 7.37 mg/kg to 277.18mg/kg and soil samples associated with *Tephrosia* ranged from 4.9mg/kg to 143.72mg/kg. High concentration of copper was found in the leaves of *Adhatoda* with maximum 600mg/kg copper, *Aerva* with maximum 400mg/kg and *Tephrosia* 150mg/kg copper. The present study reflects the elevated concentration of copper in the soils and associated plant species at the vicinity of Khetri mining sites.

Key Words: *Mining Activity, Copper, Soil Pollution, Metal Accumulation*

INTRODUCTION
Mining has been one of the most common activities since ancient times and continues to remain so in the modern world. Mining is an important part of our economy. Minerals extracted raw from earth, are processed to yield basic substances such as metals, chemicals, building materials, fuels, fertilizers etc. Industrial society could not exist without these essential commodities. A combined total of about 1150 million tones of heavy metals (copper, lead, cobalt, zinc, cadmium and chromium) have been mined by man since the Stone Age. It is further estimated that an annual output of 14 million tones of heavy metals is being mined with annual growth of 3.4% (Matagi *et al.,* 1998). The continued advancements in industrialization and the ever increasing demand for energy resources and minerals, have led to a spurt in mining activities, bringing in its wake imbalances in ecological equilibrium and many environmental hazards (Wu *et al.,* 2007; Vamerali *et al.,* 2010).
Mining activities such as crushing, grinding, washing, smelting and all other processes used to extract, concentrate generate waste products such as mine overburden and mine tailings (waste soil). As a result, very significant volumes of wastes have been deposited on soil and wild plants and animals are exposed to elements contained in the residue. People living near these sites are also exposed through wind and soil erosion. The direct effect will be loss of cultivated land, forest or grazing land, and the overall loss of production. The indirect effects include air and water pollution and siltation of water body. This will eventually lead to loss of biodiversity, amenity, and economic wealth (Yang *et al.,* 2002; Wong, 2003). The management of these waste materials is an important issue for mining industry worldwide. It is estimated that the median values of worldwide emissions of Cd, Cu, Pb, and Zn into soils were 22, 954, 796 and 1372 10^6 kg/yr, respectively; more than half of those metals were associated with base metal mining and smelting activities (Nriagu and Pacyna, 1988; Lone *et al.,* 2008).
Some heavy metals e.g., Mn, Fe, Cu, Zn, Mo and Ni are essential as micronutrient for microorganisms, plants and animals while others have no known biological function (Welch, 1995). All heavy metals at high concentrations have strong toxic effects and regarded as environmental pollutants (Nedelkoska and Doran, 2000; Chehregani *et al.,* 2005). Elevated concentrations of heavy metals pose significant risk to flora, fauna and human population. Contaminated soil negatively affects crop growth because of

interference of phytotoxic contaminants with metabolic processes and sometimes also leading to plant death (Pal and Rai, 2010). Human are at risk from polluted soils through dermal contact, ingestion, consumption of food grown on polluted soil and inhalation of dust or vapors and causes acute and chronic diseases such as gastrointestinal, respiratory, heart, brain and kidney damage and effects on skin and mucous membranes and various systemic effects on intestines, also cause DNA damage and carcinogenic effects by their mutagenic ability (Nathanail and Earl, 2001; Jadia and Fulekar, 2008; Kidd *et al.*, 2009). Contaminated soil disrupts biological cycling of nutrients, also affect the hydrosphere comprising the quality drinking water resources and threatening the aquatic ecosystem (Bilek, 2004; Sheoran *et al.*, 2008a, b).

The present research aimed to investigate the influence of mining activity on the concentration of heavy metals in the soil and vegetation surrounding copper mining sites at Khetri located in Jhunjhunu, Rajasthan, India.

MATERIALS AND METHODS

Sampling Sites

The study area Khetri is located in the Jhunjhunu District of Rajasthan, some 190 km Southwest of Delhi, and 180 km North of Jaipur (Figure 1). It is situated 550m above mean sea level. Khetri copper mines are located in northern extremity of the Khetri Copper belt between Lat. 28°03'35" to 28°04'45" and longitudinal is 75°47'40" to 75°46'45" in Jhunjhunu District. Khetri Copper Complex is a major constituent part of Hindustan Copper Ltd. (HCL), a Government of India enterprise established in November 1967. The copper deposits were mined in ancient times with some workings have dating from to the Mauryan Period, over 2000 years ago. The mines were active again in the times of the Moghul Emperiors. A report in this respect is written by Abu Fazal, a courtier of Emperor Akbar, in 1590. More recently, the mines were worked by local people who paid a royalty on production basis to the Princely State of Khetri. Two mines were functioning in the towns of Singhana and Khetri until closed by the British in 1869. Regular mining was ceased in 1872, although sporadic activity continued until 1910. From 1944 to 1955 the lease was held by the Jaipur Mining Corporation Ltd. The Geological Survey of India began prospecting the area in 1954, and exploratory mining by Indian Bureau of Mines began in 1957. The Project was handed over to the National Mineral Development Corporation in 1961 for further investigation. Initial feasibility studies were completed in 1963. By then, there was a pressing need to increase indigenous production to narrow the gap between India's own output and steadily rising demand. The decision to proceed with development of Khetri Copper Complex was taken in 1962. Shaft sinking and mine development began in 1964 and the first production of ore took place in 1970. The project was transferred to the newly-created Hindustan Copper Limited in November 1967. A fertilizer plant, based on the sulphuric acid by-product from the smelter, plus rock phosphate from southern Rajasthan, began production in 1975. There are two major operating mines in the Khetri Complex, namely- Khetri, Kolihan underground mines.

The study area consists mostly of garnetiferous chlorite quartz schist as shown in Figure 2. In the northern part of the Khetri copper mine about one kilometer long strip was selected as the sampling location along Kharkhara River which is seasonal. Most of this part is covered with alluvium soil and supported with wild plants (Fig. 2).

Plant Sampling and Analysis

The young and growing plant samples were collected. The plant samples were identified as *Adhatoda vasica* an annual shrub (1.5m) of family Acanthaceae, *Aerva tomentosa*, locally known as (Bhui), a perennial under-shrub (1m) of family Amaranthaceae, *Tephrosia villosa*, commonly known as Ruvali-biyani, and an annual herb (1m) of family Fabaceae (Bhandari, 1978) (Figure 3, 4, 5). After removing soil lumps, the plants were washed with distilled water containing 0.1-0.3% detergent and then again washed in 0.01M NaEDTA solution (sodium salt of ethylene diamine tetraacetic acid). Excess water was shaken off the plant samples and the samples were placed in the labeled polyethylene bags. Different parts of the plants (roots, stems and leaves) were pruned using tweezers. The plant tissues then dried in convection oven at 70^{0}C for 24 hours. After drying, the plant tissues were grinded, sieved to 1-mm sieve and stored in polyethylene bags (Greweling, 1976).

Figure1: Geographical location of the study area

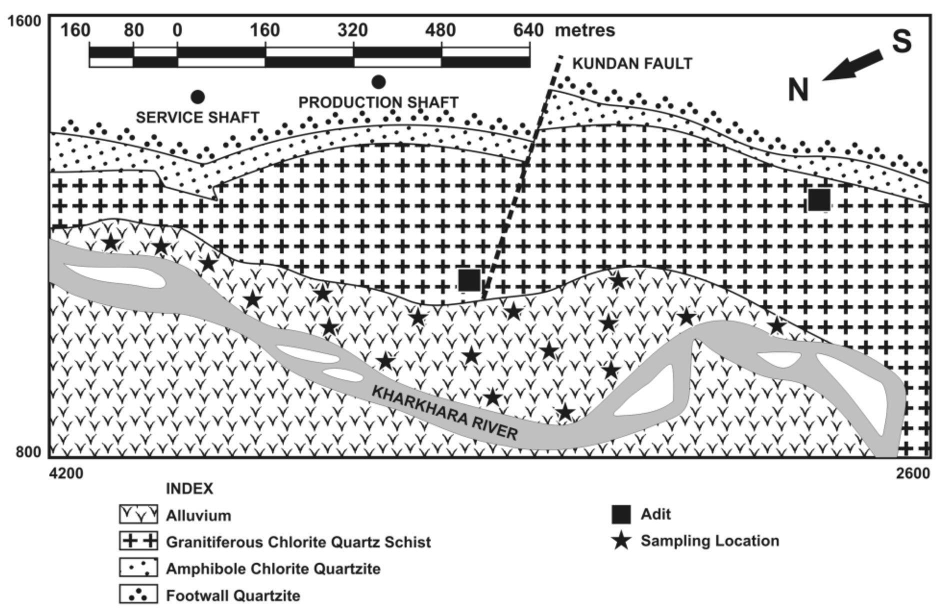

Figure 2: Geological map of the study area

Figure 3: *Adhatoda vasica*

Figure 4: *Aerva tomentosa*

Figure 5: *Tephrosia villosa*

Soil Sampling and Analysis

Along with plant samples associated soils were also collected into labeled polyethylene bags from a depth of about 15 cm at the same place. The soils were air dried and sieved through 2-mm sieve to remove unwanted material. Soil pH was measured in a 1:2.5, soil to de-ionized water ratio (Maiti, 2003). The sampling locations are indicated in Figure 2 of the geological plan of the study area.

Concentration of heavy metals (accessible for plants) in the soil was determined by DTPA-extractable method (Diethylene triamine pentaacetic acid). 5gm of soil samples were taken and 25 ml of DTPA solution (0.005 M DTPA) was added and 7.3 pH was adjusted with 0.1M TEA. This solution was shaken for two hours. After shaking the soil-solution were filtered and analyzed for Cu, by Atomic Absorption Spectrophotometer (AAS) (Lindsay and Norvell, 1978).

RESULTS AND DISCUSSION

All soil samples (except sample *Tephrosioa*-1) from where all three plant samples (*Adhatoda*, *aerva* and *tephrosia*) were collected had copper concentration higher than the normal soils i.e. higher than 5-100 mg/kg copper (Adriano, 2001). The soils from where *Adhatoda* was sampled ranges from 29.5 mg/kg to 885.54 mg/kg with a mean value of 373.88 mg/kg. The soil samples associated with plant species *Aerva* was found in range 7.37 mg/kg to 277.18mg/kg with an average value of 70.93mg/kg copper. The mean value of soil samples associated with *Tephrosia* was 43.98, ranged from 4.9mg/kg to 143.72mg/kg. The maximum soil copper concentration was 885.mg/kg. Thus the higher toxic levels of copper in soils at mining area have observed, showing soil copper pollution.

Figures 6, 7 and 8 shows copper concentration in soil and respective parts of the plants (root, stem, leaves) for *Adhatoda*, A*erva*, and T*ephrosia* arranged for each graph, from left to right, according to increasing metal concentration in soil. For most of the samples of all three plant species copper concentration is found higher than the normal value found in plants. The amount of copper required for normal plant growth is 5-20 mg/kg; concentrations below 5mg/kg are considered deficient and above 20 mg/kg as toxic to the plants (Kabata-Pendias and Pendias, 1984; Loneragan and Robson, 1981). According to Tietjen (1775) and Kabata-Pendias and Pendias (1992) 100 mg/kg copper, would be considered highly toxic to plants. From the figure 6 it is observed that for the soil copper concentration less than 100 mg/kg all the respective parts of the *Adhatoda vasiea* show copper concentration less than 20 mg/kg, thus may function as normal plant and in some cases also found deficient of copper (<5mg/kg). In most of the cases the copper concentration in *Adhatoda* samples exceeds the concentration of 30 mg/kg and even reaches to the 600 mg/kg in leaves (*Adhotoda* sample-20) with maximum soil copper concentration (≈900mg/kg). At relatively low copper concentration in soil *Adhatoda* accumulated most copper in the stem and roots. With the increase in soil copper concentration most of copper is accumulated in leaves. In *Adhatoda*, for most of the samples there is an increase in copper accumulation in leaves as the soil metal concentration increases, suggesting efficient translocation of copper from root to leaves with an increase in soil copper concentration.

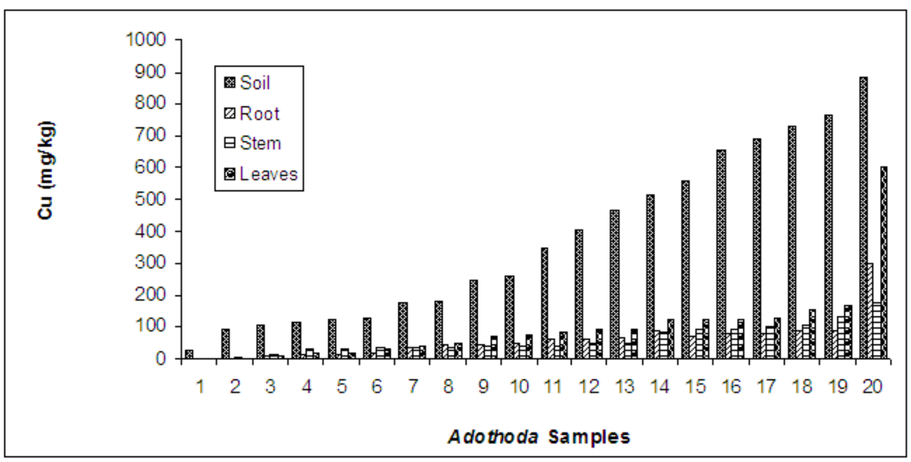

Figure 6: Copper concentrations in soil and parts of *Adhatoda vasiea*

In case of most of *Aerva* samples, for soil copper concentration less than 50 mg/kg, plant samples have shown copper concentration less than 20 mg/kg, except for stem and leaves of Aerva sample-4, where copper concentration was found at the toxic level. Above 100 mg/kg for all stem and leaves samples copper concentration was found to be higher than 30 mg/kg. *Aerva* sample-5 leaves, sample-6 stem and leaves at the soil concentration 40mg/kg also showed concentration higher than 30 mg/kg. For all soil concentrations, *Aerva* accumulated most of the copper concentration in leaves. Not in definite pattern but in most cases copper concentration in leaves increases with soil copper concentration.

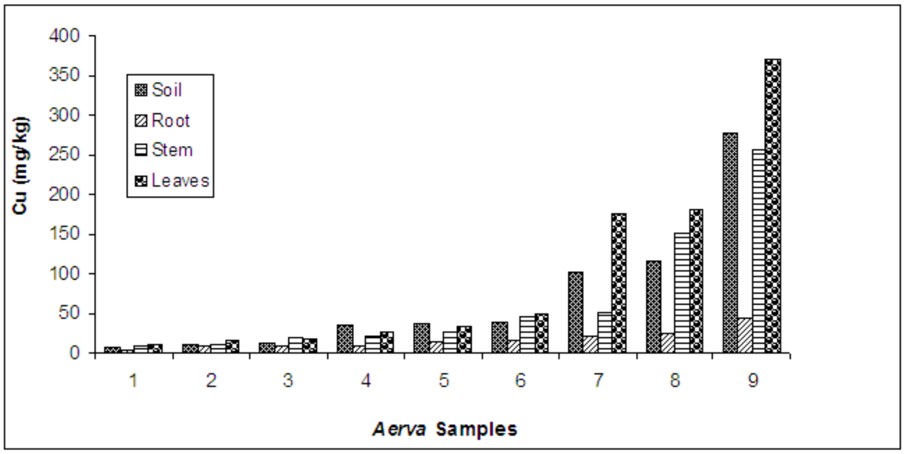

Figure 7: Copper concentrations in soil and parts of *Aerva tomentosa*

In case of *Tephrosia* samples, for the soil copper concentration up to 20 mg/kg all samples showed lower metal concentration (<20mg/kg), but in sample-3 leaves showed copper concentration higher than 30 mg/kg. Above 20 mg/kg except for sample-5 root, all samples showed concentration greater than 30 mg/kg and most of copper was found to be accumulated in leaves.

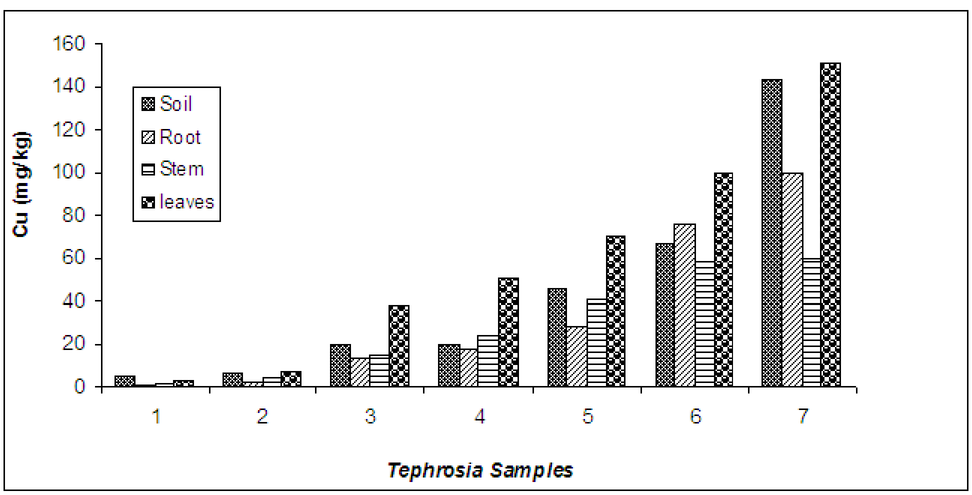

Figure 8: Copper concentrations in soil and parts of *Tephrosia villosa*

Due to continuous exposure of copper to soil by mining activity, the plant species: *adhotoda*, *tephrosia*, *aerva*, at mining vicinity have developed resistance and tolerance by accumulating copper in roots and above ground shoots. These plant species can now be called pseudometallophytes (Whiting *et al.*, 2008; Kavamura and Esposito, 2010; Sheoran *et al.*, 2011). Plants with the copper concentration range 30-500 mg/kg regarded as indicator plants (Adriano, 2001). Among these studied plant species, most of samples of *Adhatoda* and *aerva* shoots have shown the same range thus can be regarded as the copper indicator plant species.

Conclusion

Both soils and plants have found to be contaminated by elevated level of copper at the study area. All the soils examined had the copper concentration above the normal concentrations of 20 mg/kg, with the average of 373.88 mg/kg copper from where *Adhatoda* was sampled, 70.93mg/kg *aerva* associated soils and 43.98mg/kg *tephrosia* associated soils. The three plant species studied showed elevated copper content in the leaves and *Adhatoda* and *Aerva* is found as copper indicator plants. The copper concentration ranges in *Adhatoda* leaves from 18.04 to 600mg/kg, *aerva* leaves from 175.32 to 370 mg/kg for the soil copper concentration greater than 100mg/kg. The results indicated the copper pollution in the soil due to continuous mining activities and copper accumulation in studied plant species.

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