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# Geochemical fractionation of some heavy metals in soils in the vicinity of sukinda mining Area, Orissa

Bhupander Kumar<sup>1</sup>, Sanjay Kumar<sup>1</sup>, Meenu Mishra<sup>1</sup>, S. K. Singh<sup>1</sup>, Dev Prakash<sup>1</sup>, C. S. Sharma<sup>1</sup> and D. P. Mukherjee<sup>2</sup>

<sup>1</sup>Central Pollution Control Board, East Arjun Nagar, Delhi, India <sup>2</sup>Central Pollution Control Board, Rajdanga Main Road, Kolkata, India

### ABSTRACT

Geochemical fractionation of selected heavy metal in soils from Sukinda mining area was studied using single and sequential extraction technique. The concentration pattern was observed as: Al > Cr > Zn > Cu. The average concentration of total copper, chromium, zinc and aluminum was 10.18 µg g<sup>-1</sup>, 11336µg g<sup>-1</sup>, 84.64µg g<sup>-1</sup> and 20832 µg g<sup>-1</sup>, respectively. Watersoluble fraction of heavy metals were quite low (0.06-3.36%) except Cr which account 21%, but presence of chelating agents increase the bio-availability (6-34%). Sequential extraction for the speciation of elements among the geochemical phases indicates that most of the metals were associated to carbonate and reducible fraction. Data shows that most of the fractions of investigated heavy metals were in the potentially available as 96%, 97%, 93%, and 88% for Cu, Cr, Zn, and Al, respectively. Further it may be revealed that Cr is most available than Cu, Zn and Al. Gradually mobilized by biogeochemical processes and thus, soils contaminants can contaminate water supplies and impact food chain.

Keywords: heavy metal, fractionation, sequential extraction, contaminated soil.

### **INTRODUCTION**

Contaminated soils with heavy metals may be environmental hazards and sources of exposure. Environmental contamination by heavy metals may occur via various diffuse and point sources [1-3]. The fate of metals, including Cr, Ni, Cu, Mn, Hg, Cd, Pb, As, Sn and Se, in natural environment is of great concern [4], particularly near mine sites, dumps and tailing piles, but also in urban and industrial centers. In order to estimate effects and potential risks associated with elevated heavy metal concentrations that result from these activities, the fraction of total metals that is bioavailable must be identified. Heavy metals in natural environment are present in

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various chemical forms and exhibits different behavior in term of chemical interactions, mobility, biological availability and potential toxicity.

| Metal fraction and association                | Mobility  |
|---|---|
| Exchangeable (dissolved) cations              | High. Changes in major cationic compositions            |
| Exchangeable (dissorved) earlons              | may cause a release due to ion exchange                 |
| Fe-Mn oxides bound                            | Medium. Changes in redox conditions may cause a release |
| Organic matter hound                          | Medium/High. With time, decomposition/oxidation         |
| Organic matter bound                          | of organic matter occurs                                |
| Residual of metals fixed in crystalline phase | Low. Only available after weathering or decomposition   |

| Table 1: | <b>Relative mobility</b> | and availability | of metals in | geochemical form | s of soil [5]                           |
|----------|--------------------------|------------------|--------------|------------------|---|
|          |                          |                  |              | 8                | ··· • • • • • • • • • • • • • • • • • • |

Complexes or strongly bound metals are of less concern because they are most likely unavailable to organisms. The other forms i.e. exchangeable, carbonate, Fe-Mn oxide, and organic bound of heavy metals have been found to be the most important, which influence the long term effect on liability and bioavailability of metals [5]. Relative mobility and availability of metals in different geochemical fractions of soil are given in Table 1. Metals of major interest in bioavailability due to their potential for human exposure and increased health risk are listed by U. S. Environmental Protection Agency (EPA) [6].

In the scientific literature, many studies describe anthropogenic (industrial or mining) contributions to elemental abundances, and their bioavailability [7-14].

Sukinda Chromite Valley, in Jaipur district of Orissa is well known for its chromite ore deposits and accounts ~97% of India's deposits [15]. The chromite ores and waste rock material are dumped in the open ground without considering its environmental impacts. This valley has been placed fourth most polluted place in the world by Blacksmith Institute [16]. In this study, we measured heavy metals (Cr, Cu, Zn and Al) in different geochemical fractions of soils from Sukinda mining area, by applying single and sequential extraction procedures.

### MATERIALS AND METHODS

### Sampling

Soil samples in duplicate, randomly collected from different locations of mining area including, agricultural land, school playground, roadside, dry query pond, project site office and open dump ground. After removing the rocks, pebbles, samples were mixed thoroughly and a part was taken into a pre-cleaned plastic bags. The collected samples were labeled and then transferred to the laboratory for further chemical processing.

### Treatment of samples

*Total metal concentrations:* Wet samples in triplicates were processed as per USEPA method 3050 [17]. Briefly, five grams of soil sample was placed in a 50 ml screw-capped centrifuge tube, and 30 ml of digestion acid and  $H_2O_2$  was added and digested at  $90^{\circ}C$  for 30 min. The samples were centrifuged, and the supernatant was filtered through Whatman No 42 filter paper and analyzed. Moisture contents were calculated to report the results on dry weight basis.

*Single extraction:* The single extraction method was adopted after MAFF [18]. 5 g sample was extracted with 50 ml water and 0.05M EDTA (pH 7.0), respectively in a shaker for one hour at  $25^{\circ}$ C and centrifuged. The supernatants were carefully transferred to plastic bottles and analyzed for metal contents.

*Sequential extraction:* The sequential extraction of trace elements was carried out as per Tessier et al., [19]. 1 g sediment was extracted in the following order:

Fraction 1: Dissolved or Exchangeable fraction: 1M magnesium chloride (25 ml), pH 7.01 shaking for 1 hr at  $25^{\circ}$  C.

Fraction 2: Carbonate bound fraction (acid soluble): 1 M sodium acetate (25 ml), pH 5.04 with acetic acid, 6 hr shaking at  $25^{\circ}$ C.

Fraction 3: Fe-Mn oxide bound fraction (reducible): 0.04 M hydroxylamine hydrochloride in acetic acid (25% v/v), 25 ml, shaking 6 hr at  $96^{\circ}$  C.

Fraction 4: Organic bound fraction (oxidizable): 0.02 M nitric acid (6 ml) + 30% hydrogen peroxide (9 ml), 2 hrs occasional shaking at  $85^{\circ}$ C, additional 9 ml of 30% hydrogen peroxide with continuation of shaking at  $85^{\circ}$ C for 3 hrs.

Fraction 5: Residual fraction (bound to silicates and detritus materials): Total digestion with concentrated mixture of nitric acid and perchloric acid (3:1 v/v)

Centrifugation at 200 rpm for 15 min was done for separation after each extraction and supernatant was taken by pipette for analysis by Flame Atomic Absorption Spectrometry (FAAS).

| Heavy Metals | Reference value | Measured value <sup>*</sup> | Recovery (%) | SD<br>(±%) |
|--------------|-----------------|-----------------------------|--------------|------------|
| Copper       | 71              | 73                          | 103          | 3          |
| Chromium     | 168             | 162                         | 96           | 4          |
| Zinc         | 289             | 312                         | 108          | 8          |
| Aluminum     | 11,400          | 10,851                      | 95           | 5          |

Table 2: Concentration ( $\mu g g^{-1}$ ) of measured heavy metals in certified standard reference material (SW-8022 )

*Note:* \* *denote average of three replicate* 

### Instrumental analysis

Concentrations of Cu, Cr, Zn and Al were measured by Flame Atomic Absorption Spectrometry (FAAS, Thermo UK). Performance of the instrument was checked by analyzing the reference standard material solutions (Merck, USA). To compensate for matrix effects between sample and standards, blank samples were analyzed in each batch. All the samples were analyzed in triplicate. The detection limits for Cr, Cu, Zn, and Al were 0.05, 0.05, 0.01 and 0.30 mg  $1^{-1}$ , respectively. Appropriate quality assurance quality control (QA/QC) analysis was performed, including analysis of procedural blanks, random duplicate samples (Standard deviation  $<\pm5$ ), calibration curves with the  $r^2$  value of 0.999, and by analysis of certified reference material (SW 8022). The analysis results of certified reference material were comparable to the acceptable limits and were presented in Table 2. In our study, Cr and Al were less than the certified values (-4% to - 5%) while, Cu and Zn were above than the certified values (+3% to +8%).

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### **RESULTS AND DISCUSSION**

### Total metal concentration

The results of total concentrations of metals in soil samples are presented in Table 3. The concentration pattern was observed as: Al > Cr > Zn>Cu. The total concentration of copper, chromium, zinc and aluminum ranged between 6.24-13.74  $\mu$ g g<sup>-1</sup>, 2622-27963  $\mu$ g g<sup>-1</sup>, 53.10-133.45  $\mu$ g g<sup>-1</sup> and 12022-29056  $\mu$ g g<sup>-1</sup>, respectively. The average values of the chromium in this study were above environmental quality criteria guidelines stipulated by different agencies (Table 4), however, other metals were below the limits. This suggested that the soils in this region are highly contaminated by chromium. An evaluation of total metal levels in the soils may be useful as an index of contaminations, but it provides little or no indication of their bioavailability, mobility and reactivity in soils. As such, fractionation of metals may help to assess the bioavailability and possibility of mobilization of metals in the soils of this mining area.

| Hoovy Motol             | Maan  | Madian | SE*  | Ra    | nge    |
|-------------------------|-------|--------|------|-------|--------|
| neavy Metal             | wiean | Meulan | SE.  | Min   | Max    |
| Copper                  | 10.18 | 9.99   | 0.75 | 6.24  | 13.74  |
| Chromium                | 11336 | 7707   | 2553 | 2622  | 27963  |
| Zinc                    | 84.64 | 80.30  | 7.80 | 53.10 | 133.45 |
| Aluminum                | 20832 | 19868  | 1638 | 12022 | 29056  |
| *standard error –SD/\/n |       |        |      |       |        |

Table 3: Concentration range and mean of heavy metals  $(\mu g.g^{-1})$  in soils

| Table 4: Environmental | quality criteria and | earth's crust metals in soils: | comparison w | ith soils from <b>S</b> | Sukinda (ug.g <sup>-1</sup> ) |
|------------------------|----------------------|--------------------------------|--------------|-------------------------|-------------------------------|
|                        | 1                    |                                |              |                         |                               |

| Heavy Metal | EPA<br>[20] | Ind.<br>[21] | Res.<br>[22] | Normal [23] | Crust.<br>[24] | Present study |
|-------------|-------------|--------------|--------------|-------------|----------------|---------------|
| Cu          | 4300        | 60-125       | 100          | 5-20        | 55             | 10.18         |
| Cr          | 3000        | 75-100       | 8            | 0.03-14     | 100            | 11336         |
| Zn          | 7500        | 70-400       | 250          | 1-100       | 70             | 84.64         |
| Al          | -           | -            | -            | -           | 81300          | 20832         |

#### Bio-available fractions of heavy metals - single extractions

Water and EDTA extractable metals and their percentage of their 'total' are presented in Table 5 & 6. Water extractable phase contains most mobile and bio-available metals [25], whereas EDTA is capable of extracting metals in non silicate bound phase. The percentage of water extractable fraction of metals was less and it is 3.36, 0.06 and 1.16 percent for Cu, Zn and Al, respectively, whereas, Cr was 20.83 percent extractable by water. EDTA extracts higher percentage of metals from soils compared to water.

Table 5: Concentration range and mean±SE of heavy metal extracted from soil by water and EDTA-single extraction

| Hoovy Motols | Water- extractable ( $\mu g.g^{-1}$ ) |                 | EDTA-extra | ctable (µg.g <sup>-1</sup> ) |
|--------------|---------------------------------------|-----------------|------------|------------------------------|
| Heavy Metals | Range                                 | Mean            | Range      | Mean                         |
| Copper       | < 0.01-0.90                           | $0.26\pm0.09$   | 0.75-1.90  | 1.16±0.10                    |
| Chromium     | 133-6991                              | 2151±696        | 640-6198   | 2989±625                     |
| Zinc         | < 0.01-0.25                           | $0.05 \pm 0.02$ | 3.30-6.95  | 4.64±0.34                    |
| Aluminum     | 14-1837                               | 311±175         | 15-278     | 106±20                       |

The average percentage of EDTA extracting efficiency for Cr, Cu, Zn and Al was 33.85, 11.43, 5.85 and 5.48, respectively. The other reports shows that water is less capable in extraction of metals, but the presence of chelating agents (such as soluble organic species) increase the metals extractability and their bioavailability [26]. Results of present study show that most mobile, readily bioavailable water-soluble percentages of chromium was quite high and addition of chelating chemicals (i.e. EDTA) may induced extractable fraction of the other metals also.

### Geo-Chemical partitioning of heavy metals- sequential extractions

Sequential extraction provides information on the partitioning of metals into different sediment fractions which can be useful in the understanding of mobility and bioavailability.

## Table 6: Percent range and Mean±Sd of their 'total' heavy metal extracted from soil by water and EDTA-single extraction (N=24)

| Hoovy Motols | Water- extra | actable (%)      | EDTA-extractable (%) |                  |  |
|--------------|--------------|------------------|----------------------|------------------|--|
| neavy metals | Range Mean   |                  | Range                | Mean             |  |
| Copper       | <0.01-12.87  | 3.36±1.38        | 8.50-13.83           | $11.43\pm0.48$   |  |
| Chromium     | 1.52-64.61   | $20.83 \pm 5.42$ | 15.37-81.00          | $33.85 \pm 6.27$ |  |
| Zinc         | < 0.01-0.25  | $0.06 \pm 0.02$  | 3.18-9.02            | $5.85 \pm 0.56$  |  |
| Aluminum     | 0.07-6.46    | $1.16\pm0.60$    | 0.10-10.98           | $5.48\pm0.18$    |  |

The bioavailability is related to solubility of the metals then the bioavailability decrease in order: exchangeable > carbonate > Fe-Mn oxide > organic > residual [27]. In present study fractionation of heavy metals by sequential extraction was conducted in different geochemical phases of soil (exchangeable, carbonate bound, Fe-Mn oxide bound, organic bound and residual). Results observed by sequential extraction in various geo chemical phases are presented in Table 7 and their percent of 'total' metals are given in Table 8. The metal contents in individual geochemical phases are discussed below.

| Table 7: Range and mean±SE of heavy metal (µg.g <sup>-1</sup> ) in different geochemical fractions of soils -sequer | ntial |
|---|-------|
| extraction (N=24)   |       |

| Casabamiaal frastions | Heavy Metals      |             |                 |                  |  |
|-----------------------|-------------------|-------------|-----------------|------------------|--|
| Geochemical fractions | Copper            | Chromium    | Zinc            | Aluminum         |  |
| Evolongooblo          | 0.25-2.00         | 122-23476   | 0.25-1.00       | 17.7-172.4       |  |
| Excitatigeable        | $(0.75\pm0.14)$   | (6625±2763) | $(0.50\pm0.07)$ | (45.12±15.0)     |  |
| Carbonata             | 1.00-4.49         | 322-1115    | 9.73-29.21      | 3223-10358       |  |
| Carbonate             | (1.81±0.29)       | (723±75)    | (17.43±2.11)    | (7063±687)       |  |
| Fe-Mn oxides          | 3.50-11.49        | 1292-7852   | 23.99-108.93    | 4917-16664       |  |
|                       | $(7.66 \pm 0.89)$ | (3662±547)  | (58.63±8.17)    | (9812±1255)      |  |
| Organia               | 0.50-5.00         | 10-289      | 0.45-3.89       | 914-2082         |  |
| Organic               | $(1.96\pm0.39)$   | (59±23)     | (1.38±0.28)     | $(1442 \pm 113)$ |  |
| Posidual              | 0.25-1.00         | 21-1175     | 2.40-11.19      | 411-5681         |  |
| RESILUAI              | $(0.50\pm0.07)$   | (334±125)   | (6.13±0.98)     | (2471±511)       |  |

Note:-mean±SE in parentheses

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### Dissolved or Exchangeable fraction:

Heavy metals in the exchangeable fraction held by electrostatic adsorption represent the most mobile and readily available for biological uptake in the environment thus this fraction can be regarded as a pollution indicator [28].

The concentration of metals in this phase indicates the environmental impact. In the Sukinda soils the Zn and Al associated with this fraction are negligible (<1%) however; Cr and Cu concentrations were significantly higher with the average values of 33.12 and 7.52 %, respectively. Therefore, we conclude that the exchangeable fraction of Zn and Al is least bioavailable and on the other hand Cr and Cu show health risks.

### Carbonate fraction (Acid soluble):

It has been reported [29] that trace metals extracted from soil and sediments with sodium acetate (1M) adjusted to pH 5 may have also been specifically sorbed to low energy sites on the surfaces of clay minerals, organic matter and oxide minerals. Therefore, heavy metals recovered within this fraction are not strongly bound and can be released in acidic conditions (pH<5). Heavy metals extractable with 1M acetic acid adjusted to pH 5 (with acetic acid) are therefore likely to be bioavailable [30].

In the present study the carbonate fraction accounts a relatively medium amount of the 'total' metal concentrations (9.67% to 34.67%). This may be attributed to the slightly acidic nature of groundwater in this area [31]. The fractionation indicates that, Cu and Cr were observed to be less (9.67% and 10.84%), which indicates that the metal low levels of these are readily exist in this fraction. The zinc and aluminum fractions were with an average of 23.84% and 34.67% respectively. The speciation pattern of the carbonate fraction suggests greater environmental risks Zn, and Al.

| Casabamiaal frastions | Heavy Metals       |                    |                   |                    |  |  |  |
|-----------------------|--------------------|--------------------|-------------------|--------------------|--|--|--|
| Geochemical fractions | Copper             | Chromium           | Zinc              | Aluminum           |  |  |  |
| E                     | 1.96-16.30         | 1.61-83.96         | 0.34-1.14         | <0.01              |  |  |  |
| Excitatigeable        | $(7.52 \pm 1.23)$  | (33.12±10.23)      | $(0.60\pm0.07)$   | <0.01              |  |  |  |
| Carbonata             | 7.83-44.98         | 3.21-21.98         | 8.93-46.70        | 17.81-48.92        |  |  |  |
| Carbonate             | (9.67±3.63)        | $(10.84 \pm 2.11)$ | (23.84±4.20)      | (34.67±3.02)       |  |  |  |
| Fa Mn avidas          | 45.03-83.63        | 12.63-89.31        | 43.04-81.63       | 30.46-57.35        |  |  |  |
| re-will oxides        | $(63.16 \pm 4.38)$ | (51.43±8.28)       | (66.22±4.30)      | $(45.69 \pm 2.74)$ |  |  |  |
| Organia               | 4.08-16.37         | 0.04-3.81          | 0.62-4.79         | 3.36-11.50         |  |  |  |
| Organic               | (8.26±2.67)        | (0.84±0.30)        | (2.26±0.35)       | (7.37±0.72)        |  |  |  |
| Residual              | 2.50-8.56          | 0.16-15.45         | 3.93-15.30        | 3.13-31.39         |  |  |  |
|                       | (4.91±0.58)        | (5.03±1.84)        | $(7.08 \pm 1.00)$ | (12.07±2.71)       |  |  |  |
| $\mathbf{N}$          |                    |                    |                   |                    |  |  |  |

| Table 8: Range and mean±SE of heavy metal (% of 'total') in different geochemical fractions of soils from |
|---|
| Sukinda, India-sequential extraction  |

*Note:-mean*±*SE* in parentheses

### Fe-Mn oxide fraction (Reducible):

In comparison with carbonate minerals, Fe-Mn oxide minerals have relatively large area and surface site density [32]. The Fe-Mn oxide, the reducible phase of the soil under oxidizing conditions is a significant sink for the heavy metals. The fractionation results from the present

study found highest affinity of Cr (51.43%), Cu (63.16%), Zn (66.22%) and Al (45.69%) for Fe-Mn oxide minerals of soils (Table 8).

The association of higher concentration of metals with this fraction are caused by adsorption of these metals by the Fe-Mn mineral surface [33] and well explained by Zakir et al., [27]. The extent and intensity of this process will vary depending on several factors associated with oxygen dynamics in the soil. Metals associated with oxide minerals are likely to be released in reducing conditions. Reductive dissolution of the oxide minerals occurs at Eh < +250 mV for Mn oxides and +100 mV for Fe oxides [34]. Relatively small changes in Rh toward reducing conditions would cause reduction of Fe and Mn oxide species. This will cause dissolution of Fe and Mn oxide minerals [27]. The contamination risks of heavy metals of this fraction of Sukinda soils under a reducing condition will be higher.

### Organic fraction (Oxidizable):

Organic matter plays an important role in the distribution and dispersion of metals by mechanisms of chelating and cation exchange. In this phase a reaction between a metal ion and an organic ligand leading to a species which can either precipitate directly or be adsorbed on soil materials. Carboxyl, phenolic, hydroxyl and carbonyl functional groups are assumed to be primarily responsible for metal binding [35]. Metal humic complexes are reversible, and metals can be desorbed by salting out or by hydrogen ion competition. The concentration of heavy metals was found in the organic fraction are 0.84% (Cr), 8.26% (Cu), 2.26% (Zn) and 7.37% (Al). The organic fraction of metals is not considered very mobile or available because of its association with high molecular weight stable humic substances.

### **Residual fraction:**

The residual fraction is concerned with the most stable and least bioavailable of all the chemical fractions of the soil and sediments, since it is believed that metals are occluded within the crystal lattice of silicates and well crystallized oxide minerals [36]. The residual fraction is a major carrier of metals in most environmental systems. The percent of this fraction can be taken as a guide to the degree of non-availability of metals to biota or diagenetic processes except over long time scales [19,27]. The metals of the residual fraction are usually considered to be fragments of the primary mineral phase. All other fractions can be of secondary mineral phases as they involve materials formed through physical and chemical processes of weathering of primary minerals. The smaller the percentages of the metal present in this fraction, the greater the pollution of the area. In all the samples analyzed the, Cu (4.91%), Cr (5.03%), Zn (7.08%) and Al (12.07%). The relatively small amount of heavy metals in this fraction indicates their high mobility and therefore high environmental contamination risk to Sukinda soils.

### Availability of heavy metals

The environmental impact of the five-speciation fractions of the heavy metals depends upon case of remobilization [29]. Tessier et al., [19] defined a model for heavy metal association with geochemical fractions. In this model, metals found in ion-exchangeable, carbonate, reducible fraction and organic phases are those considered to be readily available to water column and the biota operationally described as bioavailable metals, while those metals in the residual phase is

considered as the non-available metal. The distribution patterns of the studied metals in various fractions were found to be as follows:-

**Copper**: reducible > acid soluble > oxidizable > exchangeable > residual **Chromium**: reducible > exchangeable > acid soluble > residual > oxidizable **Zinc:** reducible > acid soluble > residual > oxidizable **Aluminum**: reducible > acid soluble > residual > oxidizable > exchangeable



**Figure 1: The available non-available concentrations of heavy metals in soils** Note: Available= sum of metal fractions of exchangeable, carbonate, Fe-Mn oxide, and organic bound fractions. Non-available=residual fraction of metals

In present study the available forms of heavy metals are sum of first four fractions and nonavailable form of the heavy metal was considered as residual fraction, results of Sukinda soil are illustrated in Figure 1. The data shows that most fractions of all the investigated heavy metals were found in the potentially available form. Figure 1 show that the percentage potential availability of Cu, Cr, Zn, and Al were substantially high with 96%, 97%, 93%, and 88%, respectively. Gradually mobilized by biogeochemical processes and thus, soils contaminants can contaminate water supplies and impact food chain. This potential availability of the heavy metals indicates that metals have contamination risk in Sukinda Valley environment.

### CONCLUSION

Single extractions study shows that heavy metals except Cr were not readily available as indicated by the water extraction experiment, but the presence of chelating agents can render the metals more bioavailable. The geochemical fractionation study revealed that about 3-12% heavy metals in Sukinda soil are in stable form as residual fraction. On an average more than 80%

(non-residual fractions) metal contamination of the Sukinda soils were from mining activities. The speciation of elements among the five geochemical phases indicates that most of the metals were associated to carbonate and reducible fraction. Further it may be revealed that Cr is most available than Cu, Zn and Al. The overall, order of contamination was Cr > Cu > Zn > Al and indicates risk potential to biota.

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