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# CHEMICAL FRACTIONATION OF SOME HEAVY METALS IN SURFACE SOIL IN VICINITY OF COAL BASED SUPER THERMAL POWER PLANT IN KOTA CITY, INDIA

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## ABSTRACT

Soil samples were collected from fifteen different localities situated near coal based Kota Super Thermal Power Plant Station (KSTPS) in Kota City, India in summer season of 2019-20. Assessment of the soil samples was done to measure physico-chemical properties, total heavy metal concentration and chemical speciation of the heavy metals as a function of soil properties. The lability of heavy metals such as Ca, Fe, Cu, Cd, Pb and Zn in soils was measured by sequential chemical extraction procedure (SCE) to separate the metals into water soluble, $MgCl_2$, $NH_4$-acetate, hydroxylamine hydrochloride, $HNO_3/H_2O_2$ and $HF/HNO_3$ extractable fractions. Ca and Fe associated with $HF/HNO_3$ and Na-acetate extracted fractions, copper with Fe-Mn oxide and $HF/HNO_3$ extracted fractions, Cd with $HF/HNO_3$ and hydroxylamine hydrochloride extracted fractions, Pb with organic and Fe-Mn oxide bound extracted fraction & Zn with hydroxylamine hydrochloride and carbonate extracted fractions. The metals bound with hydroxylamine hydrochloride and $HNO_3/H_2O_2$ extractable fractions may be available to the plant and animals according to the pH and other physico-chemical properties of the soil.

**Keywords:** Soil samples, Kota Super Thermal Power Plant Station, Physico-chemical properties, Heavy metal, Sequential chemical extraction procedure.

## 1. INTRODUCTION

Soil pollution by heavy metals is a major environmental problem worldwide [1]. In specific, heavy metal pollution of surface soils due to acute industrialization and urbanization has become a significant concern in many emerging countries [2-5]. The agglomeration of heavy metals in surface soils is influenced by many environmental variables and human activities such as thermal power plant, industrial production, traffic, farming, and irrigation. Vast areas of Kota city are polluted by heavy metals released from coal based thermal power plant, smelters, waste incinerators, industrial wastewater, and from the application of sludge or municipal compost, pesticides, and fertilizers. Apart from the sources in the soil, accumulation of heavy metals can deteriorate soil grade, reduce crop production and the quality of agricultural products and thus perniciously affect the health of human, animals and the ecosystem [6].

In Kota city, a major thermal power plant known as Kota Super Thermal Power Station (KSTPS) generates huge amount of fly ash, which is a homogeneous mixture of various metal oxides in the atmosphere. Various industries (small and large scale) including large numbers of Kota stone factories further raise the heavy metal load in the atmosphere [7].

Alluvium soils of Kota district range in depth from shallow to very deep with lime concretion or lime encrusted gravels at varying depths. The distribution of heavy metals in soil is altered by the processes of sorption/desorption, precipitation, dissolution, redox reaction and penetration in the solid components of soil [8]. An increased tendency for the absorption and migration of metal compounds is found for the soil environments having clay minerals with a high density of negative surface charges (high CEC values), high surface areas (small sizes) and also weak vander Waal forces between the structural layer [9-10].

Consequently limited information is gathered from the results of the total concentration of heavy metals in soil, as this does not show how strongly the metal is bound to soil constituents. By possessing the knowledge of those heavy metal bearing phases and their solubility in aqueous fluids, one can conclude the potential mobility and bioavailability (lability)[11].

Several selective sequential extraction procedures have been commonly utilized for studying metal mobility and accessibility in soils and silt [12-15]. This extraction scheme allows the fractionation of the absolute metal contents into five functionally defined fractions; $MgCl_2$ extractable, acetic acid extractable, bound, hydroxyl-lamine hydrochloride extractable (reducible), nitric acid-hydrogen peroxide extractable (oxidizable), and residual fractions.

These fractions may be considered to diminish the lability from exchangeable to residual. Data on the chemical speciation of metal in a soil is therefore crucial in surveying the peril that these contaminations represent, and it can also guide the choice of remediation advances [11].

The major objective of this study is to determine the total concentrations and extractability of Ca, Fe, Cu, Cd, Pb and Zn in surface soil in the vicinity of coal based Kota Super Thermal Power Plant (KSTPS) in Kota City, India with a view of providing information on the extent of contamination. This study will reveal the chemical behaviour of heavy metals in the soil environment which is the basis of risk assessment, decontamination and remediation of soils contaminated with heavy metals because of anthropogenic activities. Since no speciation studies on heavy metals in soils in this part of the Kota city has been reported, it is expected that the results from this study would form a baseline data for future heavy metal burden in the study area.

## 2. MATERIAL AND METHODS

### 2.1. Study area

Kota, the main industrial city of Rajasthan state in India, has an area of 527 $km^2$. Kota has semi arid climate with temperature range 6°C in winter (January) to 47°C in summer (June).

With the help of GPS (Global Positioning System), 15 sampling sites were selected according to ASTM D 5111 Standards [16]. Locations of different sampling sites of Kota city has been shown in Fig. 1.

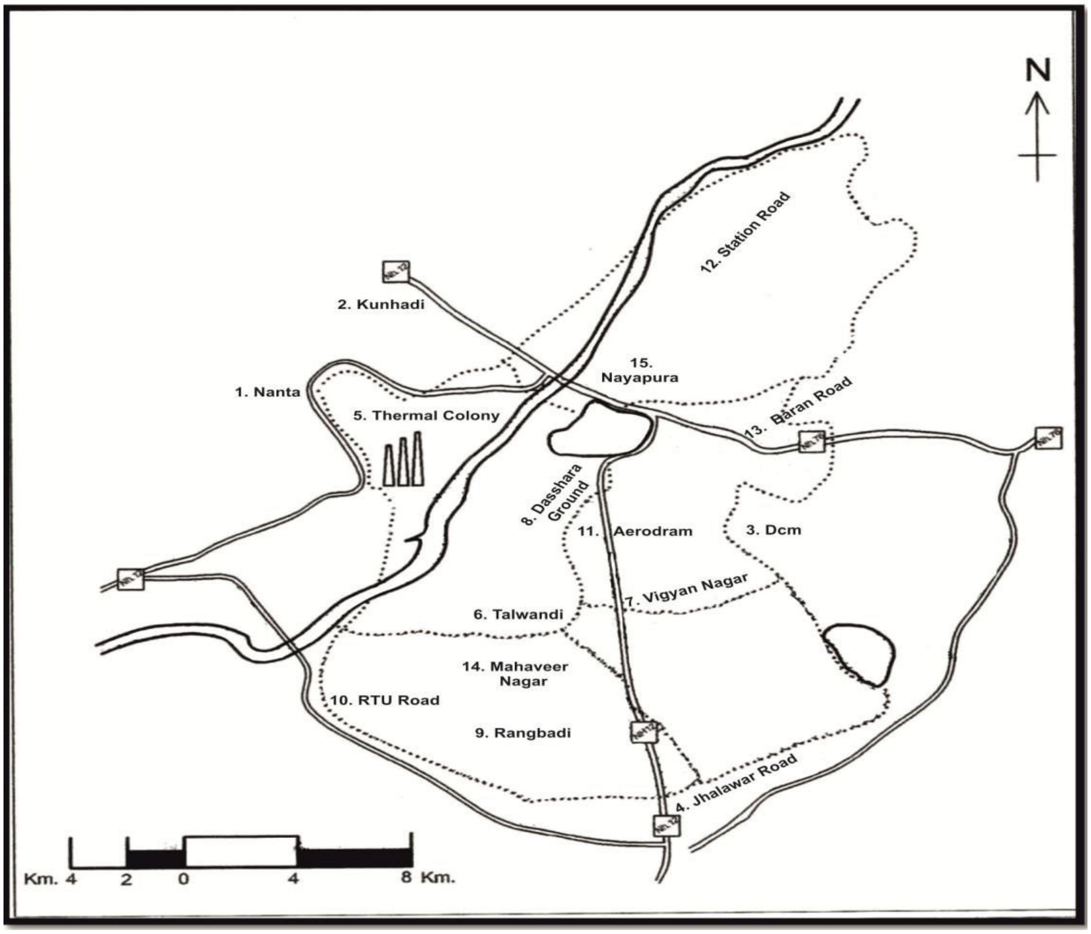

**Fig. 1: Locations of different sampling sites of Kota city.**

### 2.2. Soil Sampling and Analysis

Soil samples (n=45) in requisite quantity were collected from topsoil (0- 10 cm), at 15 selected sampling sites during summer (March, April, May) seasons of 2019-20. All samples of soil were air dried first, thereafter gently crushed in the ceramic mortar and sieved for collecting fraction smaller than 2mm. The dried samples, thus obtained, were passed through the sieves with 100 BSS openings (<149μm) followed by suitable digestion.

### 2.3. Physico-chemical Analysis of the Soil Samples

EC & pH [17], CEC [18], organic carbon content [19], particle size [20] and total heavy metals [21] were determined by the methods described in earlier research.

### 2.4. Sequential extraction procedure

The procedure of Ma and Rao, 1997 [22]; which is a modified version of a procedure described by an earlier researcher [10], was used to segregate the heavy metals into six operational defined geochemical fractions (F1 to F6). Two grams of the soil were placed in a 50 ml polypropylene centrifuge tube and subjected to the following extraction processes:

#### *2.4.1. Water-soluble fraction (F1):*

Soil extracted with 20 ml of deionized water for 2 hours.

#### *2.4.2. Exchangeable fracton (F2):*

Residue from F1 extracted with 20ml of 1molL$^{-1}$ $MgCl_2$, pH 7 for 1 hour.

#### *2.4.3. Carbonate-bound fraction (F3):*

Residue from F2 extracted with 20 ml 1molL$^{-1}$ $NH_4OC_c$ pH 5 for 5 hours.

#### *2.4.4. Fe-Mn oxide-bound fraction (F4):*

Residue from F3 extracted with 20 ml 0.04molL$^{-1}$ $NH_2OH.HCl$ in 25% (v/v) $HOA_c$ at 90°C with occational agitation.

#### *2.4.5. Organic-bound fraction (F5):*

From F4 residue extracted with 15ml 30% $H_2O_2$ at pH 2 (adjusted with $HNO_3$) for 5.5 hours (water bath, 85°C). After cooling, 5ml of 3.2molL$^{-1}$ $NH_4OA_c$ in 20% $HNO_3$ was added and shaken for 30 minutes before final dilution to 20 ml with deionized water.

#### *2.4.6. Residual fraction (F6):*

Residue from F5 digested using a $HF/HNO_3$ digestion procedure.

All the solid phases from F1 to F6 were washed with 10 ml of deionized water before further extraction. The washes were collected with supernatant from the previous fraction. After each extraction, the supernatant was separated by centrifugation at 10,000 rpm for 30 minutes. To verify the sum total of metal recovered in the sequential extraction steps, a separate total concentration of Ca, Fe, Zn, Cu, Cd, and Pb was determined on the sample after HF/aqua regia digestion.

The use of triplicates and procedural blanks was assured for quality control. In the replicate analysis of the soil samples, coefficients of variation were less than 6% for all elements. The retrieval of heavy metals in the sequential extraction steps was within 100±10%.

Following digestion, Direct Air-Acetylene Flame method (Atomic Absorption Spectrophotometer-Shimadzu-6300) was used to determine the concentrations of 6 metals (Fe, Zn, Cu, Cd and Pb). Flame Photometer (Systronics -128) method was used to measure Ca metal concentration.

### 2.5. Statistical analysis

All the data generated from the experiments were subjected to statistical analysis using SPSS version 16.0.

## 3. RESULTS AND DISCUSSION

### 3.1. Physicochemical characteristics

The physico-chemical properties of the soil samples at various sites are shown in Table 1. Soil pH is the most widely accepted factor which influences the availability of micronutrients and heavy metals in the soil to plants [23]. The pH values of the soil samples from the Mahaveer Nagar were found to be acidic (pH 5.02). The availability, mobility and toxicity of heavy metal ions in the soils were controlled by acidity. Most metals tend to be less mobile in soil with high pH as they form insoluble complexes [24]. Soil salinity is measured by electrical conductivity which indicates that movement of charge particles would be more than that of the less charge particles because there are more soluble salts in the soil samples from the all sampling sites than the control [25-26]. Organic matter acts as a major adsorbent for metals through the formation of chelates and renders them immobile [27]. Soils with low CEC are more likely to develop deficiencies in potassium ($K^+$), magnesium ($Mg^{2+}$) and other cations, while high CEC soils are less susceptible to leaching of these cations [28-29]. As the texture of the soil plays a very important role in the plant species establishment and development and also influences physical parameters of the soil. The soil texture class of all the soil samples as represented in table 2 showed that they were all sandy soils with very high percentage of sand and low clay and slit contents. Soils with high sand content exceeding 70% will have weak surface aggregation and such soils will be porous and have high rate of water infiltration and air circulation [30].

### 3.2. Total metal concentrations

Table 2 shows the heavy metal concentration and its distribution in all the sites. The soil sample showed Ca, Fe, Cu, Zn, Pb and Cd levels ranging from 251.03 - 287.13, 3.9045-7.6213, 3.1163-7.1648, 1.0021-8.6632, 1.8018-4.8485 and 0.5692-1.243 mg/kg respectively. The high concentration of Pb and Cd metals at these sites could be due to air borne sources from coal based Kota Super Thermal Power Plant Station, car exhaust fumes depositing lead and other contaminants to the environment, automobile vehicle repair process like filing and soldering of iron rods along with other metals bending processes in the Kota City and industrial activities occurring close to the automobile workshops.

**Table 1: Some physicochemical properties of surface soil in the Kota city**

| Sample sites | pH | EC (Siemens /meter) | Organic matter (%) | CEC (cmol/kg) | Sand %) | Clay (%) | Slit (%) |
|---|---|---|---|---|---|---|---|
| Nanta (S1) | 6.52 | 586.8 | 1.91 | 11.2 | 85.2 | 10.1 | 4.7 |
| Kunhadi (S2) | 8.94 | 104.8 | 2.62 | 13.3 | 83.6 | 11.6 | 4.8 |
| DCM (S3) | 6.44 | 398.4 | 3.50 | 13.2 | 78.9 | 9.1 | 12.1 |
| Jhalawar (S4) | 6.60 | 695.7 | 1.88 | 11.1 | 88.2 | 7.9 | 3.9 |
| Thermal (S5) | 8.63 | 596.1 | 2.14 | 12.2 | 79.3 | 9.9 | 10.8 |
| Talwandi (S6) | 7.56 | 491.0 | 7.53 | 20.6 | 74.1 | 11.2 | 14.7 |
| Vigyan nagar (S7) | 6.42 | 380.4 | 3.42 | 19.3 | 74.6 | 12.1 | 13.3 |
| Dashara (S8) | 6.72 | 345.5 | 3.63 | 18.9 | 76.1 | 9.9 | 14.0 |
| Rangbadi (S9) | 6.81 | 612.2 | 2.21 | 12.9 | 85.9 | 10.1 | 4.0 |
| RTU (S10) | 7.10 | 917.0 | 6.29 | 10.9 | 84.8 | 6.8 | 8.4 |
| Aerodram (S1i) | 6.69 | 442.9 | 3.94 | 18.7 | 76.1 | 12.1 | 11.8 |
| Baran road (S12) | 6.94 | 352.8 | 2.08 | 11.3 | 85.9 | 7.9 | 6.2 |
| Station road (S13) | 6.56 | 629.8 | 2.15 | 12.3 | 70.3 | 4.2 | 25.5 |
| Mahaveer nagar (S14) | 5.02 | 208.6 | 4.64 | 16.9 | 71.3 | 12.6 | 16.1 |
| Nayapura (S15) | 6.48 | 356.3 | 2.92 | 14.8 | 75.9 | 11.6 | 12.5 |

**Table 2: Characteristic levels of total heavy metals (mg $kg^{-1}$) in surface soil in the Kota city**

| Sample sites | Ca | Fe | Cu | Cd | Zn | Pb |
|---|---|---|---|---|---|---|
| Nanta | 283.18 | 7.1336 | 3.8275 | 0.8856 | 5.3311 | 2.3104 |
| kunhadi | 260.91 | 6.2426 | 3.5247 | 0.9613 | 5.6392 | 2.8878 |
| DCM | 257.86 | 5.1401 | 3.5325 | 0.7878 | 3.1199 | 3.8196 |
| Jhalawar | 287.13 | 7.6213 | 3.2508 | 0.5953 | 2.6632 | 3.0611 |
| Thermal | 251.03 | 5.6712 | 4.2755 | 0.5813 | 5.0009 | 2.9016 |
| Talwandi | 272.12 | 3.9462 | 5.1086 | 1.1235 | 7.6631 | 4.2302 |
| Vigyan nagar | 286.42 | 4.9364 | 6.8734 | 1.0224 | 8.6632 | 3.8186 |
| Dashara | 276.79 | 6.2681 | 7.1648 | 1.243 | 7.6631 | 3.0487 |
| Rangbadi | 291.34 | 5.0426 | 4.9424 | 0.7866 | 2.1113 | 2.3534 |
| RTU | 294.66 | 6.4015 | 3.9798 | 0.4944 | 1.9898 | 2.1838 |
| Aerodram | 289.93 | 5.6809 | 6.1714 | 1.3455 | 7.7892 | 4.7196 |
| Baran road | 281.87 | 7.1249 | 3.1163 | 0.4826 | 1.9664 | 1.8018 |
| Station road | 283.82 | 6.1553 | 3.6504 | 0.5692 | 1.0021 | 1.9023 |
| Mahaveer nagar | 273.18 | 3.9045 | 4.1326 | 1.0113 | 6.8813 | 3.6683 |
| Nayapura | 284.98 | 6.8062 | 5.3846 | 0.9518 | 6.6632 | 4.8485 |

### 3.3. Fractionation and Distribution of the Heavy Metals in the Soil Samples

Soil samples were fractionated for Ca, Fe, Cu, Zn, Pb and Cd using the Ma and Rao, 1997 method [22]. The quantity of metal found in an extraction fraction is expressed as a percentage of the total mass of that metal in the complete extraction fraction from a given metal.

#### *3.3.1. Calcium*

The largest portion of Calcium was concentrated in the residual fraction (F6) with a range of 38.05-41.63% in all the sites (Fig. 2). This was closely followed by the carbonate fraction (F3), organic bound fraction (F5) and Fe-Mn oxide bound (F4) with average percentages of 17.53 %, 12.65% and 11.28% respectively. The exchangeable fraction (F2) and water soluble fraction (F1) had the lowest portion with an average percentage of 9.78 % and 8.69% respectively.

#### *3.3.2. Iron*

The largest portion of iron was concentrated in the residual fraction (F6) with a range of 20.21-35.12% all the sites (Fig. 3), similar association of iron to residual fraction was reported in earlier research [31- 32].

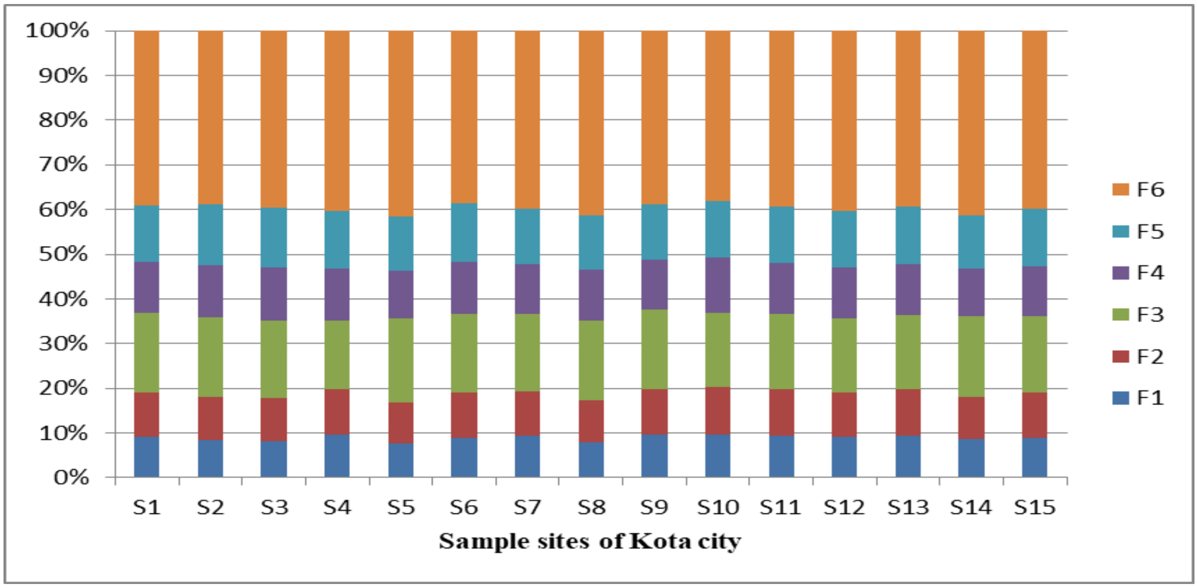

**Fig. 2: Percentage of Ca in the various geochemical phases as function of total Ca content of soil**

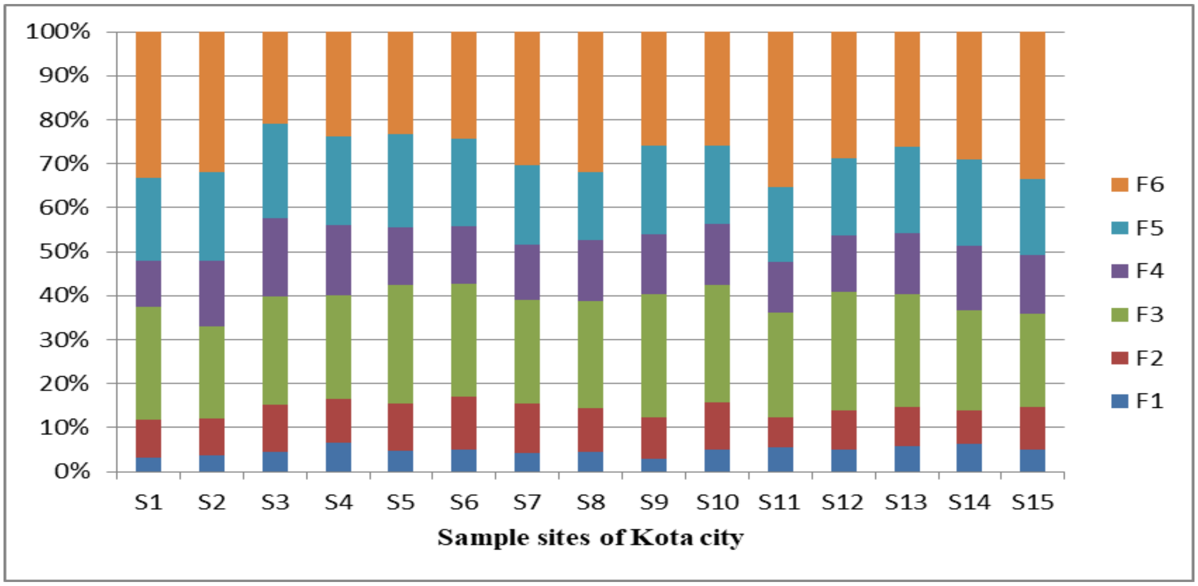

**Fig. 3: Percentage of Fe in the various geochemical phases as function of total Fe content of soil**

This was closely followed by the carbonate bound (F3), organic bound fraction (F5) and Fe-Mn oxide bound fraction (F4) with a range of 21.05-28.19 %, 15.54-21.34% and 11.46-17.69% respectively. The exchangeable fraction (F2) and water soluble fraction (F1) had the lowest portion with a range of 6.18-11.18 and 3.16-6.39% respectively. The low iron metal content in the exchangeable fraction and water soluble fraction are probably due to the fact that iron is easily absorbed and used by plants and other organisms in the soil environment [8].

### *3.3.3. Copper*

Copper was found mostly in the Fe-Mn oxide bound (F4) with a range of 22.39-28.13% (Fig. 4). The residual fraction (F6) is next with a range of 19.51-25.76 % and then organic bound fraction (F5) with a range of 17.36-19.10%.

The presence of Cu in organic fraction is supported by the high formation constants of Cu-organic complexes. Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX) analysis performed on contaminated soils confirmed the strong association of Cu with organic matter [33- 34]. The high surface area and adsorbing capacity of Fe-Mn oxides coupled with the ability of Cu to replace $Fe^{2+}$ in some Fe oxides may be responsible for such adsorption [35]. The carbonate fraction (F3), the exchangeable fraction (F2) and the water soluble fraction (F1) has 12.61-17.37%, 9.95-14.11% and 6.07-10.13% respectively.

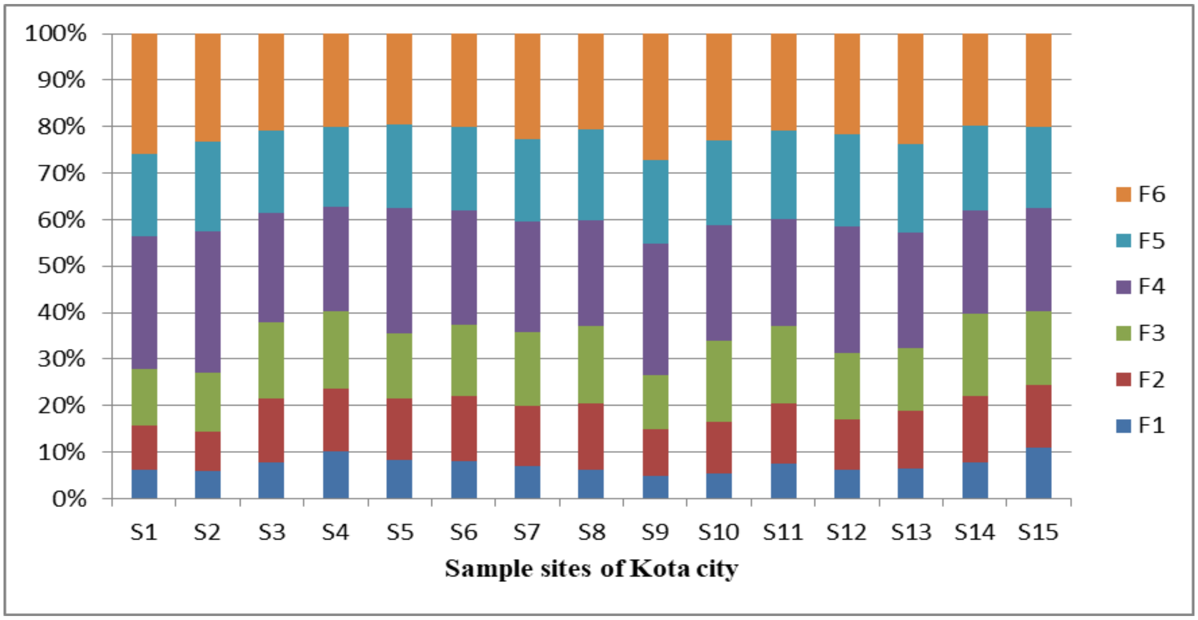

**Fig. 4: Percentage of Cu in the various geochemical phases as function of total Cu content of soil**

### *3.3.4. Cadmium*

The greatest amount of cadmium was found in the residual fraction where the range is 22.22-32.04% (Fig. 5), similar association of cadmium to residual fraction was reported in earlier research [36].

The strong binding of Cd with the residual fraction is in agreement with the observation of distribution pattern of Cd in the studied soils suggests that, the higher the total soil Cd, the higher its tendency to be associated with the residual fraction [37]. This was followed by the Fe-Mn oxide bound fraction (F4) at a range of 21.22-27.24%. The carbonate fraction (F3), exchangeable fraction (F2) and organic bound fraction (F5) were in the range of 19.25-23.85%, 14.71-20.96% and 1.93-7.40% respectively. The minor role of the organic fraction in the speciation of Cd noted in this present study is consistent with the low adsorption constant of Cd to organic matter [38]. The lowest portion of Cd was found in water soluble fraction (F1) with a range of 1.13-6.60%.

### *3.3.5. Zinc*

The largest portion of zinc was found in the Fe-Mn oxide bound fraction (F4) with a range of 29.00-50.06% (Fig. 6). Majority of Zn was associated with Fe-Mn oxide fraction, which may be due to high stability constants of Zn oxides. This was closely followed by the carbonate bound (F3) having a range of 23.64-30.69%.

The presence of Zn in this fraction might indicate a pH suitable for metal precipitation. $CaCO_3$ may act as a strong adsorbent for heavy metals and could complex as double salts like $CaCO_3.ZnCO_3$ [34]. The residual fraction (F6) is next with a range of 15.63-20.91%. The remaining fractions followed the following order: organic bound fraction (F5) > exchangeable fraction (F2) > water soluble (F1).

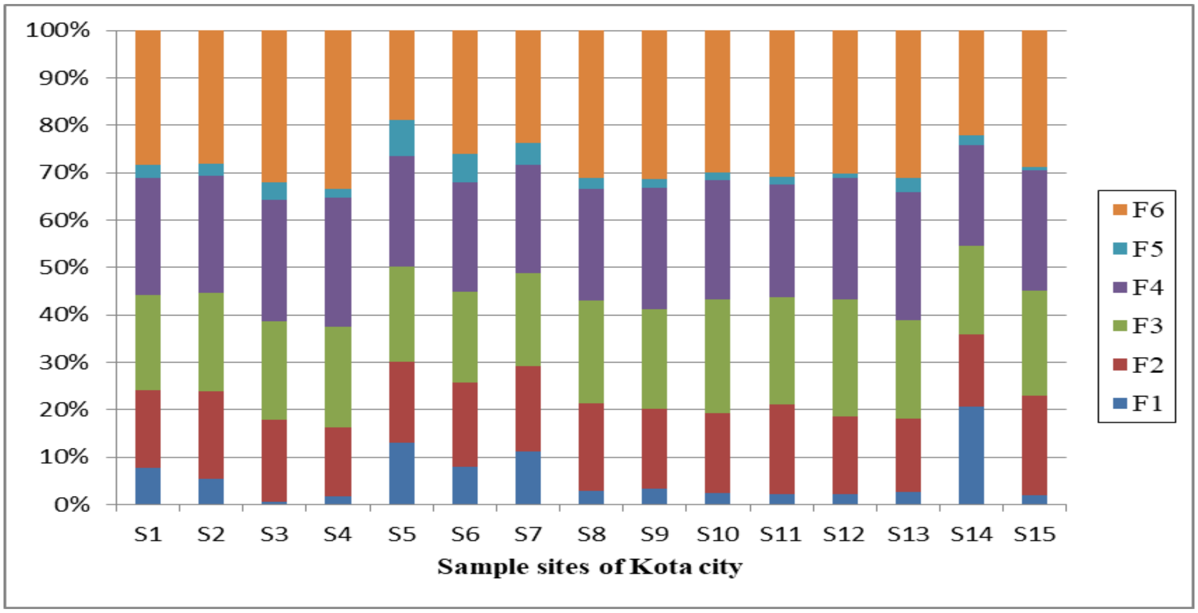

**Fig. 5: Percentage of Cd in the various geochemical phases as function of total Cd content of soil**

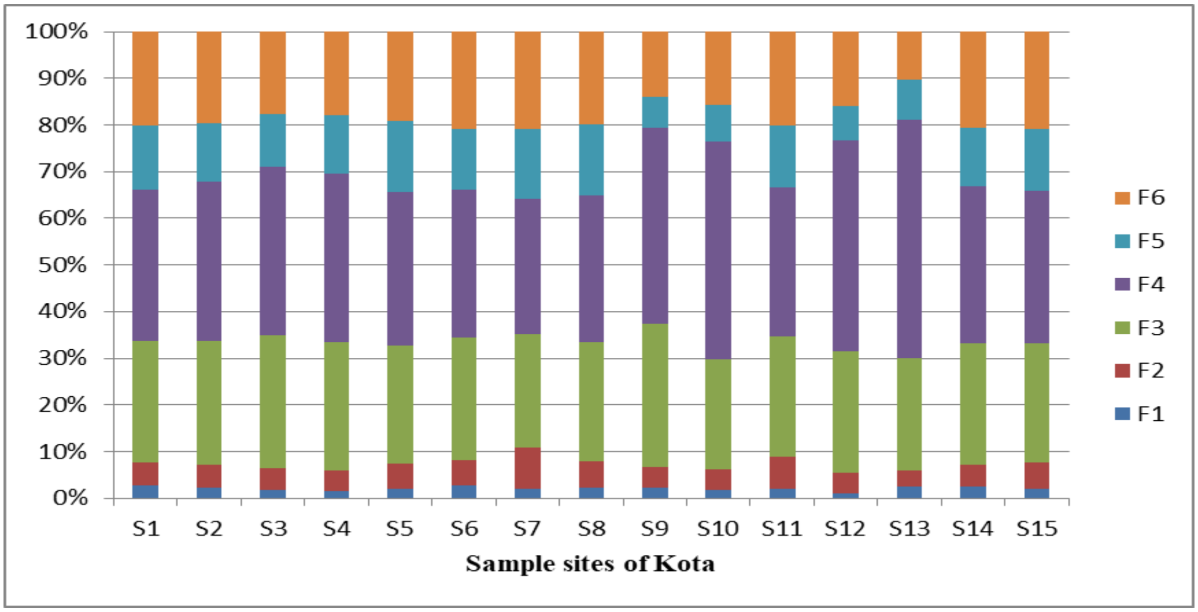

**Fig. 6: Percentage of Zn in the various geochemical phases as function of total Zn content of soil**

### *3.3.6. Lead*

Lead was mainly found in the organic bound fraction (F5) ranging from 25.08-31.29% (Fig. 7). The metal may have co-precipitated with various silicate species as a result of their adsorption into the mineral lattice because of the sandy nature of the soil [39]. This was followed by the Fe-Mn oxide bound fraction (21.25-26.50%), organic fraction (17.20-21.65%) residual fraction (12.22-18.02%) exchangeable fraction (3.41-11.52%) and water soluble (3.80-6.07%). In general, it seems that the oxide fraction is able to scavenge Pb in natural and polluted soils [38].

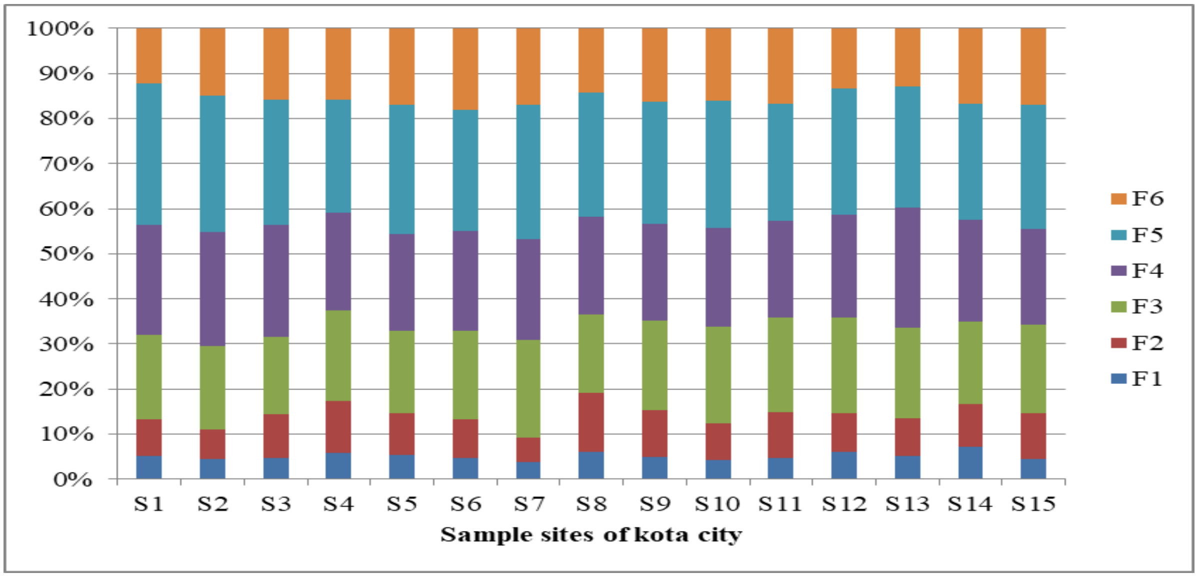

**Fig. 7: Percentage of Pb in the various geochemical phases as function of total Pb content of soil**

## 4. CONCLUSION

The presence of heavy metals in the environment represents one of the most critical environmental hazards. The results show that the soils of the studied regions are polluted with these metals, mainly given the high total concentrations which are steadily being released into the bioavailable forms and subsequently into solution which can lead to absorption into the plants system close to coal based Kota Super Thermal Power plant and cause biomagnification along the food chain. The sequential extraction used in this study is useful to indirectly assess the potential mobility and bioavailability of the heavy metals in soil. The mobility of these metals is related to their solubility and geochemical forms, and it decreases in the order of extraction sequence i.e. exchangeable>carbonate>Fe-Mn oxide bound>organic> residual. This sequence is just a generalisation and offers only qualitative information of metal mobility. The first two phases can release their metal loads by decreasing the pH and are more mobile than the other phases. Accordingly, these two phases influence the mobility and hence the bioavailability. By and large, mechanic workshop owners should be given stringent regulations to perform with full compliance so that we can decrease the extent of heavy metals introduced to the surroundings. Furthermore, remediation of the sites have to positioned into attention to lessen the amount of total metal concentration in the soil to prevent the absorption of these metals by ground water and other essential plants that are grown near to these sites.

## 5. ACKNOWLEDGEMENTS

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