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# Chemical Fractionation of Copper, Manganese and Zinc in Dumpsite Soil Samples in Kaduna Metropolis, Nigeria

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***Authors' contributions***

*This work was carried out in collaboration between all authors. Author EPA designed the proposal. Author SHA is a postgraduate student who carried out the analyses under the supervision of authors EPA and OKI. All authors wrote the draft of the manuscript, read and approved the final manuscript.*

***Original Research Article***

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## ABSTRACT

**Aims:** In this research, sequential chemical extractions were performed to fractionate copper, manganese and zinc in dumpsite soil samples into six geochemical fractions with varying mobility and bioavailability.
**Study Design:** Determination of chemical forms of metals in soils and evaluation of their mobility and bioavailability.
**Place and Duration of Study:** This study was conducted between March, 2011 and June, 2013 in the Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.
**Methodology:** Collection of soil samples from Kawo (KW), Rafin Guza (RG), Angwan Dosa (AD), Badarawa (BD), Malali (ML), Angwan Shanu (AS), Kurmi Mashi (KM), Tudun Wada (TW), Kakuri (KK) and Trikania (TK) dumpsites; sequentially extraction of samples into six fractions and determination of metal concentrations in extracts.
**Results:** Copper had high mobility factor values in the rainy season at TK (43.76%), TW (13.51%), AS (13.48%) and ML (0.14%); and in the dry season at TK (44.79%), KW (14.65%), AS (14.18%), ML (13.43%) and TW (13.31%). Manganese in the rainy season recorded relatively high mobility values at KK (2.18%), AD (2.07%), and TW (1.67%) and in the dry season at ML (2.57%), BD (2.23%), KK (2.06%) and TW (1.51%) while Zinc had

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high mobility values in the rainy season at BD (54.14%), AS (26.62%), KM (18.08%), TK (16.11%), ML (5.88%) and KK (3.54%) and in the dry season at RG (145.79%), BD (44.59%), AS (31.08%), KM (21.65%) and TK (18.19%). Copper and zinc were distributed evenly across the non-residual and residual fractions, while manganese was predominantly retained by residual fractions. The mobility and potential bioavailability of the metals in decreasing order is: zinc > Copper > Manganese.
**Conclusions:** The amount of metals bound to each fraction differed significantly according to metal type, dumpsites and seasons. The study indicates the tendency for bioavailability of the metals studied for plant uptake from soil.

*Keywords: Heavy metals; dumpsite; soil; fractionation; mobility; bioavailability.*

## 1. INTRODUCTION

The gradual increase in population and the proliferation of basic industrial processes led to emergency of civilization that has greater impact on the environment [1]. The industrial revolution gave birth to environmental pollution and the large volume of industrial chemical discharges has added to the growing load of untreated waste [2]. The disposal of domestic, commercial and industrial waste in the world is a problem that continues to grow with human civilization and no waste disposal method thus far is completely safe. Experience has shown that all forms of waste disposal system have negative consequences on the environment, public health, and local economies [3,4].

Dumpsite is an old traditional method of waste disposal similar to landfill method of waste management [5,6]. In developed countries they are often established in derelict quarries, mining or excavated pits away from residential areas with modern landfill facilities, where designated government agencies, corporate bodies and some individuals saddled with the responsibilities of waste management, deposit wastes routinely [7,8]. On the contrary, in less developed countries dumpsites are randomly located even within the residential areas thus the need to monitor the concentration of the likely environmental pollutants. In Nigeria, particularly in Kaduna Metropolis, modern landfill facilities are unavailable; consequently sorting-out of wastes into degradable, non-degradable and recyclable precious materials cannot be achieved. Thus waste are deposited at open dumpsites and poor management of these sites could create a number of adverse environmental impacts including leachate, which could pollute underground soil bed [9].

Leachate from dumpsites is said to be of particular interest when it contains potentially toxic heavy metals [6]. These metals are known to bioaccumulate in soil and have long persistence time through interaction with soil components and consequently enter into the food chain [10,11]. Household and industrial effluent discharges have been known to contain toxic metals such as arsenic, cadmium, copper, lead, manganese, mercury etc [12,13,14], which could pose as hazard to the environment by their mobility and bioavailability.

Selective sequential extraction procedures have been commonly used for studying metal mobility and availability in soils. Numerous extraction schemes for soils and sediments have been described [15,16,17]. Despite uncertainties as to the selectivity of the various extractants and to possible problems due to readsorption, extraction procedures provide qualitative evidence regarding the forms of association of heavy metals and ultimately, of their bioavailability [18].

Similar studies have been carried out in Nigeria for instance assessment of heavy metals bioavailability in dumpsites of Zaria Metropolis [19]; speciation of heavy metals in sediment of Agbabu Bitumen deposit area [20]; chemical fractionation of heavy metals in soils around the vicinity of automobile mechanic workshops in Kaduna Metropolis [21] and chemical fractionation and mobility of heavy metals in soils in the vicinity of asphalt plants in Delta State [22].

In a recent publication, authors had presented data on evaluation of the arsenic, cadmium, manganese and mercury contamination in soil and plant samples [23] and the distribution and chemical forms of arsenic, cadmium and lead in ten major dumpsites located in Kaduna Metropolis, Nigeria [24]. In continuation of this environmental case study, authors seek to also unfold the distribution and chemical forms of copper, manganese and zinc in the same study area in order to predict their behavior in soil with respect to plant uptake.

## 2. MATERIALS AND METHODS

### 2.1 Study Area

Kaduna metropolis lies at latitude 10°28N and at longitude 7°25E. It is located in the central area of what used to be called the Northern Region of Nigeria. The mean annual rainfall in the area ranges from 924.3 to 1,543.6 mm. Annual temperature varies between 29 to 38.6°C. It occupies an area of approximately 48,473.20 square kilometres and has a population of more than six million and falls into Guinea Savannah climate, which has distinct rainy and dry seasons.

Sampling was from ten municipal waste dumpsites. The study sites are Kawo (KW), Rafin Guza (RG), Malali (ML), Angwan Dosa (AD), Badarawa (BD), Angwan Shanu (AS), Kurmum Mashi (KM), Tudun Wada (TW), Trikania (TK) and Kakuri (K+K) as shown in Fig. 1. These dumpsites have been in existence from two to twenty-two years. Sample was also collected exactly 10 meters away from Badarawa dumpsites which served as the control.

### 2.2 Sample Collection and Pre-treatment

Each location was divided into four quadrant and the soil samples collected from each quadrant with the aid of a clean stainless steel spoon at 10 cm below the top soil. The samples were placed in labeled polythene bags and were then taken to the laboratory for treatment. Sampling was from August 2011 to June 2012, spanning rainy and dry seasons. Samples were air dried in air circulating oven at 30ºC overnight, homogenized, ground with an agate mortar, passed through a 2.00 mm sieve and stored in polythene bags before analysis. All the samples were collected in triplicate.

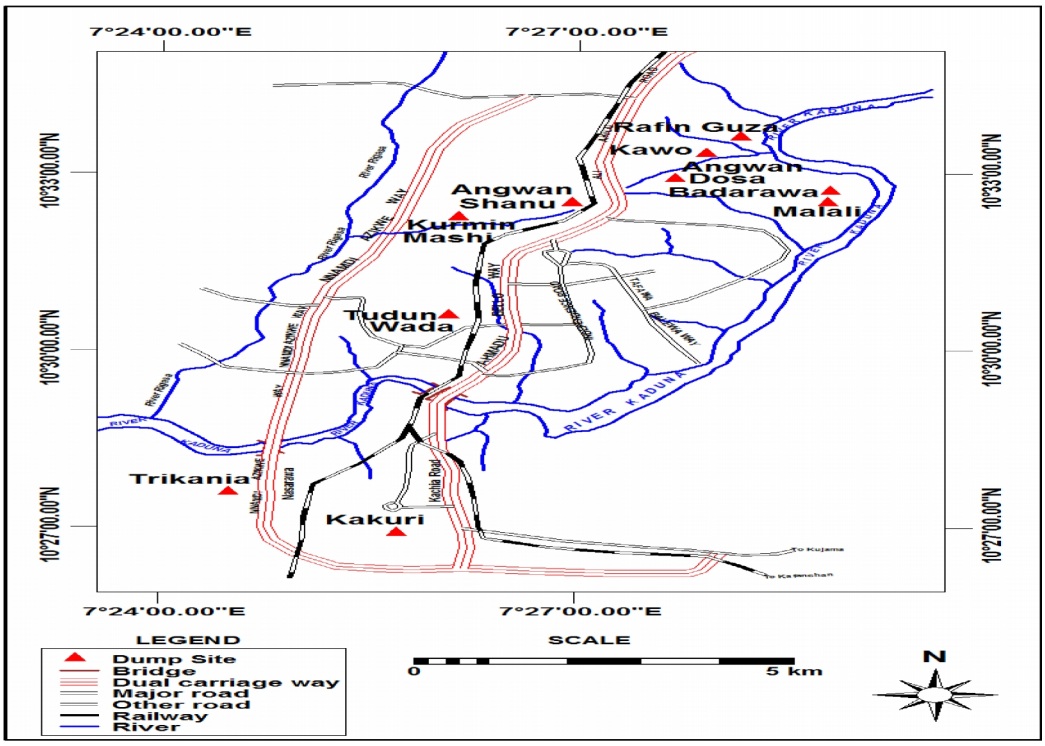



**Fig. 1. Sample collection sites located in Kaduna Metropolis, Nigeria**

## 2.3 Sequential Extraction of Metals

Sequential extraction of heavy metals was performed on the soil samples [25]. The method employed is a modification of the conventional method [26]. The modified method extracts heavy metals into six geochemical fractions as follows:

### 2.3.1 Fraction soluble in soil solution (F I)

Exactly 1.00 g air–dried soil sample was mixed with 10.00 ml of distilled/deionized water with continuous agitation using a mechanical shaker for 1 hour. This was then centrifuged and the supernatant decanted and made up to 50.00 ml with distilled/deionized water prior to analysis.

### 2.3.2 Exchangeable fraction (F II)

The residue from **F I** was leached at room temperature with 10.00 ml of 1.00 M $MgNO_3$ at pH 7.0 with continuous agitation for 1 hour, this was centrifuged and the supernatant decanted and made up to 50.00 ml with distilled/deionized water prior to analysis, $MgNO_3$ is known to displace ions electrostatically bound in the soil matrix.

### 2.3.3 Acid extractable carbonate bound fraction (F III)

Residue from F II was leached at room temperature with 10.00 ml of 1.00 M $CH_3COONa$ (at pH 5, adjusted with $CH_3COOH$) with continuous agitation for 5 hours and then centrifuged.

The supernatant was decanted and made to 50.00 ml with distilled/deionized water prior to analysis, $CH_3COONa$ solubilizes carbonates (calcite, dolomite) and releases entrapped metals.

#### 2.3.4 Reducible Fe–Mn oxides and hydroxide fraction (F IV)

Residue from F III was leached with 20.00 ml of 0.10 M solution of $NH_2OH.HCl$ (pH adjusted with 25% v/v $CH_3COOH$) at 96$^oC$ for 6 hours with occasional agitation and centrifugation. The supernatant was decanted and made up to 50.00 ml with distilled/deionized water prior to analysis; $NH_2OH.HCl$ reduces Fe and Mn oxides to soluble forms.

#### 2.3.5 Oxidizable organic matter bound fraction (F V)

To the residue from F IV, 3.00 ml of 0.02 M $HNO_3$ and 30% v/v $H_2O_2$ were added. The mixture was heated to 85$^oC$ in a water bath for 3 hours. After cooling, 5.00 ml of 1.00 M $CH_3COONa$ was then used to extract with occasional agitation for 3 hours at 85$^0C$. The mixture was centrifuged and the supernatant decanted and made up to 50.00 ml with distilled/deionized water prior to analysis. $HNO_3$ and $H_2O_2$ oxidize organic matter and solubilize sulphides. Oxidized organic matter releases complexed, adsorbed and chelated metals.

#### 2.3.6 Residual and inert fraction (F VI)

Residual from F V was digested with a mixture of 8.00 ml 5:1 mixture of HF and $HClO_4$ in acid digestion teflon cup. The mixture was dry ashed for 2 hours and evaporated to dryness. The residue was then diluted to 50.00 ml with distilled/deionized water prior to analysis.

After each successive extraction, the samples were centrifuged at 265.50 g. The supernatants were removed with pipette and filtered with Whatmann No 42 filter paper. The residue was washed with distilled/deionized water, hand shaken vigorously and centrifuged for 15 minutes before the next extraction. The volume of water for rinsing was left at a minimum to avoid excessive solubilization of solid materials. The process was carried out in triplicate for each sample.

### 2.4 Determination of Concentration of Metals in Fractions

Standard calibration curves were prepared by reading the absorbance of 0.20, 0.40, 0.60, 0.80, 1.00 and 1.20 $mgl^{-1}$ standard concentrations of Cu, Mn and Zn with a digital PG-990 atomic absorption spectrophotometer at 228.80 nm, 213.90 nm and 279.50 nm wavelengths respectively. The values obtained were used in plotting the standard calibration curves of Cu, Mn and Zn respectively from which the concentrations of Cu, Mn and Zn in every test sample was calculated. Analysis of variance (ANOVA) was used to test the significant differences in the means at $P$ = 0.05. The calculated F- value was compared with F-value from the standard F- value table based on the degree of freedom to determine whether or not the means are statistically different.

### 2.5 Determination of Mobility Factor

Mobility of metals in soil was assessed on the basis of absolute and relative content of fractions weakly bound to soil components. The relative index of metal mobility was

calculated as a mobility factor according to [27, 28] and on the basis of the following equation.

$$M = \frac{F\,(I) + F\,(II) + F\,(III)}{F\,(I) + F\,(II) + F\,(III) + F\,(IV) + F\,(V) + (VI)} x\ 100 \quad (1)$$

Where F (I) = water soluble fraction; F (II) = exchangeable fraction; F (III) = carbonate bound fraction; F (IV) = Fe - Mn Oxide fraction; F (V) = organic matter bound fraction and F (VI) = Residual fraction.

## 3. RESULTS AND DISCUSSION

### 3.1 Chemical Fractionation of Metals in Soil Samples

Assessment of the bioavailability of heavy metals in contaminated soils using sequential extraction is based on the assumption that metal bioavailability decreases with each successive extraction step in the procedure. Therefore, metals in water soluble and exchangeable fractions would be readily bioavailable to the environment, whereas the metals in the residual fraction are tightly bound and would not be expected to be released under natural conditions [29,30,31,32]. The sequential extraction procedure of [15] is one of the most thoroughly researched and widely used procedures which facilitate evaluation of the efficacy of decontamination treatments [33,34].

Sequential extraction procedure and investigation, measures the mobility and bioavailability of heavy metals in soil depending on how the metals are associated with the components of the soil. Sequence of extraction follows the order of decreasing solubility of geochemical forms of the metals [35]. Thus water soluble F (I) and exchangeable F (II) indicate the forms more mobile and bioavailable for plant uptake while the residual F (VI) indicate the forms least mobile and least bioavailable for plant uptake.

#### 3.1.1 Mobility factor

Mobility of metals in soil was assessed on the basis of absolute and relative content of fractions weakly bound to soil components. Generally, F (III) metal fractions were strongly bound to the soil components indicating less relatively mobile than the extracted water soluble F (I) and exchangeable F (II) fractions. The relative index of metal mobility was calculated as a mobility factor according to [27,28]. Mobility factor of Cu, Mn and Zn in samples showed variations especially across the sites. As presented in Tables 1 and 2 for rainy and dry seasons respectively.

*3.1.1.1 Copper (Cu)*

Previous study revealed that the organic matter content of this study area ranged from 20.30 to 36.30 gkg-1 with mean 29.28 ± 0.02 gkg-1 [23]. Cu was found high in the residual fractions though appreciable amount was present in the oxidizable organic matter bound fractions as shown in Figs. 2 and 3. These indicate the effectiveness of organic matter as a scavenger of Cu in soil. A number of studies on speciation of Cu have shown that it is mainly bound to the oxidizable phase, occurring as organic complexed metal species [36,37]. This is attributed to Cu having high affinity for humic substances which are a fraction of natural organic matter chemically active in complexing such metal [38]. Speciation trend of Cu in

deceasing order is thus given as: Residual > Organic matter bound > Fe - Mn Oxide > Exchangeable > Water soluble > Carbonate.

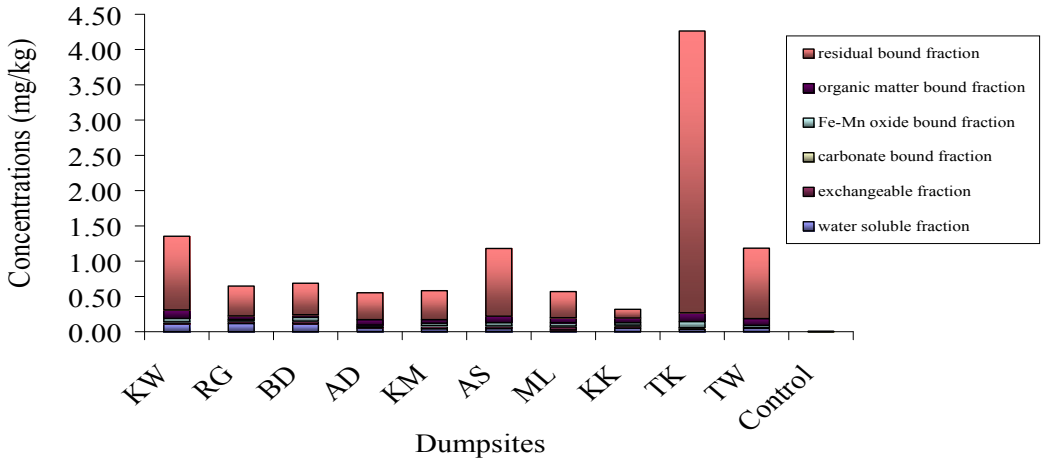



**Fig.2: Copper concentrations in soil fractions during rainy season**

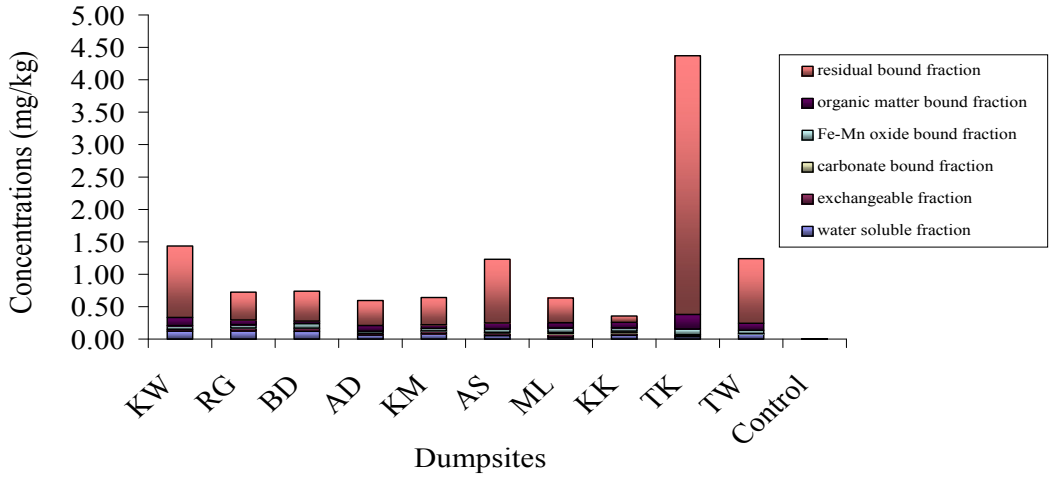



**Fig.3: Copper concentrations in soil fractions during dry season**

In the rainy season high mobility values were obtained at TK (43.76%), TW (13.51%), AS (13.48%), ML (0.14%), and BD (7.28%); while in the dry season high values were obtained at TK (44.79%), KW (14.65%), AS (14.18%), ML (13.43%), TW (13.32%) and KK (8.10%) as presented in Tables 1 and 2 respectively. This result indicates high Cu bioavailability and mobility, thus these dumpsites would be contaminated by Cu to a relatively large extent. Trend of mobility in the dumpsites during the rainy season is given as: TK > KW > TW > AS > ML > BD > RG > KK > KM > AD while dry season follows the order: TK > KW > AS > ML > TW > KK > BD > RG > KM > AD.

*3.1.1.2 Manganese (Mn)*

Mn partitioning was dominated by the residual fractions, Fe - Mn Oxide and organic matter bound fractions in the dumpsites and across the seasons as presented in Figs. 4 and 5. These results are comparable to those of [39] who reported that Cd, Fe, Mn, Ni and Pb are mostly associated with the residual fractions. These findings could be linked to the preferential incorporation of Mn into silicate lattice. Also, the high Mn level in the organic matter bound fractions may be connected to the ease of complexation and peptization between the metal and natural organic matter like humic and fulvic acids [40]. In addition, Mn contents being high in Fe - Mn Oxide fractions could be due to the high association or retention ability of the mineral crystal structure [25]. Speciation pattern of Mn in decreasing order is thus shown as: Residual > Fe – Mn Oxide > Organic matter bound > Exchangeable > Water soluble = Carbonate.

In the rainy season, relatively high mobility values were recorded such as KK (2.18%), AD (2.08%), BD (1.60%), ML (1.38%) and TW (1.67%) while in the dry season mobility values were high at ML (2.57%), BD (2.24%), KK (2.07%) and TW (1.51%) as shown in Tables 1 and 2 respectively. These values imply contamination of these dumpsites. Order of mobility in decreasing trend during rainy season is given as: KW > AS > KM > RG > TK > ML > BD > TW > AD > KK while dry season values are given as KW > AD > AS > KM > TK > RG TW > KK > BD > ML.

**Table 1. Metal mobility factor for soil samples during rainy season (%)**

| Sites | Copper | Manganese | Zinc |
|---|---|---|---|
| KW | 13.8200±0.0001 | 0.1570±0.0002 | 4.7500±0.0051 |
| RG | 6.8300±0.0005 | 0.5910±0.0003 | 1.5823±0.0021 |
| BD | 7.2800±0.0006 | 1.5960±0.0009 | 54.1400±0.0033 |
| AD | 5.7000±0.0025 | 2.0750±0.0061 | 0.0000 |
| KM | 6.2400±0.0033 | 0.4400±0.0041 | 18.0800±0.0005 |
| AS | 13.4800±0.0032 | 0.3540±0.0004 | 26.6280±0.0002 |
| ML | 0.1400±0.0021 | 1.3760±0.0003 | 5.8830±0.0003 |
| KK | 6.3170±0.0044 | 2.1800±0.0001 | 3.5400±0.0020 |
| TK | 43.7690±0.0001 | 1.2000±0.0022 | 16.1112±0.0050 |
| TW | 13.5170±0.0007 | 1.6700±0.0024 | 2.8760±0.0032 |
| Control | 10.0500±0.0001 | 30.7690±0.0004 | 0.0000 |

**Table 2. Metal mobility factor for dumpsite soils in dry season (%)**

| Sites | Copper | Manganese | Zinc |
|---|---|---|---|
| KW | 14.6500±0.0021 | 0.1990±0.0001 | 4.9100±0.0008 |
| RG | 7.7100±0.0001 | 0.5980±0.0077 | 145.7900±0.0006 |
| BD | 7.8700±0.0001 | 2.2380±0.0004 | 44.5980±0.0042 |
| AD | 6.2200±0.0002 | 0.3310±0.0003 | 0.00000 |
| KM | 7.0970±0.0005 | 0.4900±0.0046 | 21.6500±0.0021 |
| AS | 14.1810±0.0041 | 0.3790±0.0002 | 31.0840±0.0003 |
| ML | 13.4320±0.0011 | 2.5720±0.0001 | 7.6760±0.0001 |
| KK | 8.0980±0.0021 | 2.0670±0.0041 | 5.0700±0.0002 |
| TK | 44.7920±0.0022 | 0.5790±0.0002 | 18.1900±0.0003 |
| TW | 13.3170±0.0005 | 1.5110±0.0003 | 3.7330±0.0041 |
| Control | 0.0700±0.0001 | 0.5890±0.0001 | 90.3300±0.0061 |

*3.1.1.3 Zinc (Zn)*

Zn was uniformly bound to the residual fractions and the non residual fractions as depicted in Fig. 6 and 7 indicating that these fractions are of major importance as Zn carriers in soil which is in agreement with previous findings by [41]. Among the non residual fractions, Fe - Mn Oxide fractions contained the highest Zn content which may be due to the high stability constants of Zn oxides formed [42,43]. However water soluble and exchangeable fractions also contain appreciable amounts of Zn in most of the dumpsites. Decreasing order of Zn contents in the geochemical fractions is shown as: Residual > Fe - Mn Oxide > Organic matter bound > Water soluble > Exchangeable > Carbonate.

Zn has the highest mobility values of all the metals studied as seen in Tables 1 and 2, this is due to non residual fractions accumulating reasonably high amount of Zn in most of the dumpsites. The rainy season recorded high mobility values at BD (54.14%), AS (26.63%), KM (18.08%), TK (16.11%), ML (5.89%) and KK (3.54%). During the dry season however higher mobility values were obtained at dumpsites such as RG (145.79%), BD (44.60), AS (31.08%), KM (21.65%) and TK (18.19). This indicate that the risk of Zn being released and bioavailable is comparatively high, suggesting Zn is of major significance with respect to ecotoxicity during both rainy and dry seasons in these dumpsite. The mobility of Zn in decreasing order during the rainy season is given as: RG > BD > AS > KM > TK > ML > KW > KK > TW > AD while dry season trend is given as: RG > BD > AS > KM > TK > ML > KK > KW > TW > AD.

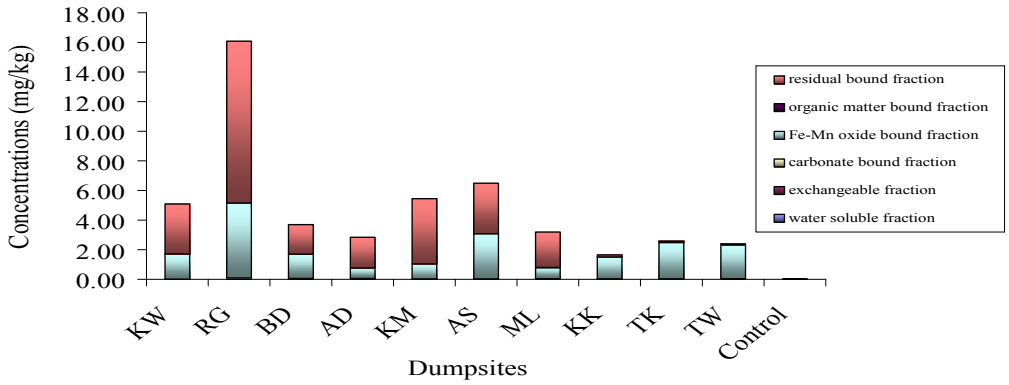



**Fig.4: Manganese concentrations in soil fractions during rainy season**

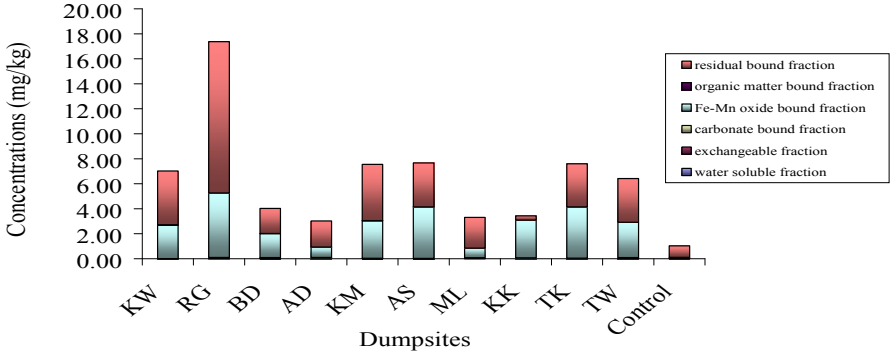



**Fig.5: Manganese concentrations in soil fractions during dry season**

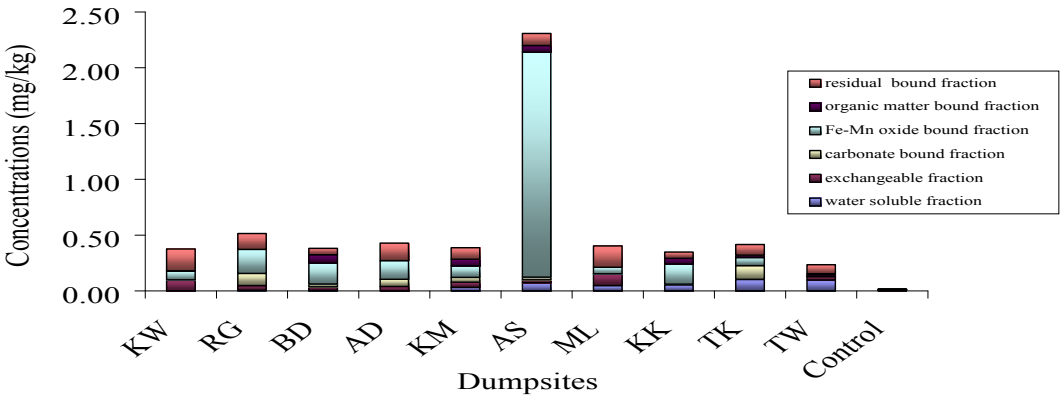



**Fig.6: Zinc concentrations in soil fractions during rainy season**

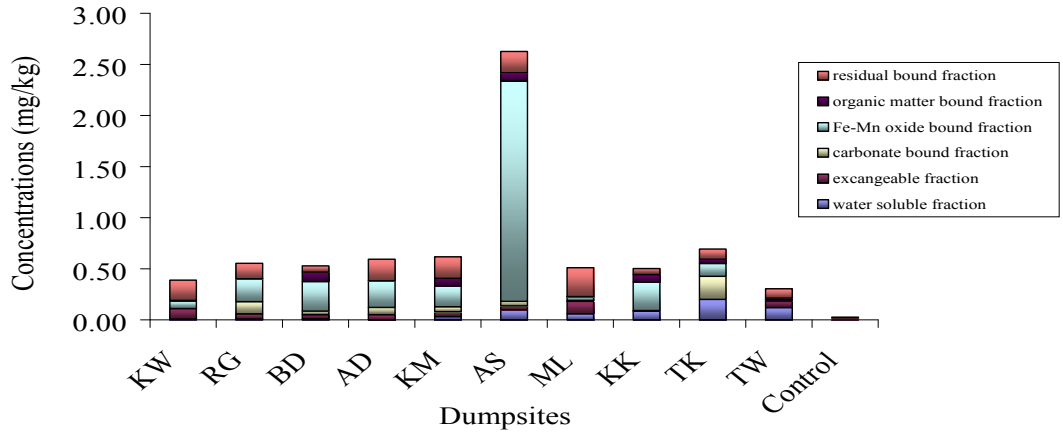



**Fig.7: Zinc concentrations in soil fractions during dry season**

## 4. CONCLUSION

Generally, mobility factor for all the metals varied significantly among the metals, dumpsites and across the seasons with the dry season values being significantly higher than rainy season values in most of the dumpsites studied. Cu and Zn were distributed almost evenly across the non-residual and residual fractions and also recorded high mobility factors in both rainy and dry seasons thus these metals would be potentially bioavailable for plant uptake and easily mobilized in soil solution. In contrast, Mn was predominantly retained by residual fractions in most of the dumpsites studied although appreciably present in the Fe - Mn oxide bound fractions. Mobility values were relatively high in most of the dumpsites indicating Mn would be potentially bioavailable for plant uptake though not as high as that for Cu and Zn. Based on the results obtained, consumption of plants grown on these dumpsites should be discouraged in order to avoid the risk of ingestion of the heavy metals studied.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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