

Seasonal Chemical Fractionation of Metals in Some Dumpsites Soils in Zaria Metropolis, Nigeria

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Abstract

The study was aimed at investigating the chemical fractionation, bioaccumulation and bioavailability of Hg, Cd, Cu, Pb and Zn in the refuse waste soils of some dumpsites across the seasons (wet and dry) in Zaria metropolis. The heavy metals in the waste soils were sequentially extracted and measured using atomic absorption spectrophotometry. The results revealed that high concentrations of metal in dry season. The non-residual fraction was found to be the most abundant pools for all the metals across the seasons (wet and dry). Also, significant amounts of Hg, Cd and Cu were mostly found in the bioavailable fractions across the sites in the seasons. Thus, these metals would readily be bioavailable to the environment. Overall, the order of mobility and bioavailability of these metals across the seasons (dry and wet) followed the pattern; Hg > Cd > Pb > Zn > Cu and Hg > Cd > Cu > Zn > Pb respectively. Tendencies of health risk for human and livestock due to the spread of the metal pollution from waste dumpsites to agricultural areas is high. Bioaccumulation of cadmium and mercury cause liver, brain and intestinal disorders, irreversible damage to nervous system and brain, protoplasmic poisoning etc.

Keywords: Metals, Bioavailability, Dumpsites, Human Toxicity, Soil.

1. Introduction

The disposal of heavy metals is a consequence of several activities like chemical manufacturing, painting and coating, etc. (Awokunmi *et al.*, 2010), pollution by these metals cause serious problems to human health and life in general. The introduction of industrial and municipal solid wastes into our environment has been identified as the principal sources of soil contamination by metals (Kebir and Bouhadjera, 2011). Inadequate treatment of these wastes and subsequent use as organic manure may result in high metal concentrations in soils which are mobilized into the flora and fauna and subsequently into man with deleterious health effects (Adefemi and Awokunmi, 2009; Abdallah *et al.*, 2012).

According to FEPA (1995), solid wastes are useless, unwanted and discarded materials that arise from man's activities and cannot be discarded through sewer pipe. The non-glowing or sticky nature of solid waste gives rise to the accumulation of solid waste on some habitable parts of the earth surface. Places with accumulated solid wastes are called refuse dumps but a designated place for dumping of refuse is known as dumpsite (Awokunmi *et al.*, 2010). Although solid waste is an asset when properly managed, its volume has continued to increase tremendously in recent times in Nigeria, as a result of socio-economic development. In Nigeria, much has been and is being invested on municipal solid waste management in cities but little progress has been made because of several financial, technological and institutional constraints within the public and private sectors apart from erratic growth of housing units in the inner core of urban cities (Ojeshina, 1999; Adefemi and Awokunmi, 2009).

Zaria metropolis is located at latitude 11°3'N and longitude 07°40' and is presently one of the most important cities in northern Nigeria. It faces problems of environmental sanitation such as improper disposal of refuse near residential areas due to poor refuse collection and handling. Also, it is a common practice to find huge refuse dumpsites within the residential areas and along some minor and major roads (Uba *et al.*, 2008).

As many studies have shown, municipal refuse may increase heavy metals concentrations in soil and water (Carlson, 1976; Albores *et al.*, 2000; Uba *et al.*, 2008) which may have effects on the host soils, crops and human health (Smith *et al.*, 1996; Nyle and Ray, 1999). Thus, the environmental impacts of municipal refuse are greatly influenced by their heavy metal contents. However, while total metal contents is a critical measure in assessing risk of refuse dumpsites, total heavy metal contents alone does not provide predictive insights on the bioavailability, mobility and fate of the heavy metal contaminants (Albores *et al.*, 2000; Uba *et al.*, 2009). Thus, is the chemical form or species of the heavy metals that is an important factor in assessing their impacts on the

Past investigations on the heavy metals impacts due the solid waste disposal in Nigeria were mostly concerned with the total heavy metal determinations (Bamgbose *et al.*, 2000; Okoronkwo *et al.*, 2006) and few data on the chemical fractionation of these metals in the dumpsite soils (Uba *et al.*, 2008). There has been no report on the seasonal variation of metals fractions in soils. Hence, the present study is therefore aimed to investigate the seasonal chemical fractionation of Cd, Cu, Pb, Hg and Zn of some refuse dumpsites in Zaria metropolis with a view to determine their mobility, bioavailability and fate in order to assess the human health and ecological risks associated with the refuse dumpsites.

2. Materials and Methods

2.1 Dumpsite Description

Soils from ten dumpsites were collected in the four major settlements in Zaria metropolis. These dumpsites were Samaru (S), Railway station (R), Babban Gwari (B), Shafi road (SH), Dandaji (D), Jeka da uwarinka (GK), NTC (NT), Kusfa (K), Prince road (P), Alkali gae (A) and Control (CTR). Fig. 1 below show ruminant animal feeding on some of waste at one of the dumpsite map.



Figure 1: One of the Dumpsite at Babban gwani, Zaria city

2.2 Refuse Characterization

To ascertain the percentage composition of the waste types known weight (1kg) of the refuse samples were sorted and weighed which revealed the presence of the following; plastics, bones, papers, polythene bags, textiles, waste leaves, wood, metal scraps, rubber tubes and charcoal in various compositions.

2.3 Refuse Waste Soil Collection

Refuse waste soils were collected from ten dumpsites (as in section 2.1) in Zaria metropolis across the seasons (both hot and wet seasons) in 2012, composite samples were made in the laboratory for each season and for each

2.4 Quality Assurance

All reagents used were of analytical grades. Double distilled de-ionized water was used. Glasswares and polythene sample bottles were washed with liquid soap, rinsed with water and soaked in 10% HNO₃ for 24 hours. Then cleaned thoroughly with double distilled de-ionized water and dried. The analytical results obtained were validated with the spiked samples. The analytical precision was confirmed by the triplicates digestion throughout the study.

2.5 Sequential Extraction of Metals in Waste Soils

The extraction was carried out with an initial mass of 1.0g dried soil in polypropylene centrifuged tube of 50ml capacity. The modified method of Tessier (1979) according to Finzgar *et al.* (2007) which fractionates the soil into six geochemical fractions was used. Mg(NO₃)₂ was used instead of MgCl₂ to avoid an increase in the solubility of heavy metals within the soil solution matrix. The extraction was carried out on three sub-samples in each step as follows:

- i. **Water Soluble Fractions:** 1g of the air dried soil sample (2mm sieve) were mixed with 10ml of de-ionized water with continuous agitation for 1 hour, centrifuged and the supernatant decanted and made up to 50ml with de-ionized water prior to analysis.
- ii. **Exchangeable Phase:** The residue in (i) above is shaken at room temperature with 16ml of 1M Mg(NO₃)₂ at pH 7.0 for 1 hour, centrifuged and supernatant decanted and made up to 50ml with double distilled de-ionized water.
- iii. **Oxidized Phase (bound to organic matter):** Residue from (ii) above +10ml of 8.8M H₂O₂ + 6ml of 0.02M HNO₃ was shaken for 5 + 1 hrs at 98°C. 10ml of 3.5M CH₃COONH₄ was added as an extracting agent, the resulting mixture was then centrifuged and supernatant made up to 50ml with distilled water prior to analysis.
- iv. **Acid Soluble Base (bound to carbonates):** 25ml of 0.05M Na₂EDTA was added to the residue in (iii) above and shaken for 6 hrs and centrifuged. The supernatant was decanted and made up to 50ml with distilled water prior to analysis.
- v. **Reducible Phase (bound to Fe–Mn oxides):** Residue from (iv) above + 17.5mlNH₂ON.HClO.1M + 17.5ml CH₃COONH₄3.5M, shaken for 1 hr, centrifuged, the supernatant decanted and made up to 50ml with distilled water prior to analysis.
- vi. **Residential Phase (bound to silicates and deferential materials):** Residue from (v) above was digested by using HCl – HNO₃/HF (0.35:12 w/v solid solution) in acid digestion, Teflon cup. It was then dry ashed for 2 hrs and evaporated, filtered and diluted to 50ml with double-distilled de-ionized water.

After each successive extraction, the sample was centrifuged at 3000rpm for 15 minutes. The supernatants was then removed with pipette and filtered with Whatman No. 42 filter paper. The residue in each case was washed with de-ionized water followed by vigorous handshaking and then 15 minutes centrifugation before the extraction.

3 Results and Discussion

3.1 Quality Assurance

The recovery of the added metal ions for both total metal and sequential extraction methodology as shown in Table 1 by spiking experiment were found to be 90.07 – 98.10 and 92.63 – 100.75% respectively. All these ranges are within the acceptable range. This difference is attributed to the difference in the leaching time, reagents and the total volume of extractions (Ciba *et al.*, 1999). Similar ranges have already been reported in literature for sequential extraction (Albores *et al.*, 2000).

Table 1: Percentage recovery of the sequential extraction compared with the aqua-regia digestion

Metals	Sequential Extraction (%)	Total metal (%)
Pb	92.63	90.07
Cu	100.10	85.02
Cd	100.05	97.85
Zn	100.75	98.10
Hg	99.50	95.00

3.2 Sequential Extraction

The sequential extraction scheme is useful in accessing the mobility and bioavailability of heavy metals in the waste soils. Figures 2 - 11 showed percentages of the bioavailable, residual and the non-residual fractions across the sites for all the metal. The extractable fractions of zinc across the season are presented in Figures 2 and 3.

Zinc

The total extractable zinc in most of the dumpsites across the seasons as shown in Figs. 2 and 3 were above the USEPA (2000) permissible limits of 300mg/kg with few exceptions. During the wet season, the total extractable fractions ranged from 251.437 (D) to 1135.270 mg/kg (S) while the total concentrations across the sites ranged from 81.117 to 771.15 (B) mg/kg in the dry season. The results indicate the range of the percentage of the residual fractions during the wet season was between 4(NTC) – 43.56% (DD), the control site (CTR), had the least percentage of zinc in the residual fraction, However, the non-residual fraction ranged from 56.44 (CTR) – 95.882% (NTC) which showed that the metal will be readily released into the environment. It's interested to note that during the wet season, the highest concentration of 1,135.27mg/kg was obtained but only 35.61% of this fraction was readily available to the environment (bioavailable) while 86.62% was found in the residual fraction and still 51.01% of the residual fraction was acid soluble fraction which is unavailable to the environment. The potential mobility and bioavailability of this metal in the refuse waste soils during the wet season followed the pattern: NTC > K > S > A > D > B > J > P > R > SH > CTR.

Conversely, the percentage of the bioavailability fraction at the dry season ranged from 8.190 (NTC) to 79.075% (BG). The lowest and the highest concentrations obtained at NTC and BG dumpsites respectively. The potential mobility and bioavailability of this metal at dry season is: B > CTR > A > P > K > D = S > R > SH > JK > NTC.

Moreover, the percentage of the residual fraction in this season ranged from 5.297 (B) to 48.503% (P) indicating that this metal is readily bioavailable to the environment across the sites with a few exception this study compared well with the fractionating pattern recorded in the wet season. Overall, the order of availability of this metal is both dry and wet seasons were: Acid soluble > residual > oxidisable > reducible > water soluble > exchangeable and Residual > acid soluble > reducible > water soluble > exchangeable > oxidisable respectively.

Among the residual fractions, sites A, B, J, SH, R and P had the highest amount of Zn in the reducible fractions. This may be partly attributed to the high stability constraints of zinc oxides. Several other workers have also founds zinc to be associated with reducible fractions (Kuo *et al.*, 1983, Ramos *et al.*, 1994 and Uba *et al.*, 2008). There was significant difference in the concentrations of Zn across the sites at $P < 0.05$ except fraction III which is not significantly different at $p < 0.05$.

Lead

The bioavailable, residual and the non residual fractions of the lead across the sites and seasons (wet and dry) are presented in Figures 4 to 5. 20% of the total extractable fractions contributes to the mobile phase in most of the study areas (B, D, SH, R, P & NTC) while more than 49% of the total extractable fraction were found in the non-residual fraction with the exception of site CTR which as >91% in the residual fraction. Overall, the potential bioavailability of this metal in the different fractions followed the pattern: Residual > reducible > oxidisable > acid soluble > water soluble > exchangeable. Similarly, the order of the mobility and bioavailability of this metal in the refuse waste soils revealed the following pattern: BG > SH > NTC > R > D > P > JK > A > K > CTR.

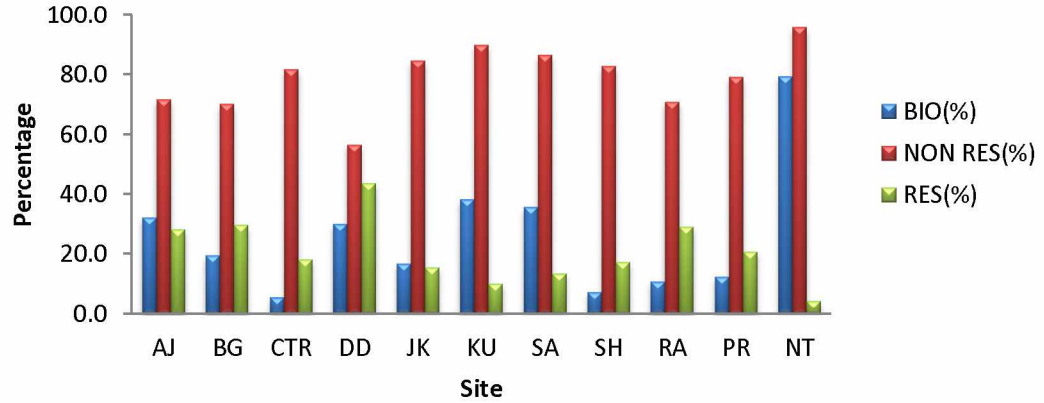


Figure 2 : Bioavailable, residual and non-residual Zinc in the wet season dumpsites soils

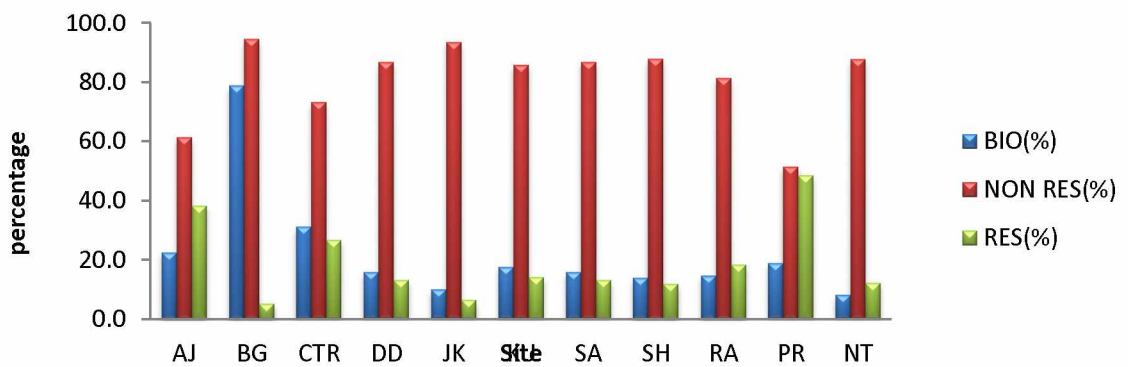


Figure 3: Bioavailable, residual and non-residual Zinc in the Dry season dumpsites soils

The total concentrations obtained across the sites were within the tolerable limits of 30 – 300mgkg⁻¹ (USEPA, 1986). Based on the mobile fractions, sites B, D, SH, R, P and NTC were at risk of lead contamination with time due to accumulative effects. Similar concentration range was reported by Kabata-pendias and Pendias (1984).

Furthermore, the total concentrations range recorded lead in the dry season was 23.706 (B) to 133.255mg/kg (R). The highest concentration was recorded at site R and the lowest was observed at site B. The range of the bioavailable fractions across the sites ranged from 9.726 (R) to 39.649% (CTR) most of the fractions were dominant in the non-residual fraction (>60%). However, the residual fractions constitute 8.70(B) to 34.085% (SH). Overall, sites A, B, CTR, D, K, S, SH and P were at risk of metal contamination based on the concentrations of bioavailable fractions in these sites, the order of mobility and the bioavailability of this metal across the sites in this season is:

CTR > B > SH > A > K > P > S = D > JK > NTC > R.

Moreover, availability of the metal among the fractions followed the trend; Acid soluble > residual > reducible > exchangeable > oxidisable > water soluble. On comparing the concentration of this metal among the fractions across the site there was no significance difference between the metal across the sites at P < 0.05.

Copper

The concentrations of copper in the waste soils of the ten dumpsites and a control site across the season (wet and dry) is shown in Figures 6 and 7. The total extractable fractions in all the analyzed samples across the seasons ranged from 1.642(SH) to 80.993(JK) mgkg⁻¹ and 1.940(B) to 1553.046mgkg⁻¹(R) for the wet and dry seasons respectively.

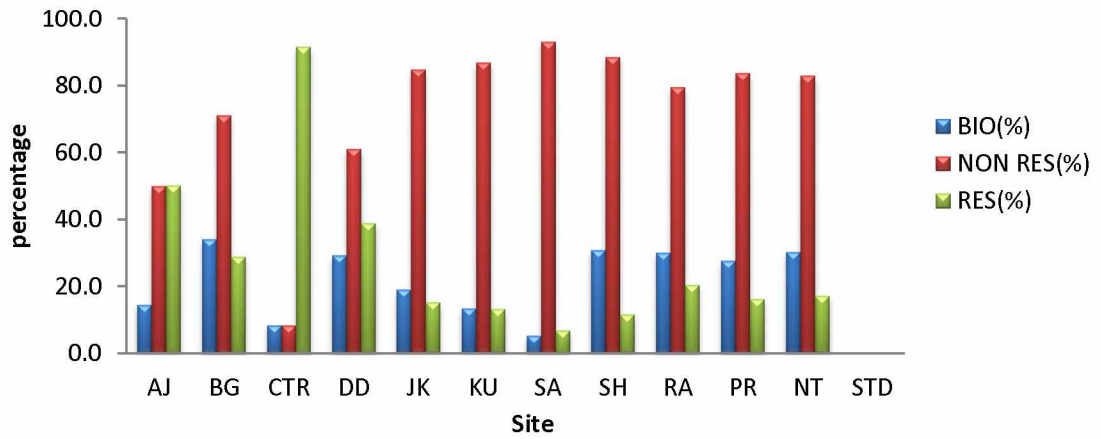


Figure 4: Bioavailable, residual and non-residual Lead in the wet season dumpsites soils

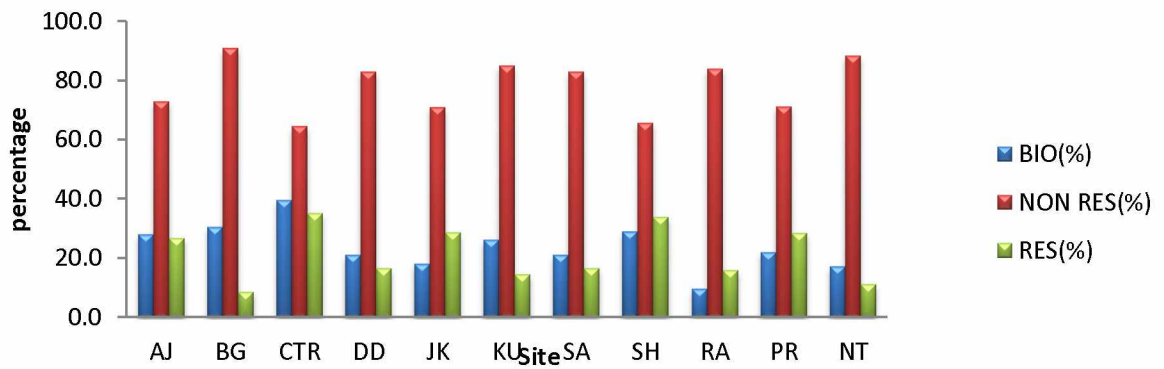


Figure 5: Bioavailable, residual and non-residual Lead in the Dry season dumpsites soils

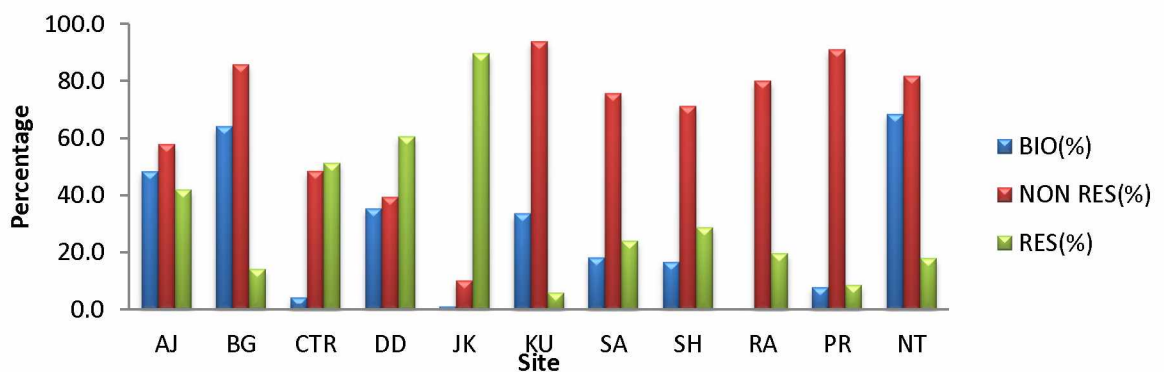


Figure 6: Bioavailable, residual and non-residual Copper in the wet season dumpsites soils

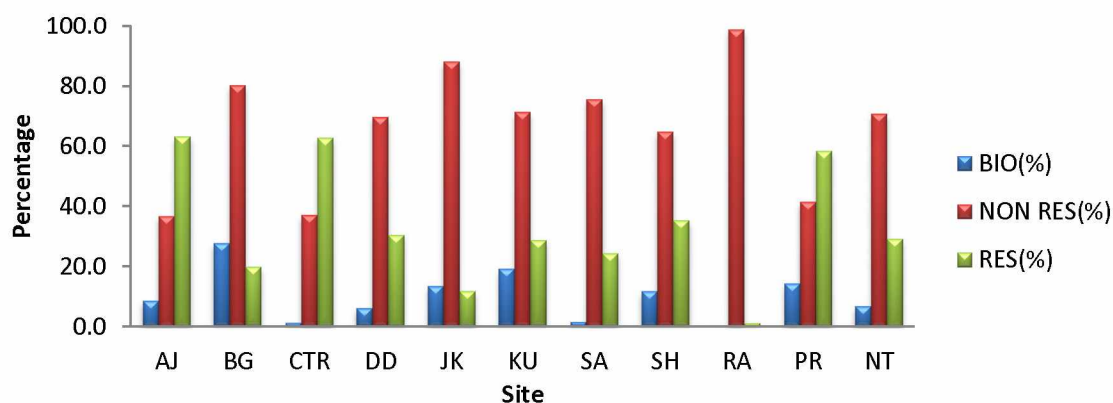


Figure 7: Bioavailable, residual and non-residual Copper in the dry season dumpsites soils

The levels of copper in all the analyzed samples were below the toxic limit of 250mgkg^{-1} (USEPA, 1986) except site R which is far above this limit. The mobile fraction across the sites for the wet and hot seasons ranged from BDL (CTR) to 65.741% (D) and 28.139(SH) to 56.738% (A) respectively. Sites A, B, D, K and NTC have reasonable percentage of the total extractable fractions in the mobile phase (>30%) indicating that these metals are readily bioavailable to the environment. The range of the extractable fractions in the non-residual and residual phase across the sites were; 75.833 (CTR) – 85.350% (P) and 13.42 (SH) – 24.167% (D) for the wet season respectively. The potential mobility and bioavailability of this metal in the waste soils of the dumpsites were found to be in the order; NTC > B > A > D > K > SH > P > CTR > JK > R

Furthermore, the bioavailability trend of this metal among the fractions was: Residual > oxidisable > acid soluble > reducible > water soluble > exchangeable. The percentage range of the non-residual and residual fractions for the dry season across the sites ranged from 37.179 (CTR) – 98.831% (R) and 1.169 (R) – 63.265% (A) respectively. The potential mobility and bioavailability of the metal across the sites in this season ranged; B > K > P > JK > SH > A > NTC > D > S > CTR > R.

The bioavailability pattern of this metal among the fractions is; residual > acid soluble > reducible > oxidisable > water soluble > exchangeable. This metal was found to concentrate more in the last four fractions in all the dumpsites waste soils across the sites which are consistent with the findings of Gupta and Chen (1975), and Hickey and Kittrick (1984) and Uba *et al.*, (2008). However, among the four fractions acid soluble contain the highest fraction especially at sites D, JK, K, S, SH, R, and NTC dumpsites. Significant percentage of the total extractable fractions were present in the residual fraction at site A, P and CTR indicating that the metal may not be readily bioavailable to the environment at these sites. This is not unconnected with the high formation constant of the organic copper complexes (Stumm and Morgan, 1981, Uba *et al.*, 2008).

Cadmium

Figures 8 and 9 showed the percentages of the residual, non-residual and bioavailable metals across the seasons (wet and dry). The average ranges for the metal across the seasons (wet and dry) were 1.629 (SH) – 4.602mgkg^{-1} (S) and 1.741 (B) – 5.845mgkg^{-1} (R) respectively. The highest and lowest concentrations were observed at sites S and SH for the wet seasons while sites B and R had the lowest and highest concentrations in the dry seasons. However, it is not the total metal contents that determine the potential bioavailability of the metal but its presence in the mobile phase. Considering the percentage of the bioavailable and mobile phase of this metal in the wet season, the range is BDL (CTR) – 65.741% (D) indicating that site D had 65.741% of the extractable fraction in the mobile phase. S dumpsites although had the highest concentrations of the total extractable fraction across the sites had only 41.62% of the mobile phase which is not as bioavailable as site D. The non-residual and residual fractions ranged from 73.148 (D) – 89.344% (A) and 10.65 (A) – 23.485 (%) (NTC) respectively. The trend of the mobility and bioavailability of this metal across the sites is D > SH > JK > K > NTC > A > S > P > B > R > CTR.

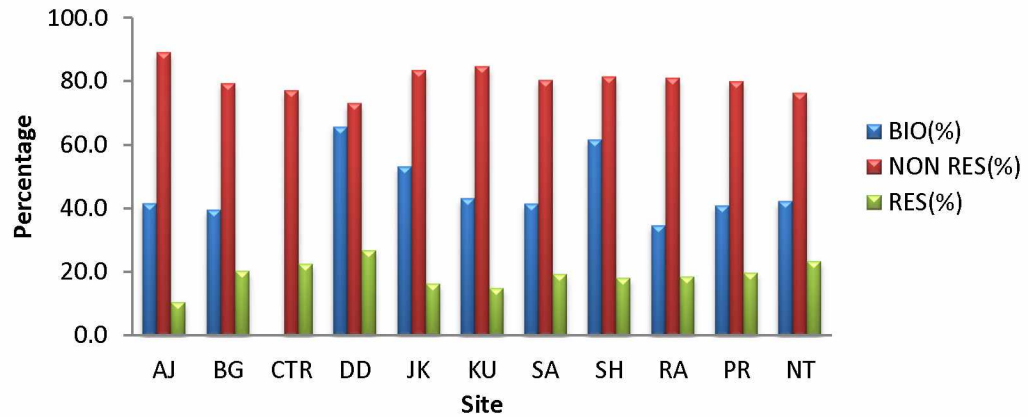


Figure 8: Bioavailable, residual and non-residual Cadmium in the wet season dumpsites soils

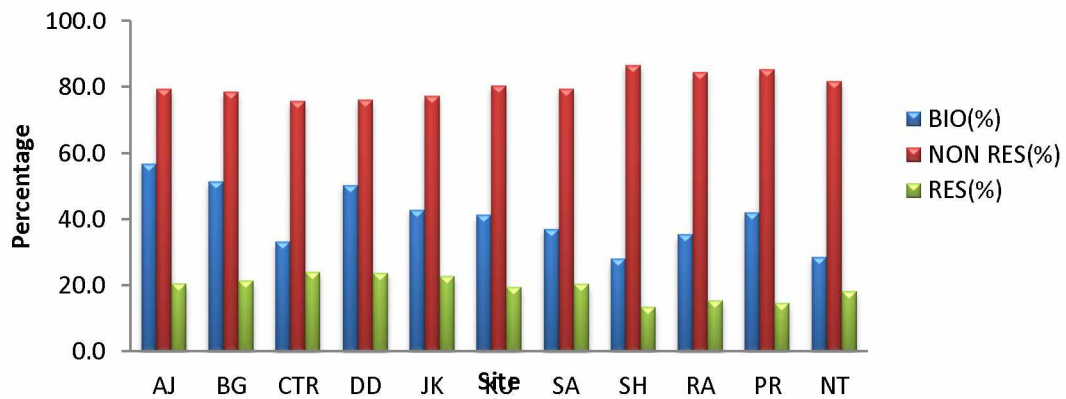


Figure 9: Bioavailable, residual and non-residual Cadmium in the Dry season dumpsites soils

Similarly, the bioavailability of the metal among the fractions followed the pattern: acid soluble > oxidisable > residual > reducible > exchangeable > water soluble. The bioavailable fractions in the wet season contribute >39% of the total extractable cadmium with the exception of CTR this showed that the metal is readily bioavailable to the environment.

Furthermore, the range of the bioavailable fraction in the dry season is from 28.139 (SH) to 56.738% (AJ) and the residual and the non-residual fractions were found to be; 13.42 (SH) to 24.167 (%) (CTR) and that most of the extractable fractions were concentrated in the non-residual fractions and > 28% of the non-residual fractions were found in the mobile phase. The potential mobility and bioavailability of this metal across the sites in the dry season is followed the trend: A > B > D > JK > P > K > S > R > CTR > NTC > SH. This indicates that the extractable fractions of cadmium across the sites are more bioavailable at site A and less bioavailable at site SH for the dry season. The availability of this metal among the fraction is; Residual > acid soluble > exchangeable > water soluble > reducible > oxidisable

The presence of the appreciable percentages of the total extractable fraction in the mobile phase suggests that Cd in these soils was potentially more bioavailable for plant uptake (Xian, 1989, Uba *et al.*, 2008). The result obtained in this study was in agreement with the observations of Harrison (1981), Miller and Mcfee (1983), Kuo *et al.* (1983) who reported similar Cd concentrations levels in waste soils of dumpsites. There was significant difference of the cadmium concentration among the fraction at $P < 0.05$ except at fraction IV and V which were significantly not different at $p < 0.05$ across the seasons.

Mercury

Figures 10 and 11 showed the percentages of the bioavailable, residual and the non residual fractions of the mercury across the seasons (wet and dry). The levels of mercury in both seasons and among the fractions were above the critical concentration of 0.13mg/kg^{-1} . The total extractable fraction of mercury in the wet season ranged from 232.183 (JK) – 792.592 (B). The highest and the lowest concentrations were recorded at sites B and JK respectively. The concentrations of this metal across the sites exceed the tolerable limit of 0.13mg/kg . The percentage range of the bioavailable fraction across the sites was 24.068 (SH) – 76.848% (B), this suggests the bioavailability of the metal to the immediate environment by leaching activities in the wet season. The highest percentage of the bioavailable fraction was recorded at site B while SH dumpsite had the least bioavailable fraction indicating the dominance of the extracted fractions in the residual fraction.

The residual and non-residual fractions of the metal across the sites ranged from 4.058 (B) – 20.317% (S) and 79.683 (S) – 95.942% (CTR). Overall, the percentage of the bioavailable fraction across the sites was $>24.068\%$. The potential mobility and bioavailability of this metal follows the pattern: $B > JK > S > A > CTR > D > P > K > R > NTC > SH$. Similarly, the availability of this metal among the fractions across the sites followed the pattern; oxidisable $>$ exchangeable $>$ water soluble $>$ acid soluble $>$ reducible $>$ residual, the highest concentrations of this metal have been obtained in the non-residual fraction. Among the non-residual fractions, the bioavailable fraction constitute more than 43% with the exception of the SH site constituting only 24% of the bioavailable fraction which is less bioavailable compared to the other sites.

Furthermore, the range of the total extractable fraction across the sites is 203.701 (B) – 1949.155 (CTR) mg/kg, sites B and CTR had the highest and the lowest concentrations respectively. The concentration of this toxic metal is far above the permissible concentration of 0.013mg/kg (WHO). The non-residual fraction constitutes 80.523% (B) – 96.516% (A) and the residual fraction had 3.484 (A) – 19.477% (B) respectively. The non-residual fractions showed the highest percentage of the extracted metals and constitute 17.351 (A) – 80.523% (B) of the bioavailable metals across the sites. The non-residual fraction was the most abundant pool for all the metals studied. A significant amount of Hg, Cd, Cu were associated with the bioavailable phase (mobile phase), this indicates that these metals will be potentially more bioavailable to the environment.

The potential mobility and bioavailability of this metal in the dry season was found to be; $B > S > R > K > JK > D > P > CTR > NTC > SH > A$. The highest bioavailable fraction was obtained at site B and the least bioavailable fraction was noted at site A. the availability of the metal among the fraction follows the pattern; oxidisable $>$ acid soluble $>$ water soluble $>$ exchangeable $>$ reducible $>$ residual. More than 49% of the metal is bioavailable to the environment with the exception of site A which has the least fraction of the extractable fraction in the mobile phase. The t-test for comparing the mean at $P < 0.05$ showed that there is no significant difference between the fractions. The metal was positively correlated across the seasons.

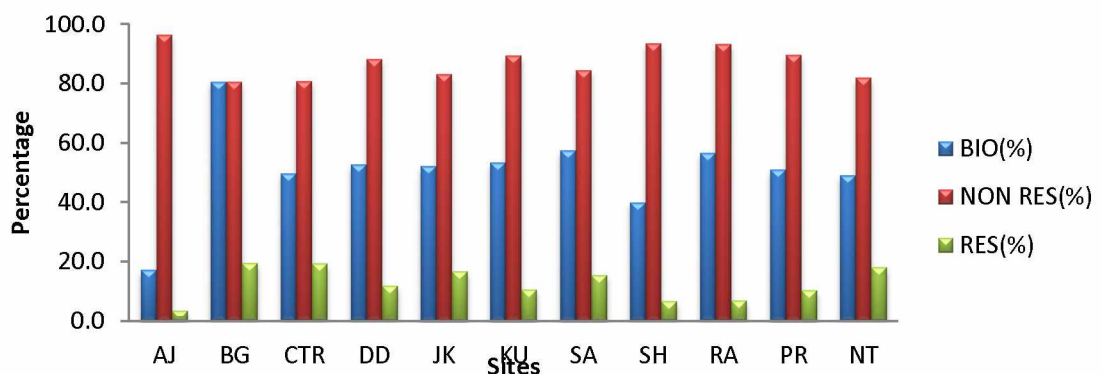


Figure 10: Bioavailable, residual and non-residual Mercury in the wet season dumpsites soils

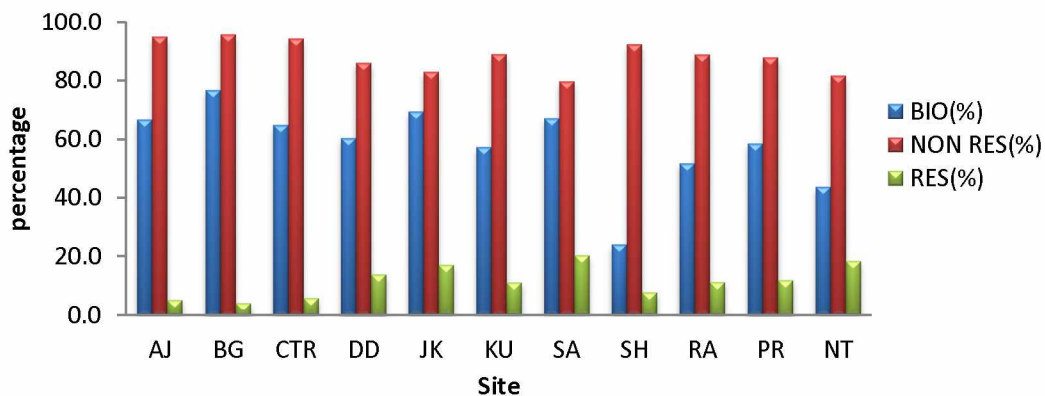


Figure 11: Bioavailable, residual and non-residual Mercury in the Dry season dumpsites soils

Conclusion

The present study indicates that the overall concentration of metals was high at dumpsites soils compared to the concentrations recorded in the wet seasons. A sequential extraction was used to fractionate Zn, Cu, Pb, Cd and Hg present in the refuse waste soils of the ten dumpsites in Zaria metropolis, northern Nigeria and a control site located 300m away from the dumpsites.

Dry

Hg: Oxidisable > acid soluble > water soluble > exchangeable > reducible > residual
 Cd: Acid soluble > oxidisable > residual > reducible > exchangeable > water soluble
 Cu: Residual > acid soluble > reducible > oxidisable > water soluble > exchangeable
 Zn: Residual > acid soluble > reducible > water soluble > exchangeable > oxidisable

Wet

Hg: Oxidisable > exchangeable > water soluble > acid soluble > reducible > residual
 Cd: Acid soluble > exchangeable > water soluble > reducible > oxidisable
 Cu: Residual > oxidisable > acid soluble > reducible > water soluble > exchangeable
 Pb: Residual > reducible > acid soluble > water soluble > exchangeable
 Zn: Acid soluble > residual > oxidisable > reducible > water soluble > exchangeable

Overall, the order of mobility and bioavailability of the studied metals in both the wet and dry seasons followed the patterns; Hg > Cd > Zn > Pb and Hg > Cd > Pb > Zn > Cu respectively. The fractionation scheme presented may be used to examine the bioavailability of metals in dumpsite waste soils across the seasons (wet and dry). The distribution patterns of metals among the fractions were found to be different for all the metals across the season. Furthermore, it was observed from the sequential extraction data, as the total extractable metal contents increases, the percentage of fractions also increases in soils. The sequential extraction indicates the extractability of these metals relative to each other. It was also observed, the total metal contents of the waste soil in the dry season were higher than the concentrations recorded in the wet season this is due to the leachability of these metals in the wet season.

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REFERENCES

- Abdallah, S. A., Uzairu, A., Kagbu, J. A. and Okunola O. J. (2012). Assessment of heavy metals bioaccumulation by *Eleusine indica* from refuse dumpsites in Kaduna Metropolis, Nigeria. *Journal of Environmental Chemistry and Ecotoxicology*, **4(9)**: 153 – 160.
- Adefemi, O. S. and Awokunmi E. E. (2009). The Impact of Municipal Solid Waste Disposal in Ado Ekiti Metropolis, Ekiti State, Nigeria. *Afr J. Environ. Sci. Tech.*, **3(8)** – 189.
- Albores, A F., Perez-cid, B., Gomes, E. F., Lopez, E. F. (2000). Comparison between Sequential Extraction Procedures and Single Extraction Procedure and for Metal Partitioning in Sewage Sludge Samples. *Analyst*, **125**:1353-1357.
- Awokunmi, E. E, Asaolu, S. S. and Ipinmoroti, K. O. (2010). Effect of Leaching on Heavy metal Concentrations of Soil in some Dumpsites. *Afr. J. Env and Technol.*, 3(8): 495 – 499.
- Bamgbose, O., Arowolo, T. O. A. and Odukoya, O. (2000). Earthworms as Bioindicators of Metal Pollution in Dumpsites of Abeokuta, Nigeria. *Rev, Biol. Trop.*, 48.
- Carlson, C. W. (1976). Land Application of Waste Materials. Soil Conservation. Soc. Am. Ankeny, IOWA, Pp3-7.
- Ciba, J., Korlewicz, T. and Turek, M. (1999). The Occurrence of Metals in Composted Municipal Waste and their Removal . *Water Air, Soil Pollut.*, **111**:159 – 170.
- Finžgar, N. Tlustos, P. and Leštan, D. (2007). Relationship of soil properties to fractionation, bioavailability and mobility of lead and zinc in soil. *Plant Soil Environ.*, **5**: 225 – 238.
- Gupta, S. K. and Chen, K. Y. (1975). Partitioning of Trace Metals in Selective Chemical Fractions of near shore Sediments. *Environ. Letter*, **10**: 129 - 158.
- Harrison, R. M. (1981). Chemical Association of Pb, Cd, Cu and Zn in Street Dusts and Roadside Soils. *Environ Sci.Technol.*, **15**: 1378 – 1383.
- Hickey, M .G. and Kittrick, J. A. (1984). Chemical Partitioning of Cd, Cu, Ni, and Zn in Soils and Sediments Containing High Levels of Heavy metals. *J. Environ. Quality*, **13**: 372 - 376.
- Kabata-Pendias, A. and Pendias, H. (1984). Trace Elements in Soils and Plants. CRC Press, Boca Raton, USA. PP. 365.
- Kebir, T and Bouhadjera, K. (2011). Heavy metal concentrations in agricultural soils and accumulation in plants growing near of dumpsite of Ghazaouet (West Algeria). *International Journal of Current Research*, **2(2)**: 042 – 049.
- Kuo, S., Heilman, P. E. and Baker, A. S. (1983). Distribution and Forms of Cu,Zn, Cd, Fe and Mn in Soils ear a Copper Smelter. *Soil Sci.*, **135**: 101 – 109.
- Miller, W. P. and Mcfree, W.W. (1983). Distribution of Cd, Zn, Cu and Pb in Soils of Industrial Northwestern Indiana. *J. Environ. Qual.*, **12**: 29 - 33.
- Norwell, W. A. (1984). Comparison of chelating agents as extractants for metals in diverse soil material. *Soil Sci. Soc. Am. J.*, **48**: 1285 – 1292.
- Nyle, C. B. and Ray, R. N. (1999). The Nature and Properties of Soils. 2nd ed. USA. Pp. 743-785.
- Okorokwo, N. E., Igwe, J. C. and Onwuchekwe, E. C. (2005). Risk and health implication of polluted soils for crops production. *African Journal of Biotechnology*, **4(13)**: 1521 – 1524.

- Ojeshina OA (1999). Sanitary and Hazardous Waste: Landfill as a Waste Disposal Strategy for Nigerian settlement. A paper presented at a one day workshop as part of the activities to mark FEPA's 10th year anniversary, Nigeria.
- Smith, C. J., Hopmans, P. and Cook, F. J. (1996). Accumulation of Cr, Pb, Cu, Ni, Zn and Cd in Soil following Irrigation with Untreated Urban Effluent in Australia. *Environ. Pollut.*, **94(3)**: 317 - 323.
- Tessier, A., Campbell, P. G. C. and Bisson, N. (1979). Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Anal Chem.*, **51(7)**: 844 – 861.
- Uba, S., Uzairu, A., Harrison, G. F. S., Balarabe, M. L. and Okunola, O. J. (2008). Assessment of Heavy Metals Bioavailabilty in Dumpsites of Zaria Metropolis. *African Journal Biotechnol.*, **7(2)**: 122-130.
- Uba, S., Uzairu, A. and Okunola, O. J. (2009). Content of Heavy Metals in *Lumbricus Terrestris* and Associated Soils in Dump Sites. *Int. J. Environ. Res.*, **3(3)**: 353 – 358.