



Research Paper

Geochemical Partitioning of Some Heavy Metals in Dumpsite Soils in Kaduna Metropolis, Nigeria

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(Received 05th June 2013, Accepted 04th July 2013)

Available online at: www.ijrce.org

Abstract: Heavy metals are potentially toxic to human life and the environment. Metal toxicity depends on chemical associations in soils. Therefore determination of the chemical form of metals in soils is important in order to evaluate its mobility and bioavailability. Sequential extraction was used to fractionate Arsenic (As), Cadmium (Cd), and Lead (Pb) from ten dumpsites soils in Kaduna metropolis, Nigeria into six geochemical fractions: water soluble, exchangeable, carbonate, Fe-Mn oxide, organic, residual fraction. On the average, amount of heavy metals bound to each fraction differed significantly according to metal type, sites and across the seasons. The heavy metals were distributed almost evenly across the non-residual and residual fractions. The apparent mobility and potential bioavailability for these three metals in the soils were: $Cd > Pb > As$. Metal distributions in different chemical fractions in these samples depended on respective total metal concentrations, except for Cd. The study indicated that consumption of plants grown on these sites could pose health hazard to man.

Keywords: Soil, extraction, heavy metals, mobility, bioavailability, determination.

Introduction

Contamination of the environment by heavy metals is of major concern because of their toxicity and threat to human life and the environment [1-3]. Anthropogenic contamination sources of heavy metals in soils include urban infiltration, industrial and domestic waste as well as inputs from vehicle exhausts, use of pesticides, burning of fossil fuels, open air incineration of solid waste and petroleum activities [4,5]. Other sources are paper mills, organic chemicals, alkalis, petroleum refining, asbestos products, cements, basic steel works, fertilizers, textile mill products and leather industries [6, 7].

Human require varying amounts of some heavy metals for instance iron, cobalt, copper, manganese, molybdenum, and zinc. All metals are toxic at higher concentrations. Excessive levels could be detrimental to health. Other heavy metals such as mercury, arsenic, cadmium and lead are toxic and have no known vital or beneficial effects on organisms and their accumulation over time in the bodies of animals could have detrimental effect [8-11]. Accumulation of lead for example has been recorded to causes damage

to the brain and kidney while cadmium causes kidney and lung problem as well as high blood pressure [12]. Therefore, it is advisable to monitor the levels of these heavy metals in the soils in areas of high population density and high human activities.

Based on primary accumulation mechanisms in sediments and soils, heavy metals could be classified into five categories: adsorptive and exchangeable, bound to carbonate phases, bound to reducible phases for instance Fe and Mn oxides, lattice metals bound to organic matter and sulphides [13,14]. Heavy metals present in these categories have different remobilization behaviours under changing environmental conditions [15, 16]. Geochemical forms of heavy metals in soil affect their solubility, which directly influences their bioavailability. Therefore, determining total content of heavy metals is insufficient to assess the environmental impact of contaminated soils [17, 18], because it is the chemical forms that determine metal behaviour in the environment and the remobilization ability.

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 [19, 20]. Despite uncertainties as to the selectivity of the various extractants and to possible problems due to re-adsorption, extraction procedures provide qualitative evidence regarding the forms of association of metals and indirectly, their bioavailability [23, 24]. The present study is on investigation of the chemical partitioning of arsenic, cadmium and lead in ten major dumpsites located at Kaduna Metropolis, Nigeria.

Material and Methods

Study Area: Kaduna Metropolis is located between longitude 30° east of the Greenwich meridian and latitude 900 and 1130° North of the equator. 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 Figure 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.

Sample Collection and Pre-treatment: Each location was divided into four quadrant and the soils 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 labelled 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 30°C overnight, homogenized, ground with an agate mortar, passed through a 2.00 mm sieve and stored in polythene bags before analysis.

Sequential extraction of metals: Sequential extraction of heavy metals was performed on the soil samples [22]. The method employed is a modification of the conventional method [20]. The modified method extracts heavy metals into six geochemical fractions as follows:

Fraction soluble in soil solution (F I): Exactly 1.00 g air-dried soil sample was mixed with 10.00 ml of deionised 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 deionised water prior to analysis.

Exchangeable Fraction (F II): The residue from F I was leached at room temperature with 10.00 ml of 1.00 M MgNO₃ 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 deionised water prior to analysis, MgNO₃ displace ions electrostatically bound in the soil matrix.

Acid Extractable Carbonate bound Fraction (F III): Residue from F II was leached at room temperature with 10.00 ml of 1.00 M CH₃COONa (at pH 5, adjusted with CH₃COOH) with continuous agitation for 5 hours and then centrifuged. The supernatant was decanted and made to 50.00 ml with deionized water prior to analysis, CH₃COONa solubilises carbonates (calcite, dolomite) and releases entrapped metals.

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 NH₂OH.HCl (pH adjusted with 25% v/v CH₃COOH) at 96°C for 6 hours with occasional agitation and centrifugation. The supernatant was decanted and made up to 50.00 ml with deionized water prior to analysis, NH₂OH.HCl reduces Fe and Mn oxides to soluble forms.

Oxidisable Organic Matter Bound Fraction (F V): To the residue from F IV, 3.00 ml of 0.02 M HNO₃ and 30% v/v H₂O₂ were added. The mixture was heated to 85°C in a water bath for 3 hours. After cooling, 5.00 ml of 1.00 M CH₃COONa was then used to extract with occasional agitation for 3 hours at 85°C. The mixture was centrifuged and the supernatant decanted and made up to 50.00 ml with deionised water prior to analysis. HNO₃ and H₂O₂ oxidise organic matter and solubilise sulphides. Oxidised organic matter releases complexed, adsorbed and chelated metals.

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 HClO₄ 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 deionised water prior to analysis.

After successive extraction, the sample was centrifuged at 265.50 gravity. The supernatants were removed with pipette and filtered with Whatmann No 42 filter paper. The residue was washed with deionised water followed by vigorous hand shaking and then followed by 15 minutes of centrifugation before the next extraction. The volume of the water for rinsing was left at a minimum to avoid excessive solubilisation of solid materials. The process was carried out in triplicate for a particular sample. Appropriate reagent blanks were prepared and analyzed for each extraction type. Arsenic, cadmium

and lead concentrations in all extracts were determined with atomic absorption spectrophotometry.

Results and Discussion

Assessment of 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 [23]. The procedure of [20] is one of the most thoroughly researched and widely used procedures to evaluate the efficacy of decontamination [24, 25]. The sequential extraction procedure and analysis, measures the mobility and bioavailability of heavy metals in soil depending on how the metals are associated with the components of the soil. The mobility and bioavailability of metals serves to predict the behaviour of heavy metals in the soil. Sequence of extraction follows the order of decreasing solubility of geochemical forms of the metals [26]. Thus water soluble F(I) and exchangeable F(II) indicate the forms more mobile and bioavailable for plant uptake while

the non-residual (FVI) indicates the forms least mobile and least bioavailable for plant uptake.

Arsenic (As): Figures 2 and 3 illustrate the concentration of As in the soil samples during the wet (rainy) and dry seasons respectively. It was mostly present in residual and organic matter bound fraction and least concentrated in water soluble, exchangeable and carbonate bound. This indicates that the residual fractions serve as pool for As in the soil, therefore As would not be bioavailable for plant uptake in most of the dumpsites studied and even across the seasons.

However AD, ML and RG sites across the seasons contained greater amount of As in the non residual fractions specifically, water soluble fraction, exchangeable and carbonate bound fractions. This implies significant amount of As would be released into the environment for plant uptake, thus consumption of plants grown in the environment could pose health risk to man. Trend in soil fractions across the seasons in decreasing order is given as: Residual > Organic matter bound > Fe - Mn Oxide = Water soluble = Exchangeable = Carbonate bound.



Figure 1: Sample collection sites located in Kaduna Metropolis, Nigeria

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Cadmium (Cd): Figures 4 and 5 illustrate the concentration of Cd in the soil samples during the wet (rainy) and dry seasons respectively. Cd was associated with the residual fraction F (VI) and non residual fractions in particular exchangeable F (II) and Fe - Mn Oxide F (IV) which served as pool for cadmium in some sites and across the seasons. This is an evidence that the speciation pattern for Cd in the

soil is variable with sampling sites, which is in agreement with results obtained by other researchers [22, 29]. Generally, Cd trend in decreasing order across the seasons is as follows: Residual > Exchangeable > Fe - Mn Oxide > Organic matter > Carbonate = Water soluble.

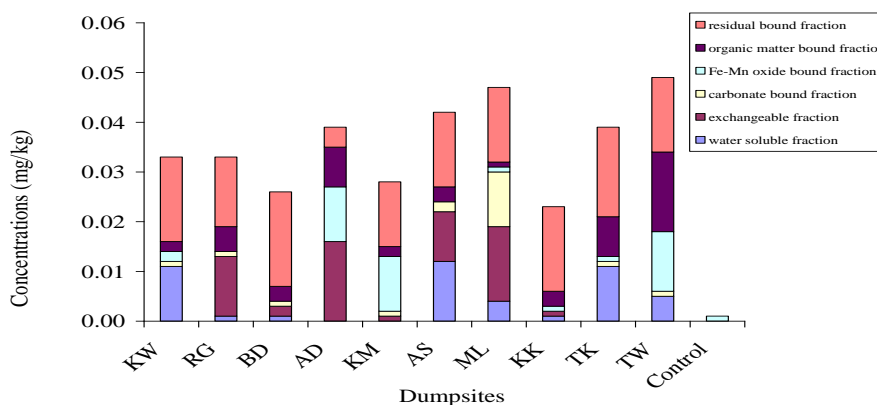


Figure 2: Arsenic concentrations in soil fractions during rainy season

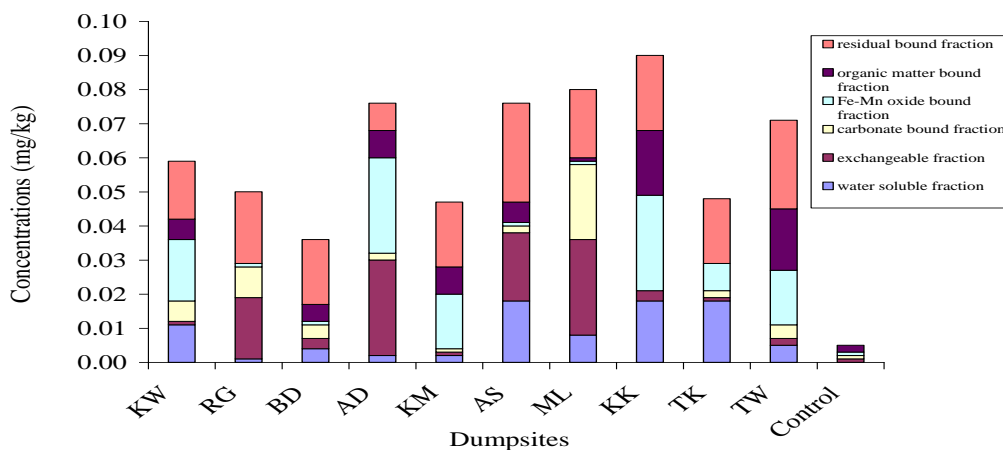


Figure 3: Arsenic concentrations in soil fractions during dry season

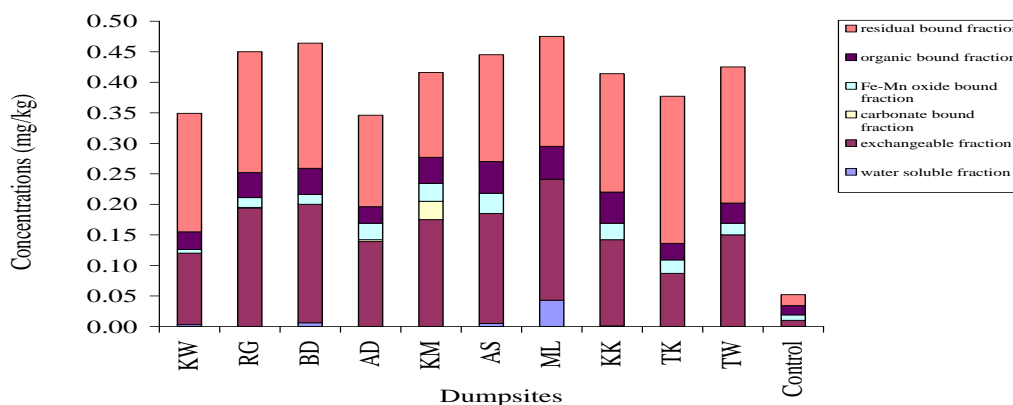


Figure 4: Cadmium concentrations in soil fractions during wet season

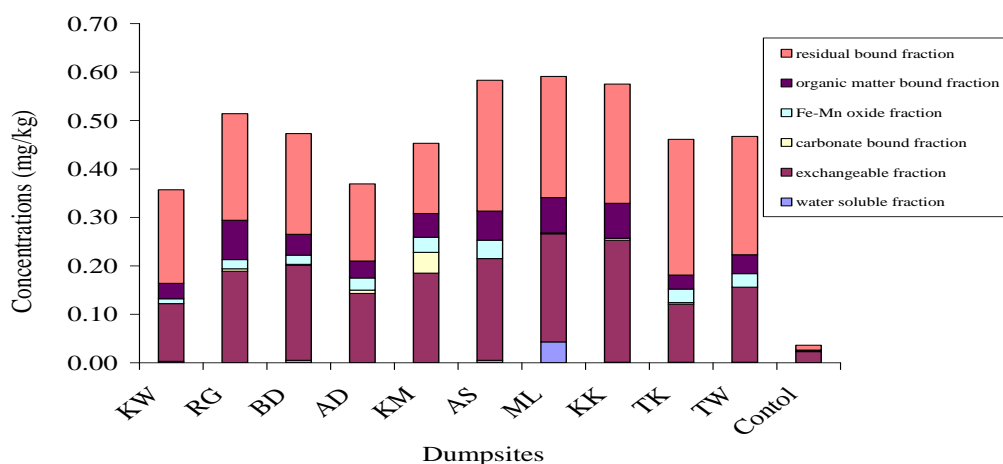


Figure 5: Cadmium concentrations in soil fractions during dry season

Lead (Pb): Figures 6 and 7 illustrate the concentration of Pb in the soil samples during the wet (rainy) and dry seasons respectively. Pb was found to be concentrated in the residual and organic matter bound fractions, where they are strongly bound and not easily released for plant uptake. Exceptions were however observed in some sites where greater amount of Pb were present in

non residual fractions. These findings agree with results obtained by another researcher [28]. Thus environmental pollution due to Pb would be minimal in most of the studied sites. Decreasing order of Pb concentration in the soil fractions is in the following order: Residual > Organic matter bound > Fe - Mn Oxide > Exchangeable > Carbonate > Water soluble.

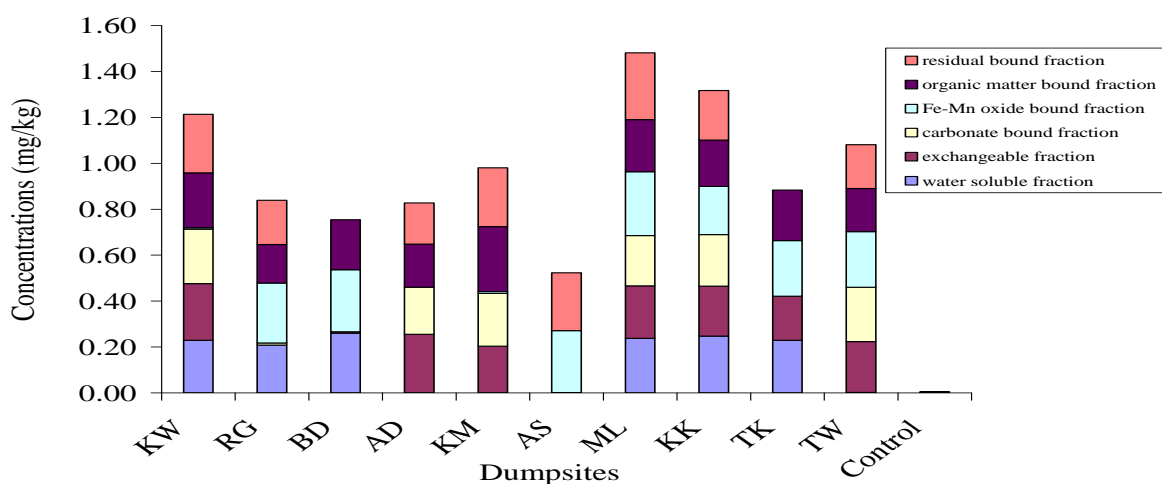


Figure 6: Lead concentrations in soil fractions during wet season

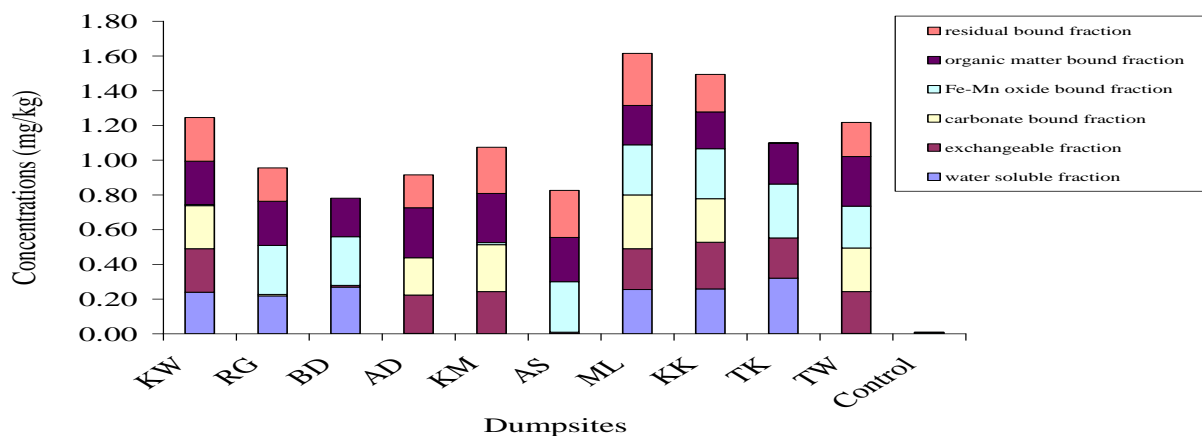


Figure 7: Lead concentrations in soil fractions during dry season

Table 1
Metal mobility factor for soil samples during wet season (%)

| Sites | Arsenic | Cadmium | Lead |
|---------|----------------|---------------|-----------------|
| KW | 1.2390 ±0.0007 | 4.6600±0.0001 | 24.9490±0.0007 |
| RG | 10.4500±0.0041 | 0.0000 | 8.8230±0.0015 |
| BD | 0.2800±0.00060 | 6.5800±0.0004 | 7.6000±0.0021 |
| AD | 0.0000 | 0.0000 | 0.0000 |
| KM | 0.0000 | 0.0000 | 0.0000 |
| AS | 2.1870±0.0010 | 6.2500±0.0002 | 0.0000 |
| ML | 28.1200±0.0003 | 6.7300±0.0012 | 26.3410±0.0052 |
| KK | 0.2400±0.0005 | 5.5500±0.0031 | 24.4190±0.0063 |
| TK | 1.2990±0.0014 | 0.0000 | 10.7500±0.0033 |
| TW | 2.4900±0.0040 | 0.0000 | 223.4500±0.0031 |
| Control | 0.0000 | 0.0000 | 0.0000 |

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

| Sites | Arsenic | Cadmium | Lead |
|---------|----------------|----------------|-----------------|
| KW | 6.0550±0.0006 | 4.7600±0.0004 | 25.3370±0.0044 |
| RG | 90.6800±0.0005 | 0.0000 | 9.9630±0.0021 |
| BD | 10.3900±0.0023 | 10.6900±0.0002 | 7.9370±0.0014 |
| AD | 11.0400±0.0044 | 0.0000 | 212.3600±0.0021 |
| KM | 5.4800±0.0051 | 0.0000 | 0.0000 |
| AS | 2.0710±0.0007 | 7.9300±0.0004 | 8.3400±0.0021 |
| ML | 28.5800±0.0004 | 8.3730±0.0043 | 30.6570±0.0011 |
| KK | 0.9300±0.0033 | 48.2700±0.0042 | 27.3590±0.0006 |
| TK | 1.6010±0.0003 | 35.8100±0.0021 | 13.3100±0.0003 |
| TW | 5.7300±0.0001 | 6.2200±0.0022 | 237.3200±0.0002 |
| Control | 0.0000 | 0.0000 | 5.0900±0.0001 |

Mobility Factor: Mobility of metals in soil could be assessed on the basis of absolute and relative concentration in fractions weakly bound to soil components. Metals present in fractions F (III) were strongly bound to the soil components (relatively less

mobile) than those extracted in water soluble F (I) and exchangeable F (II). Therefore the relative index of metal mobility was calculated as a mobility factor ^{129, 301} on the basis of the equation 1.

$$MF = \frac{F(I) + F(II) + F(III)}{F(I) + F(II) + F(III) + F(IV) + F(V) + (VI)} \times 100 \quad (1)$$

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

Mobility factors of the heavy metals showed variations especially across the sites. Tables 1 and 2 present the mobility factors of the heavy metals in the rainy and dry seasons respectively. As had low mobility values due to residual fraction accumulating higher amount of As in most of the sites. Exceptions were however observed at sites RG (90.68%), ML (28.58%), AD (11.04%) and BD (10.39%) in the dry season, where reasonably high mobility factor values were obtained due to non residual fractions (water soluble and acid exchangeable fractions) containing higher amount of As. This indicates that As would be bioavailable for plant uptake and would easily leached

down the subsoil thereby contaminating underground water in these sites. Thus As could pose health risk on organisms that consume plants grown on these sites and further get into the food chain. Mobility trend in decreasing order for rainy season is as follows: ML > RG > BD > TW > AS > TK > KW > KK > AD = KM. Dry season trend is also given as: RG > ML > AD > BD > KW > TW > KM > AS > TK > KK.

Cd was seen to have the very low mobility especially at RG, AD and KM where mobility factor was 0.00% across the seasons. Since higher amount of its contents are accumulated in the residual fraction of

the dumpsites, Cd would not be released into the environment. However, with respect to mobility factor values were obtained in the dry season at KK (48.27%), TK (35.81%) and BD (10.69%) indicating mobility and bioavailability of Cd at these sites, thus posing health risk on man. Mobility trend for Cd at the dumpsites in rainy season is as followings: ML > BD > AS > KK > KW > RG = AD = KM = TW = TK while trend in dry season is as shown: KK > TK > BD > ML > AS > TW > KW > RG = AD = KM.

Mobility values obtained for Pb also vary significantly across sites. Relatively high values were recorded at TW (237.32%), AD (212.36%), ML (30.65%), KK (27.35%) and KW (25.335) in the dry season, indicating high Pb mobility and uptake by the plants grown in these sites. Some sites recorded 0.00% mobility factor across the seasons for instance KM which recorded 0.00% even across the seasons implying Pb contamination would be minimal. These results could be attributed to the nature of the soil fractions Pb associated with in the various sites. Mobility of Pb in decreasing trend is given in the rainy season as: TW > ML > KW > KK > TK > RG > BD > AD = KM = AS. For dry season mobility factor in decreasing order is given as: TW > AD > ML > KK > KW > TK > RG > AS > BD > KM.

Conclusion

Mobility factors for all the metals varied significantly among the metals and across the seasons with the dry season values being significantly higher than rainy season values in most of the sites studied. On the average, amount of heavy metal bound to each fraction differed significantly according to metal type, sites and across the seasons. All the heavy metals were distributed almost evenly across the non-residual and residual fractions, therefore these metals would be potentially available for plant uptake and easily mobilized in soil solutions. The mobility and bioavailability for these three heavy metals is given as: Cd > Pb > As. Metal distributions in different chemical fractions in these soils depended on respective total metal concentrations, except for Cd. Based on these findings, consumption of plants grown on these sites could pose health hazard to man.

References

1. Abdelatif M. A., Wan Norazmin S. Evaluation of groundwater and soil pollution in a landfill area using electrical resistivity imaging survey. *Environmental management* 28 (2001)
2. Adriano D. C., Trace Elements in terrestrial Environments (2nd Ed.). New York: Springer-Verlag.(2001)
3. Alloway B. J., (Ed.) Heavy metals in Soils. (2nd ed.) London: Blackie Academic and Professional. (1995)
4. Enger E. D., Smith B. F., Environmental Science. (8th Ed.). McGraw - Hill. (2002)
5. Nadal M., Schuhmacher M., Domingo J. L., Metal pollution of soils and vegetation in an area with petrochemical industry. *Science of the Total Environment*. 321, 59–69 (2004)
6. Kumar G. P., Growth of *Jatropha curcas* on heavy metal contaminated soil amended with industrial wastes and *Azotobacter* – a greenhouse study. *Bioresource Technology*. 99, 2078–2082 (2008)
7. Beaven R. P., Walker A. N., Evaluation of the total pollution load of MSW, Proceedings Sardinia '97, 6th International Landfill Symposium. CISA: Cagliari, Italy, 57–71 (1997)
8. Dalal R. C., Moloney D., Sustainability indicators of soil health and biodiversity, In Management for sustainable ecosystems, ed. P. Hale, A. Petrie, D. Moloney, and P. Sattler. Brisbane: Centre for Conservation Biology, University of Queensland. 101–108 (2000)
9. Esakku S., Palanivelu K., Joseph K., Assessment of heavy metals in a municipal solid waste dumpsite, Workshop on sustainable landfill Management. 3-5 December, Chennai, India. 139-145 (2003)
10. Vaird B., Pihan F., Promeyrat S., Pihan J. C., Integrated assessment of heavy metal (Pb, Zn and Cd) highway pollution: bioaccumulation in soil, Graminaceae and land snails. *Chemosphere*. 55, 1349–1359 (2004)
11. Suman M., Ravindra K., Dahiya R., Chandra A., Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environmental monitoring and assessment*. 118, 435–456 (2006)
12. Biswas A. K., Kumar S., Babu S. S., Bhattacharya J. K., Chakrabarti T., Studies on environmental quality in and around municipal solid waste dumpsite, Resource Conservation and Recycling. 55, 129-134 (2010)
13. Albores A. F., Perez-Cid B., Gomes E. F., Lopez, E. F., Comparison between sequential extraction procedures and single extraction procedures for metal partitioning in sewage sludge samples. *Analyst*. 125, 1353-1357 (2000)
14. Aydinalp C., Marinova S., Distribution and forms of heavy metals in some agricultural soils. *Polish Journal of Environmental Studies*. 12(5), 629-630 (2003).
15. Gumgum B., Ozturk G., Chemical speciation of heavy metals in the Tigris river sediment. Chemical speciation and bioavailability. 13, 25–29 (2001)
16. Olanipekun E. O., Fagbote E. O., Speciation of heavy metals in soil of bitumen deposit impacted area of

- western Nigeria. *European Journal of Scientific Research*, Eurojournals publishing Inc. **47(2)**, 265-277 (2010)
17. Prudent P., Domeizer M., Massiani S., Chemical sequential extraction as decision making tool. *Application to Municipal Solid Waste*. **2**, 32-36 (1996)
18. Uba S., Uzairu A., Harrison G. F. S., Balarabe M. L., Okunola O. J., Assessment of heavy metals bioavailability in Dumpsites of Zaria Metropolis, Nigeria. *African Journal of Biotechnology*. **7(2)**, 122-130 (2008)
19. Tessier A., Campbell P., Bisson M., Sequential extraction procedure for the speciation of particulate trace metals. *J. Anal. Chem.* **51**, 844-851 (1979)
20. Finzgar N., Tlustos P., Lestan D., Relationship of soil properties to fractionation, bioavailability and mobility of lead and zinc in soil. *Soil Science Journal*. **5**, 225-238 (2007)
21. Manjunatha B. R., Balakrishna K., Shanker R., Mahalingam T. R., Geochemistry and assessment of metal pollution in soils and river India. Components of a monsoon –dominated environment near Karwar, southwest Coast. *Environmental Geology*. **40**, 1462-1470 (2001)
22. Okunola O.J., Uzairu A., Gimba C.E., Kagbu J. A., Geochemical partitioning of heavy metals on roadside surface soil of different grain size along major roads in Kano metropolis, Nigeria. *British Journal of Applied Science and Technology*. **1(3)**, 94-115 (2011)
23. Olanipekun E. O., Fagbote E. O., Speciation of heavy metals in soil of bitumen deposit impacted area of western Nigeria. *European Journal of Scientific Research*, Eurojournals publishing Inc. **47(2)**, 265-277 (2010)
24. Pardo R., Barrado E., Perez L., Vega M., Determination and speciation of heavy metals in sediments of the Pisuerga River. *Water Res.* **23**, 73-379 (1990)
25. Vicente-Beckett V. A., Pascual C. B., Kwan C. S., Beckett R., Levels and distribution of trace metals in sediments of Laguna Lake (Philippines) and its tributary rivers. *Int. J. Environ. Anal. Chem.* **45**, 101-116 (1991)
26. Ma Q. L., Rao N. G., Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soil. *Journal of Environmental Quality*. **26**, 259-264 (1997)
27. Yuan C., Shi J., He B., Liu J., Lung L., Jiang G., Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environmental International Journal*, **30**, 769-783 (2004)
28. Ramrez M., Massolo S., Fraiche R., Correa J. A., Metal speciation and environmental impact on sandy beaches due to El. Salvador Copper mine, Chile. *Marine Pollution Bulletin*. **50**, 62-71 (2005)
29. Yusuf K. A., Sequential extraction of Pb, Cu, Cd and Zn in soil near Ojota waste site. *Journal of Agronomy*. **6(2)**, 331-337 (2007)
30. Kabala C. I., Singh B. R., Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter. *Journal of Environmental Quality*. **30**, 485-492 (2001)