

HEAVY METALS MOBILITY AND BIOAVAILABILITY IN SOME SELECTED DUMPSITES OF OKENE METROPOLIS, NIGERIA

*U. Abdulmumuni, E. D. Paul and S. E. Abechi

Department of Chemistry, Ahmadu Bello University, Zaria. Nigeria.

Accepted:20/10/2015

*Corresponding Author: umarabdulmumuni75@gmail.com

Abstract

The chemical fractionation and bioavailability of Cd, Cu, Mn, Pb and Zn in the refuse waste soils of some dumpsites in Okene metropolis were investigated. The heavy metals in the waste soils were sequentially extracted and analysed using atomic absorption spectrometry. The sites from which the samples were collected were Inike (INI), Idoji (IDO), Ammco (AAM), Lafia (LAF), Iruvuchebe (IRU), Idogido (IDG), Oboroja (OBO) and Idichie (IDI). The means of total extractable metals in the samples ranged between 63.80 (INI) to 236.65 mg/kg (IDO) for Cd, 36.80 (AAM) to 312.00 mg/kg (LAF) for Cu, 192.00 (IRU) to 472.62 mg/kg (INI) for Mn, 98.30 (IDG) to 214.45 mg/kg (IRU) for Pb, and 269.35 (OBO) to 1898.15 mg/kg (IRU) for Zn. The non-residual fractions were found to be the most abundant pools for all the metals across the sites. Cadmium, Manganese and Lead were mostly found to be in the mobile phase of the samples indicating that these metals are potentially more bioavailable to the environment. This spread of metal pollution from waste dumpsites to agricultural areas can lead to health risks for human and livestock. The resulting bioaccumulation of Cadmium, Manganese and Lead can lead to damages to the liver and brain. Irreversible nervous system disorders and brain protoplasmic poisoning are typical. This study indicates that consumption of plants grown on these sites can pose health hazard to man. The observed mobility trend of the metals in this study is Cd > Mn > Pb > Cu > Zn.

Key words: Heavy metals, Okene, dumpsites, mobility, bioavailability.

Introduction

Okene is in the north central of Kogi state and is located at Latitude: 7° 37' 56" N Longitude: 6° 14' 48" E, Okene itself is a large local government area with a geographical area of 328,000 hectares, and the second most populated council area in Kogi State (NPC 2006). As at 2006 census the city has Population density of 320,260 [1]. Dumpsite is an old traditional method of waste disposal similar to landfill method of waste management [2, 3].

According to Khan and Ghouri, (2011), pollution is a worldwide problem, and its potential in influencing health of the human population is great. The impact of pollution in the vicinity of overcrowded cities and automobiles has reached a disturbing magnitude and is arousing public awareness [4]. As many studies have shown, municipal refuse may increase heavy metal concentration in soil and underground water [5] which may have effects on the host soils, crop and human health [6, 7]. However, total heavy metal concentrations is important measure in assessing risk of a refuse dumpsite, but cannot alone bring about insight on bioavailability, mobility and the fate of the heavy metal contaminant [8].

Leachate from dumpsites is said to be of particular interest when it contains potentially toxic heavy metals [9]. 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 which have been known to contain toxic metals such as cadmium, copper, lead,

manganese and zinc e.t.c, [12, 13], 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 bioavailability in soils. Numerous extraction schemes for soils and sediments have been described [14, 15, 16]. 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 [17].

Similar studies have been carried out in Nigeria for instance assessment of heavy metals bioavailability in dumpsites of Zaria Metropolis [8] according to Uba *et al*, the non-residual fraction was the most abundant pool for all the metals studies except copper. And also chemical fractionation of Copper, Manganese and Zinc in dumpsite of soil sample in Kaduna metropolis, Nigeria [18]. According to ekwumemgbo *et al*, Cu and Zn were distributed almost evenly across the non-residual and residual fractions and also recorded high mobility factors thus these metals would be potentially bioavailable for plant uptake and easily mobilized in soil solution.

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 behaviour in soil with respect to plant uptake.

Materials and Methods

Quality assurance

All reagents used for this analysis were of analytical grade, de-ionized water was used. Glassware and polythene sample bottles were washed with liquid soap, rinsed with distilled water, soaked in 10% HNO₃ for 24 h, cleaned thoroughly with de-ionized water and dried.

Dumpsite description

Soils from eight dumpsites were collected from eight different major settlements in Okene metropolis and a control which is 85m away from Inike dumpsite. These dumpsites are: Idoji (IDO), Idichie (IDI), Aamco (AAM), Idogido (IDG), Lafia (LAF), Iruvucheba (IRU), Inike (INI) and Oboroja (OBO).

Sample Collection and Pre-treatment

Each location was divided into four quadrants and the soil samples collected from each quadrant with the aid of a clean stainless steel spoon at 15cm below the top soil. The soil samples were placed in labelled polythene bags and were then taken to the laboratory for treatment. The soil samples were air dried in air circulating oven at 30°C overnight, homogenized and 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 [19]. The method employed is a modification of the conventional method [20]. This method extracts heavy metals into six geochemical fractions as follows: Fraction I (Fraction soluble in soil solution), Fraction II (Exchangeable fraction), Fraction III (Acid-Extractable – Carbonate bound fraction), Fraction IV (Reducible Fe-Mn Oxides and hydroxide fraction), Fraction V (Oxidizable – Organic Matter Bound Fraction), Fraction VI (residual and Inert fraction)

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 solubilisation of solid materials.

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 [24, 25]. Appropriate blank reagents will be prepared and analysed for each extraction type. All extracts were analysed for heavy metals (Cd, Cu, Mn, Pb and Zn) by Atomic Absorption Spectrometry.

Results and Discussion

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 [21,22, 40]. 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.

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 [24, 25]. Mobility factor of Cu, Mn and Zn in samples showed variations across the sites.

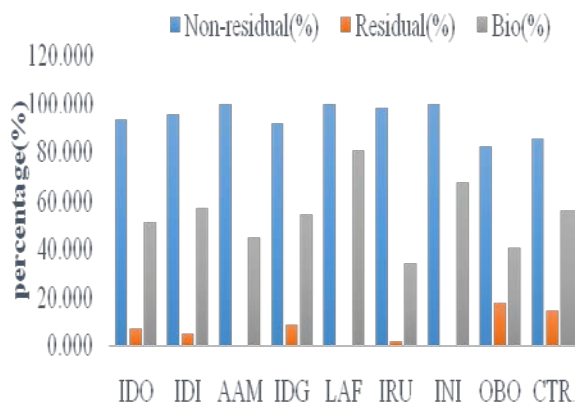


Figure 4.5:1 Chemical fractions of cadmium (mg/kg) in the waste soils of the dumpsites

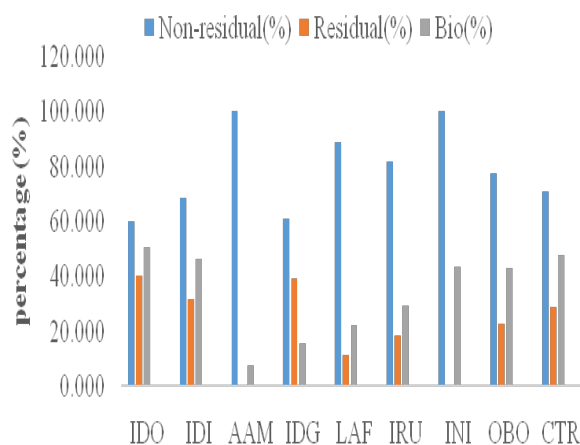


Table 4.5:2 Chemical fractions of copper (mg/kg) in the waste soils of the dumpsites

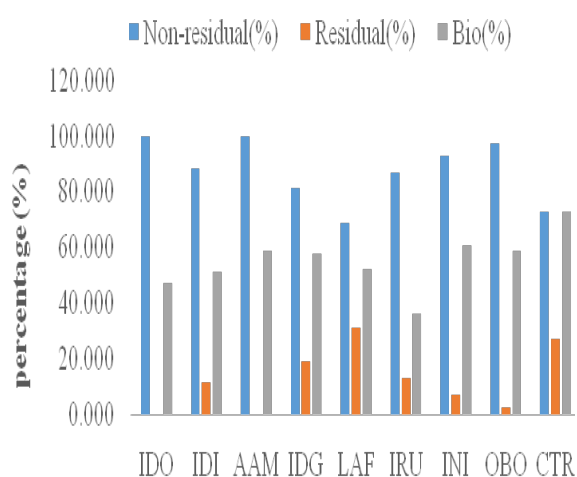


Figure 4.5:3 Chemical fractions of Manganese (mg/kg) in the waste soils of the dumpsites

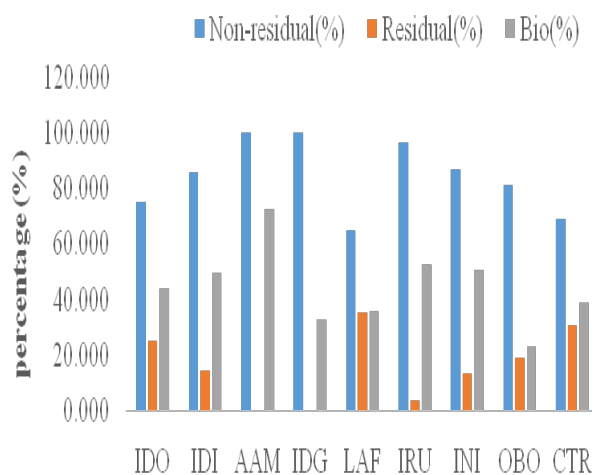


Figure 4.5:4 Chemical fractions of lead (mg/kg) in the waste soils of the dumpsites

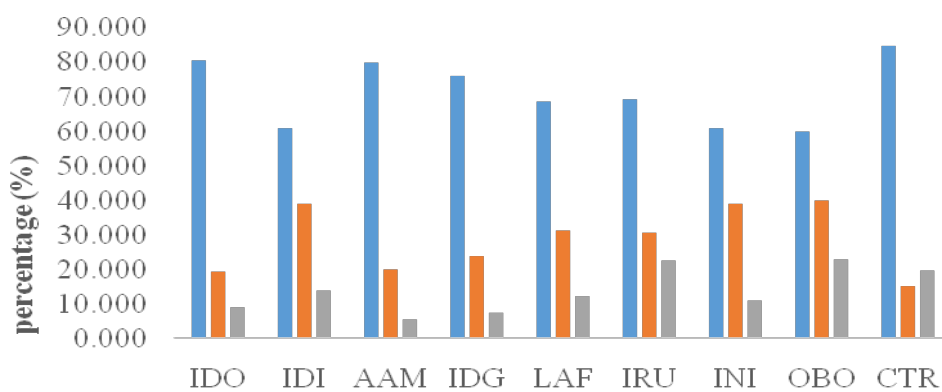


Figure 4.5:5 Chemical fractions of zinc (mg/kg) in the waste soils of the dumpsites

The concentration level in the six fractions step of the waste dumpsite soil of eight dumpsites studied are presented in Figure 4.5.1. From the results presented, total extractable Cadmium was found to be above permissible limit set by European Union (1986) concentration, 3.0mg/kg. Cadmium were mostly present in greater amount in non-residual fractions, specifically, water soluble fraction, exchangeable and carbonate bound fractions. This implies significant amount of cadmium would be released into the environment for plant uptake and thus consumption of such plants overtime could pose health risk on man. In residual fraction it is least present except in Oxidizeable-organic matter bound fraction in IDO and IDI sites hence it would not be bioavailable for plant uptake.

The mobile phase contained 33.894 (IRU) to 80.597 (LAF)% of the total extractable fraction of the metal which indicate that this metal will be readily bioavailable to the environment. The availability of this metal in the sequential extracted fractions follows the order. Organic matter bound > Carbonate bound >

Fe - Mn Oxide > Water soluble > Exchangeable > Residual.

The potential mobility and bioavailability of this metal in the waste soils of the dumpsites were found to be in the order: LAF > INI > IDI > IDG > IDO > AAM > OBO > IRU.

The findings in this investigations is in agreement with the observation of Harrison (1981) [26]. Miller and Mcfee (1983) [27] and Kuo *et al* (1983) [32] who reported similar Cd concentration levels in waste soils of dumpsites.

Copper

The concentration levels of copper in six fractions for the waste soils in eight dumpsite studied are presented in (figure 4.5.2). The concentration of copper in all refuse waste soils studied were below the toxic limit of 140mg/kg (EU 1986). Copper was dominated by the reducible Fe - Mn Oxide fraction, though appreciable amount is present Oxidizeable organic matter bound fraction. This indicates the effectiveness of organic matter as a scavenger of Cu in soil. A number of studies on speciation of copper have shown

that it is mainly bound to the Oxidizable phase, occurring as organically complexed metal species [28,29]. This is attributed to copper having high affinity for humic substances which are a fraction of natural organic matter chemically active in complexing such metal [30].

The major association of copper with organic fraction in these soils may be due to high formation constant of organic copper complexes [31].

Speciation trend in decreasing order as reducible Fe - Mn Oxide > organic matter bound > Residual > acid extractable - carbonate > Exchangeable > Water soluble.

The potential mobility and bioavailability amongst the dumpsites followed the pattern

IDO > IDI > INI > OBO > IRU > LAF > IDG > AAM.

Lead

Fractionation of Lead (Pb) is shown in figure 4:5.4. More than 80% of this metal was found to be in the non-residual fraction. Greater amount of Pb were present in non-residual fractions. All the dumpsites waste soils did not exceed the toxic limit of 300mg/kg (EU 1986). [2] reported similar results. Based on the mobile fraction, none of the dumpsite soil is at risk for lead contamination but it will be readily bioavailable for plant uptake. This finding is in agreement with Ramrez *et al.* (2005) [18]. Thus environmental pollution due to lead would be at minimum in most of the studied dumpsites. High amount of lead in organic matter bound fraction reflects the greater tendency for lead to be unavailable for plant uptake or less mobile in the soil [Ma and Rao, 1997]

Decreasing order of Pb contents in the soil fractions shows: Organic matter bound > Exchangeable > Carbonate > Water soluble > Fe - Mn Oxide > Residual.

Mobility of Pb in decreasing trend is given as: AAM > IRU > INI > IDI > IDO > LAF > IDG > OBO.

Manganese

Figure 4:5.3 shows fractionations of manganese in dumpsite soil. Manganese is mostly present in greater amount in non-residual fractions specifically Exchangeable and carbonate bound fractions. This implies significant amount of manganese would be released into the environment for plant uptake, and it would more bioavailable to the plants.

In addition, Mn contents been high in Fe - Mn Oxide fraction could be due to the high association or retention ability of the mineral crystal structure [32]. And could also be due to the precipitation of amorphous hydrous oxides of manganese during ageing of the dumpsites [33]. The order of bioavailability of this metal in different fractions followed the pattern: Exchangeable > Fe - Mn Oxide > Carbonate > Organic matter bound > Water soluble > Residual.

The potential mobility and bioavailability amongst the dumpsites followed the pattern: INI > OBO > AAM > IDG > LAF > IDI > IDO > IRU.

Zinc

Fractionation of Zinc, in dumpsite soils is shown in figure 4:5.5. It shows that extractable fractions of zinc in most dumpsite soils were above the EU (1986) maximum permissible limit (300mg/kg). The result also indicated that Zinc was primarily bound to the residual fraction followed by reducible Fe - Mn Oxide fraction. Figure 4.8 indicating that these fractions are of major importance as zinc carriers in dumpsites soil. This is in agreement with previous findings by Lee *et al.* (2005). High amount of zinc in the residual fraction reflects the greater tendency for zinc to be unavailable for plant uptake or less mobile in the soil [Ma and Rao, 1997]. Among the non-residual fractions, Fe - Mn Oxide fraction contained the highest Zn content with exceptions in OBO site. This may be due to the high stability constants of Zn Oxides formed. Several works have also found Zn to be associated with Fe - Mn Oxide (Kuo *et al.*, 1983; Ramos *et al.*, 1994; Gao *et al.*, 2008). Zinc contents in water soluble and exchangeable fractions in the soil are on the average relatively low. Although larger amount of total zinc was present in the residual fraction. Zinc mobility and bioavailable in decreasing order is shown as: Fe - Mn Oxide > Organic matter bound > Residual > Carbonate bound > Water soluble > Exchangeable.

In general, mobility factor for all the metals varied significantly among the metals. Values in most of the dumpsites studied are high, hence consumption of plants grown on some of the dumpsites through food chain could pose health hazard on man depending on the metal predominantly bound to the non-residual fractions.

Conclusion

Sequential extractions were used to fractionate Cd, Cu, Mn, Pb and Zn in the refuse waste soils in some selected dumpsite in Okene metropolis. Generally, mobility factor for all the metals varied significantly among the metals in the dumpsites studied. Cu and Zn were distributed almost evenly across the non-residual and residual fractions and also recorded high mobility factors across the site, thus these metals would be potentially bioavailable for plant uptake and easily mobilized in soil solution. In contrast, cadmium, lead and manganese was predominantly retained by non-residual fractions, which indicates that these metals will be potentially more bioavailable to the environment. 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. Overall, the order of mobility and bioavailability of the metals was Cd > Mn > Pb > Cu > Zn.

References

1. TWG (2007). Current population figures for cities, towns and Administrative Divisions of the World. <http://www.world-gazetter.com//home.htm>.
2. A.M. Odukoya, and A.F. Abimbola, (2010) Contamination assessment of surface and groundwater within and around two dumpsites. *International Journal Environmental Science and Technology*. 7(2):367-376.
3. O. Osibanjo, (1995). National waste management profile for Nigeria. Paper presented at the project steering committee meeting of the international maritime organization (IMO) FEPA Nigeria. Case study Input into the Global Waste survey. Presidential Hotel Port Harcourt 31st Jan.;1-15.
4. A. Begum, M. Ramaiah, I. Khan, and K Veena, (2009). Heavy metal pollution and chemical profile of CauveryRiver water. *Environmental Journal of Chemistry*; 6: 47-52.
5. N.E. Okorokwo, J.C. Igwe, and E.C. Onwuchekwe, (2005). Risk and health implication of polluted soils for crops production. *African Journal of Biotechnology*. 4(13): 1521 – 1524.
6. C.B. Nyle, and R.N. Ray, (1999). The Nature and Properties of Soils. 2nd edition USA. Pp. 743-785. C.B. Nyle, and R.N. Ray, (1999). The Nature and Properties of Soils. 2nd edition USA. Pp. 743-785.
7. C.J. Smith, P. Hopmans, F.J. Cook (1996). Accumulation of Cr, Pb, Cu, Ni, Zn and Cd in soil following irrigation with untreated Urban effluents in Australia, *Environ. Pollut.* 94(3): 317-323.
8. S. Uba, A. Uzairu, G.F.S. Harrison, M.L. Balarabe, and O.J. Okunola, (2008) Assessment of heavy metals bioavailability in dumpsites of Zaria Metropolis, Nigeria. *African Journal of Biotechnology*. 7(2):122-130.
9. A.M. Odukoya, and A.F. Abimbola, (2010) Contamination assessment of surface and groundwater within and around two dumpsites. *International Journal Environmental Science and Technology*. 7(2):367-376.
10. O.O. Dosumu, N. Salami, and F.A. Adekola, (2003) Comparative study of trace element levels. *Bull Chemical Society Ethiopia.* ;17(1):107-112.
11. S. Vasiliadou, and C. Dordas, (2009) Increased concentration of soil cadmium effects on plant growth, dry matter accumulation, Cd, and Zn uptake of different Tobacco cultivars (*Nicotiana tabacum* L). *International Journal Phytoremediation*. 11:115-130.
12. P. Bhattacharya, A.B. Mukherjee, J. Jacks, and S. Nordqvist, (2002) Metal contamination experimental studies and remediation. *Journal of Environmental Science*. 290:165-180.
13. W.R. Berti, L.W.P. Jacobs, (1996). Chemistry and Phytotoxicity of soil trace elements from repeated sewage sludge application. *Journal of Environmental Quality*. 25:1025-1032.
14. A. Tessier, P.G.C. Campbell and M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*. 51:844-851.
15. E.D. Paul, C.E. Gimba, J.A. Kagbu, G.I. Ndukwe, And G.I. Okibe, (2011). Spectrometric determination of fluoride in water, soil and vegetables from the precinct of river basawa, Zaria, Nigeria. *Journal of basic and applied chemistry*. 1(6):33-38.
16. L.M. Shuman, (1985) Fractionation method for soil microelements. *Soil Science*. 140:11-22.
17. B.R. Manjunatha, K. Balakrishna, R. Shanker, and T.R. Mahalingam, (2001) 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.
18. P.A. Ekwumemgbo, K.I. Omoniyi, H.A. Sanni, (2013) Geochemical partitioning of some heavy metals in dumpsite soils in Kaduna Metropolis, Nigeria. *International journal Resources Chemical Environment*. 3(3):125-131.
19. O.J. Okunola, A. Uzairu, C.E. Gimba, and J.A. Kagbu, (2011). 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.
20. N. Finzgar, P. Tlustos., and D. Lestan, (2007). Relationship of soil properties to fractionation, bioavailability and mobility of lead and zinc in soil. *Soil Science Journal*, 5: 225-238.
21. E.O. Olanipekun, and E.O. Fagbote, (2010) Speciation of heavy metals in soil of bitumen deposit impacted area of western Nigeria. *European Journal of Science Resources, Eurojournals publishing Inc*. 47(2):265-277.
22. O. Osibanjo, (1995). National waste management profile for Nigeria. Paper presented at the project steering committee meeting of the international maritime organization (IMO) FEPA Nigeria. Case study Input into the Global Waste survey. Presidential Hotel Port Harcourt 31st Jan.;1-15.
23. X. Xian, (1989) Effect of chemical forms of cadmium, zinc, and lead in polluted soils on their uptake by cabbage plants. *Journal Plant Soil*. 113:2165-2175.
24. C.I. Kabala, and B.R. Singh, (2001). 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.
25. K.A. Yusuf, (2007) Sequential extraction of Pb, Cu, Cd and Zn in soil near Ojota waste site. *Journal of Agronomy*. 6(2):331-337.
26. R.M. Harrison, (1981). Chemical association of Pb, Cd, Cu and Zn in street dusts and roadside soils. *Environ. Sci. Technol*. 15: 1378-1383.

27. W.P. Miller, W.W. McFee, (1983). Distribution of Cd, Zn, Cu and Pb in soils of industrial northwestern Indiana. *J. Environ. Qual.* 12: 29-33.
28. K. Fytianos, A. Lourantou (2004) Speciation of elements in sediment samples collected at Lakes Volvi and Koronia, Greece. *Environ Int. J.* 30:11-17.
29. R. Pardo, E. Barrado, Y. Castrillejo, M.A. Velasco, and M. Vega, (1993) Study of the contents and speciation of heavy metals in river sediments by factor analysis. *Analytical Letters.* 26:1719-1739.
30. J. Pempkowiak, A. Sikora, E. Biernacka, (1999) Speciation of heavy metals in marine sediments vs their bioaccumulation by mussels. *Chemosphere.* 39:313-321.
31. W. Stumm, J.J. Morgan, (1981). *Aquatic chemistry: An introduction emphasizing chemical equilibria in natural water.* 2nd ed. John Wiley and Sons, New York.
32. O.J. Okunola, A. Uzairu, C.E. Gimba, and J.A. Kagbu, (2011). 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.
33. N. Staelens, P. Parkpian, C. Polprasert, (2000). Assessment of Metal Speciation in Sewage Sludge Dewatered in Vertical flow Reeds beds using a Sequential Extraction Scheme. *Chem. Speciat. Bioavail.* 12: 97-107.
34. P.K. Lee, S.T. Yun, B. Mayer, (2005) Metal contamination and solid phase partitioning of metals in urban roadside sediments. *Chemosphere.* 60:672-689.
35. Q.L. Ma, and N.G. Rao, (1997) Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soil. *Journal of Environmental Quality.* 26:259-264.
36. S. Kuo, P.E. Heilman, A.S. Baker, (1983). Distribution and forms of Cu, Zn, Cd, Fe and Mn in soils near a copper smelter. *Soil Sci.* 135:101-109.
37. L. Ramos, L.M. Hernandez, M.J. Gonzalez, (1994) Sequential fractionations of copper, lead, cadmium, and zinc in soil from or near Donana National park. *J. of Environ Qual.* 23:50-57.
38. X. Gao, S. Chen, Long A. (2008) Chemical speciation of twelve metals in surface sediments from the northern South China Sea under natural grain size. *Baseline/Marine Pollut. Bull.* 56:770-797.