



Full Length Research Paper

**SPECIATION, DISTRIBUTION AND BIOAVAILABILITY OF SOME HEAVY METALS IN
DUMPSITE SOILS FROM OGBOMOSO, NIGERIA**

A.M.O. Abdul Raheem* ; Z.O. Isiaka

Department of Chemistry, University of Ilorin, P.M.B. 1515, Ilorin-Nigeria

*Corresponding e-mail: modinah4@yahoo.co.uk; Tel: +2348035952356

ABSTRACT

The chemical speciation and bioavailability of cadmium (Cd), iron (Fe), zinc (Zn), and lead (Pb) in refuse dump soils of some dumpsites in Ogbomosho metropolis were investigated. The heavy metals in the soil samples were sequentially extracted and analysed using Buck scientific model 210VGP Atomic Absorption Spectrophotometer. The result showed that majority of Fe and Pb were associated with the residual and organic matter fractions. The exchangeable and carbonate fractions were the most important fractions for Cd and Zn. The total concentrations of Zn ranged from 2.15 - 230.30 (mg/l), the highest followed by Fe which ranged from 0.16 - 107.42 (mg/l), and then, Pb and Cd ranged from 0.23 - 4.57 (mg/l), and 0.01 - 0.91 (mg/l) respectively. The bioavailability factor for metals in all the sites ranged from 9.59 - 90.41 % for Fe; 75 - 100 % for Cd; 83.75 - 94.33 % for Zn; and 22.04 - 71.98 % for Pb, following the order Cd > Zn > Fe > Pb. The relatively high bioavailability factors observed for Cd in some sites coupled with its comparatively high concentration in the exchangeable fraction, indicates high mobility, and lability in the soils studied.

Keywords: Chemical speciation, Bioavailability, Heavy metals, Dumpsites

INTRODUCTION

The behaviour and fate of metals are governed by a range of different physicochemical processes which dictate their availability and mobility in the soil or sediment system. The knowledge of the chemical forms of soluble heavy metals or of heavy metals associated with particulates or colloids is essential for estimating the bioavailability, mobility and chemical reactivity in soils and sediments (Hickey and Kittrick, 1984). To assess the bioavailability of heavy metals, sequential extraction procedure is normally employed, this consists of a series of chemical extractants, each being more drastic in action and of different nature than the previous one (Chaudhary and Banerjee, 2008). Heavy metals are associated with various soil components in different ways and these associations determine their mobility and availability (Ahumada *et al.*, 1999).

One of the major challenges to human health and environmental quality is the contamination of the environment by potential toxic elements which are of major concern to the environmental scientists (Olajire *et al.*, 2003). There is a very large set of health consequences from exposure to soil contamination depending on pollutant type, pathway of attack and vulnerability of the exposed population. For example, it has been noted that lead (Pb) is especially hazardous to young children and pose high risk of developmental damage to the brain, while to all population, kidney damage is a risk. Although, many potential contaminants are required in trace amounts by plants for food production, they become hazardous when they bioaccumulate over time in the soil (Tokalioglu *et al.*, 2003). Once there is an introduction of metal contaminants into the environment, it can exist in various chemical forms and the form in which these metals exist is much more important as the degree of metal toxicity has been closely related to their chemical forms (Eisler, 1986).

In recent years there has been increased interest in the studies on speciation or chemical forms of heavy metals in polluted soils using sequential extraction techniques because it provides knowledge on metal affinity to soil components and the strength with which they are bound to matrix (Kotoky *et al.*, 2003). The use of sequential extraction procedure, although more time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals (Tessier *et al.*, 1979). Among the numerous extraction schemes described in literature is the procedure of Tessier *et al.*, (1979) which is one of the most thoroughly researched and widely used procedures to evaluate the possible chemical association of metals in soils and sediments.

MATERIALS AND METHODS

The study Area: The study area, Ogbomosho, is located in the South-Western part of Nigeria, which lies within the coordinates of latitude 8.08° N to 8.13° N and longitude 4.15° E to 4.25° E.

The two dumpsites used are at Ogbomosho town, the first dumpsite is in Sabo area which is located in the northern region of Ogbomosho, along Ogbomosho - Ilorin road, Oyo State, Nigeria. Sabo lies approximately on latitude 8.15° N and longitude 4.24° E. This area is majorly occupied by the Hausa traders, students, transporters, artesian, market men and women. The second dumpsite is in Pakiotan, behind new Sawmill located on the highway where human activities are minimal. This area lies approximately on latitude 8.13° N and longitude 4.27° E.

Sampling and Analysis

Soil samples were collected from two dumpsites at depths of 0 - 15 cm, 15 - 30 cm, and 30 - 45 cm, representing top, sub, and bottom soils respectively. The samples collected were taken to the laboratory where their composites were made. The composites were picked, air-dried, grounded and sieved using 2mm aperture sieve which ensures particles of < 2 mm diameter for adequate reaction contact (i.e. intimate contact with solid and liquid phases).

METHODOLOGY

The sequential extraction procedure developed by Tessier *et al.*, (1979) was used to determine the speciation of the metal forms in each soil. This procedure speciates the heavy-metal distribution into an easily extractable (exchangeable) form, a form bound to carbonates, a form bound to Fe–Mn oxides, a form bound to organics, and a residual form using 5g of dry soil in the following five steps:

Fraction 1 (exchangeable form) – 5 g of soil sample were continuously mixed and reacted with 40 ml of 1 M sodium acetate solution (pH adjusted to 8.2 with acetic acid) for one hour. Then the suspension was centrifuged (30 mins, 10,000 rpm) and the supernatant was analysed for metals. The soil residue was mixed with 40 ml of deionized water and centrifuged (30 mins, 10,000 rpm) and the supernatant was discarded to remove the added chemicals.

Fraction 2 (carbonate-bound form) – the residual soil sample from fraction 1 was treated with 40 ml of 1 M sodium acetate (pH adjusted to 5.0 with acetic acid) and mixed for 5 hours. The suspension was centrifuged (30 mins, 10 000 rpm) and the supernatant was analyzed for metals. The remaining soil residue was then washed with 40 ml of deionized water as before.

Fraction 3 (Fe–Mn oxides-bound form) – the residual soil sample from fraction 2 was treated with 100 ml of 0.04 M hydroxylamine hydrochloride (NH₂OH. HCl) in 25 % (v/v) acetic acid and heated to 96 °C, with occasional agitation for 6 hours. The suspension was centrifuged (30 mins, 10 000 rpm), and the supernatant was analysed for metals. The soil residue was washed with 40 ml of deionized water as before.

Fraction 4 (organic-bound form) – 15 ml of 0.02 M nitric acid (HNO₃) and 25 ml of 30 % hydrogen peroxide (pH adjusted to 2.0 with nitric acid) were added to the washed residual soil sample from fraction 3 and heated to 85 °C for 2 hours with occasional agitation. Then, 15 ml of 30 % hydrogen peroxide (pH adjusted to 2.0 with nitric acid) were added and heated again to 85 °C for 3 hours with occasional agitation. The mixture was cooled to room temperature of 26 °C and 25 ml of 3.2 M ammonium acetate (NH₄OAc) in 20 % (v/v) HNO₃ were added. Finally, the sample was diluted to 100 ml with deionized water and mixed continuously for 30 mins. The suspension was centrifuged (30 mins, 10 000 rpm) and the supernatant was analysed for metals.

Fraction 5 (residual metals): The washed residue from fraction 4 was digested with a mixture of nitric acid and perchloric acid, and the supernatant was analysed for metals.

At the end of each extraction procedure, the mixtures were centrifuged at 10,000 rpm for 30 min. The supernatants were removed by pipette and filtered with Whatman No.1 filter paper into sample container. Then residue was used for next stage of extraction consecutively. The filtrates were analysed for metal contents with the aid of Buck Scientific Model 210 VGP Analytical Atomic Absorption Spectrometer (AAS).

RESULTS AND DISCUSSION

Table1: Sampling points areas coordinate description

Sampling point	Area	Coordinates
A	Soil sample from Sabo dumpsite	Lat. 8.15°N and Long. 4.24°E
B	Soil sample from pakiotan dumpsite	Lat. 8.13°N and Long. 4.27°E

The sampling points, areas and coordinates are as shown in table 1

Tables 2-4 represent the concentrations of the metals in various geochemical fractions (F1-F5) of the soil.

Table 2: Concentrations of iron (Fe) (mg/l) in various geochemical fractions of the soil

Sampling sites	F1	F2	F3	F4	F5	% Bioavailable	% Non-Bioavailable
Composite A	0.16	1.28	57.94	33.65	81.41	34.04	65.96
0-15cm	0.35	0.54	32.19	48.56	72.55	21.45	78.55
30-45 cm	0.48	1.13	46.62	91.82	27.83	28.05	71.95
Composite B	8.26	6.55	73.57	12.69	63.95	53.56	46.44
0-15 cm	3.34	1.95	16.85	148.57	60.05	9.59	90.41
30-45cm	0.32	0.97	37.78	43.82	107.42	20.53	79.47

Key: (F1 = Exchangeable, F2 = Carbonate, F3 = Iron-manganese Oxide, F4 = Organic matter, F5 = Residual); % Metal Bioavailability Factor (MBF) = $[\Sigma F1, F2, F3 / \Sigma F1, F2, F3, F4, F5] \times 100$ (Adekola *et al.*, 2010)

% Metal Non – Bioavailability Factor (MNBF) = $100 - MBF$

The majority of iron in the soils was associated with the residual fraction. This is consistent with the results of Horsfall and Spiff (2005). The residual fraction is considered the most stable, less reactive and less bioavailable since it is occluded within the crystal lattice layer of silicates and well crystallized oxide minerals (Abeh *et al.*, 2007; Schwarzenbach *et al.*, 1993). The fraction can be taken as a guide to the degree of pollution of the soil. The smaller the percentages of the metal present in this fraction, the greater the pollution of the area (Horsfall and Spiff, 2005). The high percentage of iron found in residual fraction is an important repository of iron in the soil. In sandy soil that contains little clay, iron oxide could be leached through the soil and impact ground water quality.

The low concentration of iron in the exchangeable and carbonate fractions observed is in line with the earlier work (Horsfall and Spiff, 2005). The carbonate and exchangeable fractions are released into solutions of low pH, which can be related to stomach conditions (Evans *et al.*, 1992). The association pattern of iron in the different phases is in the order: residual > Fe-Mn oxide > organic > carbonate > exchangeable.

Table 3: Concentrations of cadmium (Cd) (mg/l) in various geochemical fractions of the soil

Sampling sites	F1	F2	F3	F4	F5	% Bioavailable	% Non-Bioavailable
Composite A	0.07	0.02	0.00	0.00	0.03	75.00	25.00
0-15cm	0.35	0.19	0.48	0.07	0.01	92.73	7.27
30-45 cm	0.26	0.20	0.13	0.01	0.00	98.33	1.67
Composite B	0.02	0.03	0.02	0.00	0.01	87.50	12.50
0-15 cm	0.67	0.07	0.02	0.00	0.00	100	0.00
30-45cm	0.91	0.14	0.19	0.04	0.00	96.64	3.36

Key: (F1 = Exchangeable, F2 = Carbonate, F3 = Iron-manganese Oxide, F4 = Organic matter, F5 = Residual)

In all the soil samples subjected to chemical speciation, Cd was found to be most associated with the exchangeable fraction and the carbonate fractions. Also, the concentration of cadmium decreases as the depth of the soil decreases. Researchers have reported various concentrations of Cd in different fractions, high percentage of Cd in the Exchangeable fraction and carbonate fraction was also reported by Iwegbue, (2007).

Table 4: Concentrations of Zinc (Zn) (mg/l) in various geochemical fractions of the soil

Sampling site	F1	F2	F3	F4	F5	% Bioavailable	% Non-Bioavailable
Composite A	230.35	80.81	59.13	23.90	17.42	89.96	10.04
0-15cm	50.31	39.39	47.46	11.30	7.20	88.12	11.88
30-45 cm	22.48	15.96	20.37	5.04	4.35	86.23	13.77
Composite B	107.42	26.61	21.77	3.25	6.12	94.33	5.67
0-15 cm	51.24	8.68	11.18	11.65	2.15	83.75	16.25
30-45 cm	30.55	8.17	16.20	6.83	7.54	79.26	20.74

Key: (F1 = Exchangeable, F2 = Carbonate, F3 = Iron-manganese Oxide, F4 = Organic matter, F5 = Residual)

In all the samples subjected to chemical speciation, zinc was found to be most concentrated in exchangeable fraction and the carbonate fraction. The concentration of Zn is seen to be decreasing in each fraction as the depth increases and follows the order exchangeable > carbonate > Fe-Mn oxide > Organic > residual fraction. However, some researchers have reported varying concentration of Zn in different fractions, high concentration of Zn in the residual and organic fractions was reported (Fayun *et al.*, 2008) in a soil collected around industrial zone.

Table 5: Concentrations of Lead (pb) (mg/l) in various geochemical fractions of the soil

Sampling site	F1	F2	F3	F4	F5	% Bioavailable	% Non-Bioavailable
Composite A	0.92	0.47	0.69	3.06	0.94	34.21	64.79
0-15cm	0.59	0.48	0.72	1.76	4.57	22.04	77.96
30-45 cm	0.48	1.13	46.62	91.82	27.83	36.19	63.81
Composite B	8.26	6.55	73.57	12.69	63.95	71.98	28.02
0-15 cm	3.34	1.95	16.85	148.57	60.05	54.47	45.53
30-45 cm	0.32	0.97	37.78	43.82	107.42	40.41	59.99

Key: (F1 = Exchangeable, F2 = Carbonate, F3 = Iron-manganese Oxide, F4 = Organic matter, F5 = Residual)

In all of the samples subjected to chemical speciation, there is no regular pattern for Pb except that fraction bound to Carbonate and Fe-Mn oxide are associated with the least concentration. This is in accordance with the work of (Abdus-Salam *et al.*, 2011) while fractions bound to the exchangeable and residual forms have the highest concentrations.

Bioavailability Factor

The exchangeable bond to carbonates species and Fe-Mn oxides, corresponding to the first three fractions, are generally called “bio-available”, as they exhibit mobility relative to the environment and are potentially available for plants. Chemical speciation procedure was used to determine the potential mobility and bioavailability of heavy metals in the dumpsites. The five geochemical forms (F1-F5) of metals are operationally defined by careful Chemical fractionation order that follows a decreasing solubility and increasing strength of extractants (Xian, 1989). The ease of extraction is related to the degree of solubility and bioavailability of metal form depends on the solubility. Therefore, the metal bioavailability factor (MBF) is defined as (Adekola *et al.*, 2010):

$$\frac{F1 + F2 + F3}{F1 + F2 + F3 + F4 + F5} \quad \text{i.e. The bio-available fraction}$$

The operational fractions whose conditions are not easily attainable in the geochemical conditions of the soil are regarded as non bioavailable fractions, NBF. The fate of these metals in an environment is determined by the ease of availability; and the higher the level of bioavailability, the higher the impact on the target system. Fe has the lowest bioavailable factor in all of the samples subjected to chemical speciation. This study shows that Zn has the highest bioavailability factor in the two (Composite Samples A & B) composite samples but decreases in the individual samples while Cd is generally considered highest in this study because all of the

depths apart from the composite have a high percentage of Cd. The range is as follows: Fe 9.59-53.59%, Cd 75-100%, Zn 79.26-94.33%, and Pb 22.04 - 71.98%. The high percent bioavailability is an indication of poor retention in the residual geochemical form partly due to saturation or old age of the dumpsites. The bioavailability levels of the metals in each dumpsite are depicted in Figures 1-6 below:

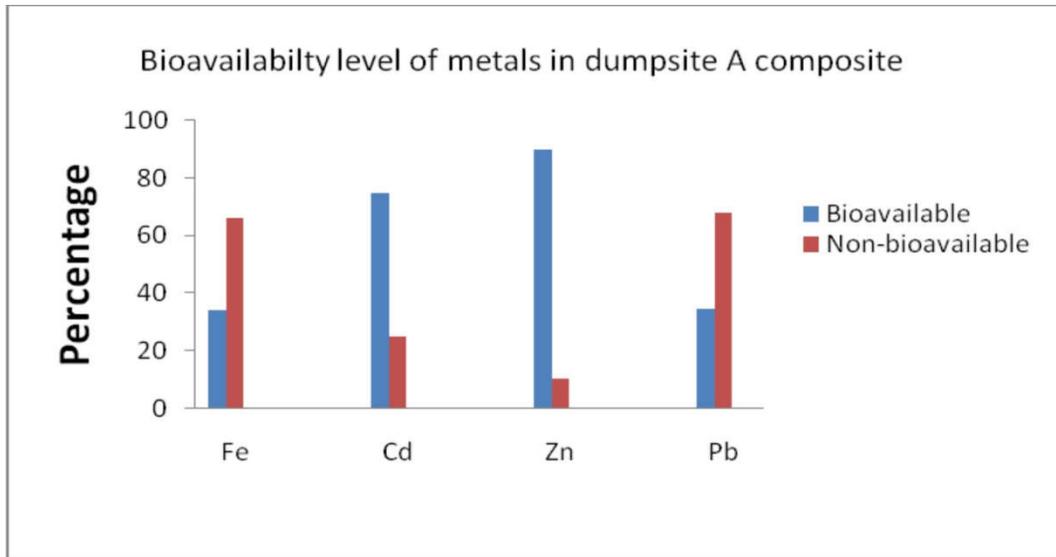


Figure 1: Bioavailability of Fe, Cd, Zn and Lead in the dumpsite A (composite)

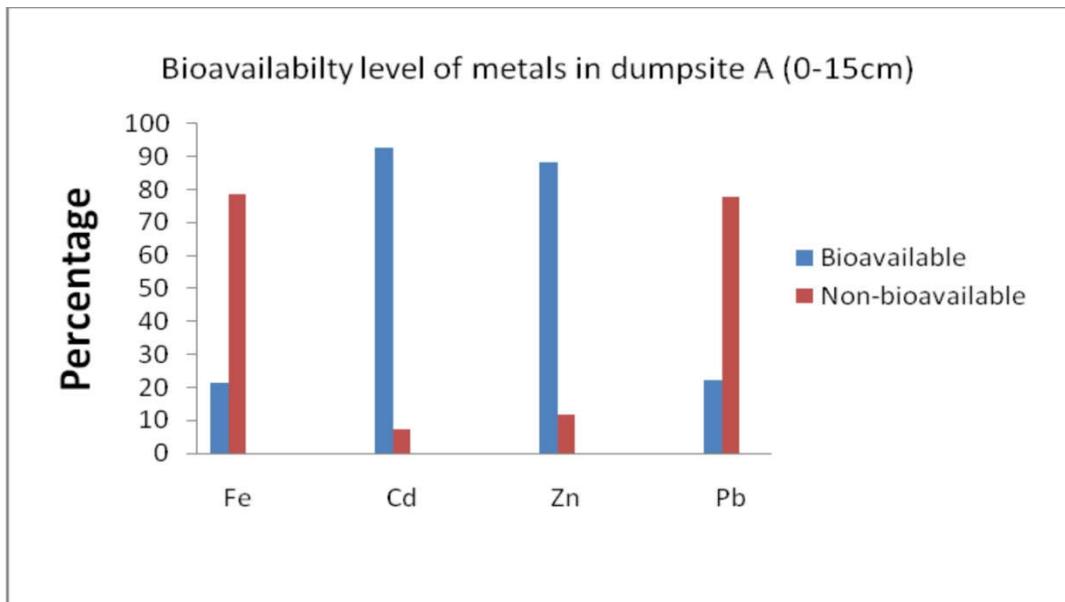


Figure 2: Bioavailability of Fe, Cd, Zn and Lead in the dumpsite A (0-15 cm)

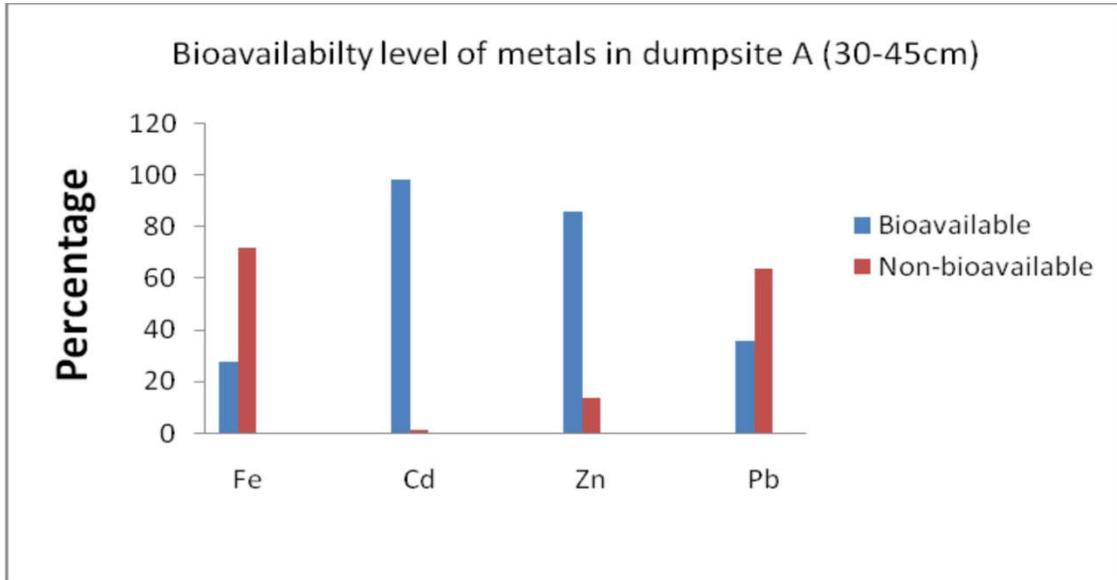


Figure 3: Bioavailability of Fe, Cd, Zn and Lead in the dumpsite A (30-45cm)

The bio-availability level of cadmium and zinc, is very high in this site for the composites as well as the individual depths; this high concentration could be as a result of the anthropogenic activities. Cadmium is ubiquitous in the human environment and has been known as one of the most deleterious heavy metal pollutant (Robards and Worsford, 1991). It may enter the food chain and this causes an adverse effect on human health. Among heavy metals polluting soils, Cd is of major concern because of its potentially harmful effect not only on humans and animals, but also on microbial biomass and its activity which plays an important role in the biological cycle of almost all the major plant nutrients cycling and soil fertility (Smith, 1996).

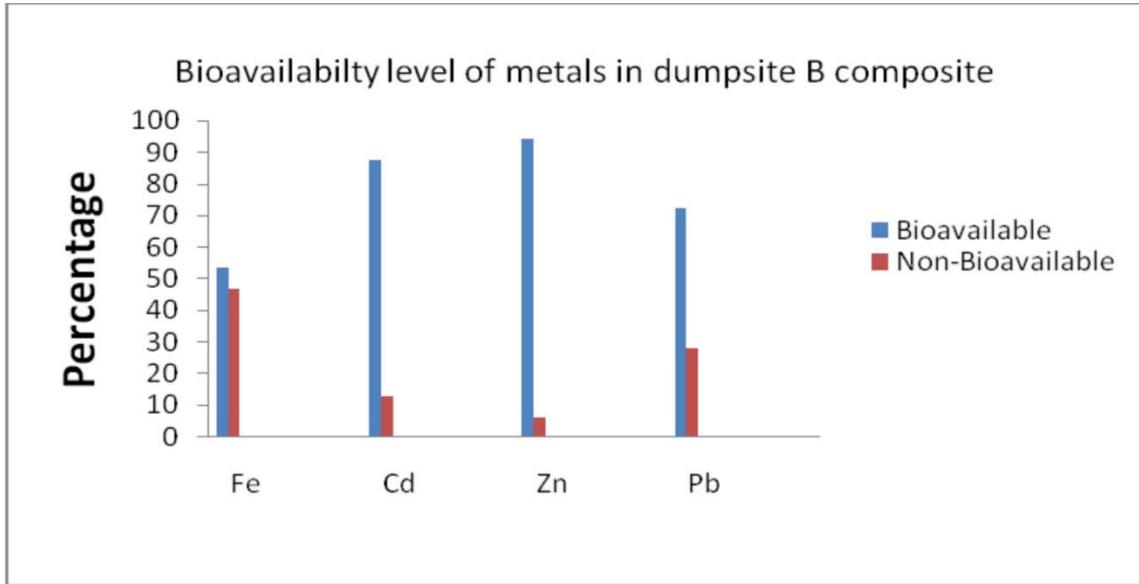


Figure 4: Bioavailability of Fe, Cd, Zn and Lead in the dumpsite B (composite)

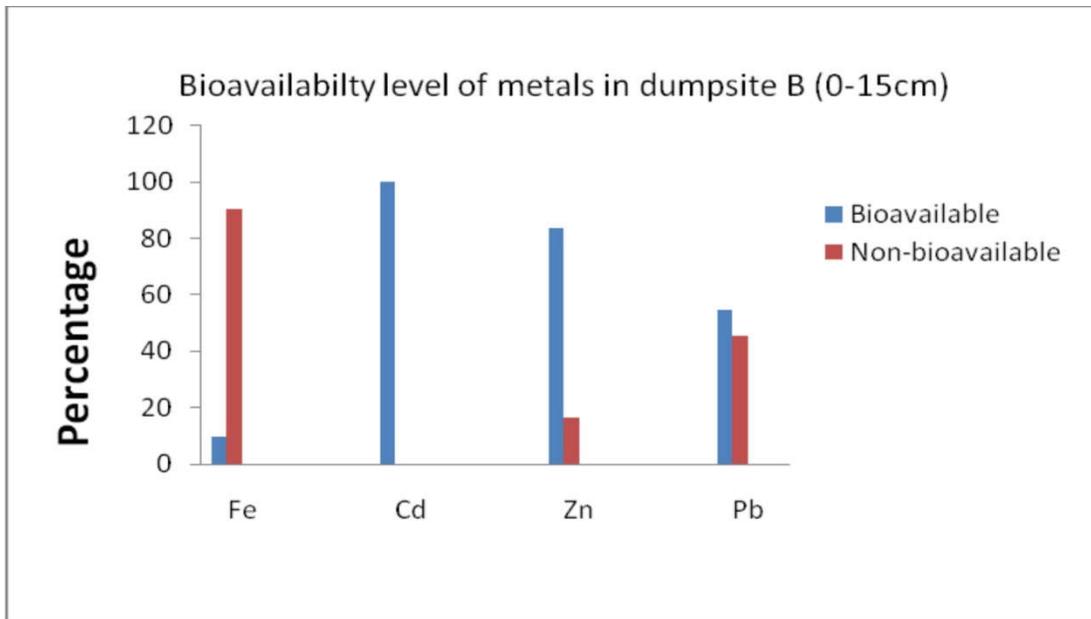


Figure 5: Bioavailability of Fe, Cd, Zn and Pb in the dumpsite A (0-15 cm)

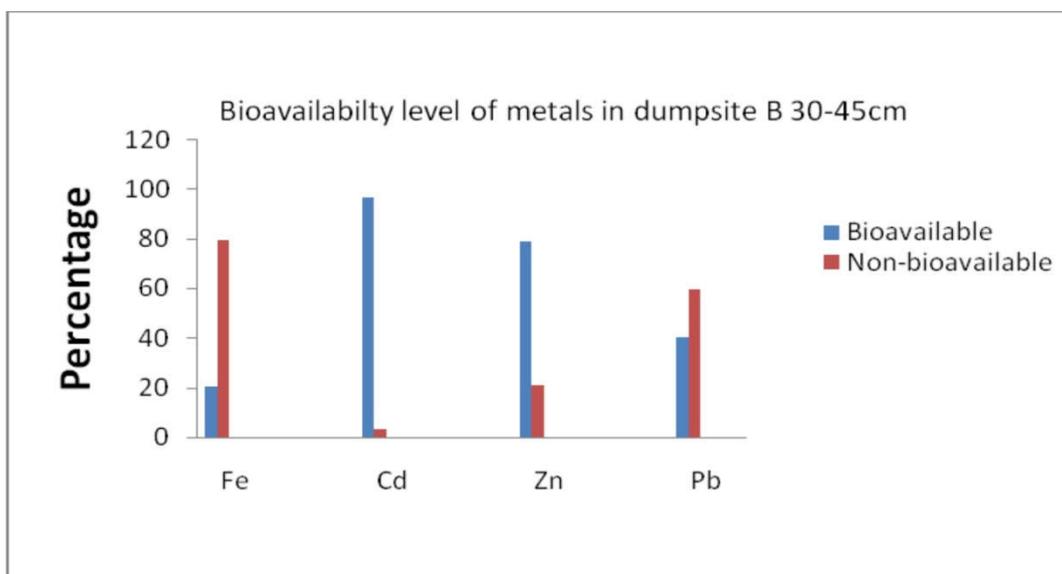


Figure 6: Bioavailability of Fe, Cd, Zn and Pb in the dumpsite A (30-45 cm)

However, for the second site, the bioavailability levels of zinc, cadmium and also lead is higher than the first site, this could be as a result of the anthropogenic activity. Cd and Pb are among the most toxic elements in nature making our dumpsites un-save as repository for wastes; particularly where wastes are not sorted and dumpsites are not well prepared. In these present conditions of the dumpsites, it poses danger to the aquifer due to ease of leaching of these toxic metals especially during rainy season. Overall, the order of mobility and bioavailability of the metals is $Cd > Zn > Pb > Fe$.

CONCLUSION

The increase of the total metal (Fe, Cd, Pb, Zn) content in the soil is due to human activities. The main source of which is the composition of the solid waste. Once in the soil, Cd binds preferably to the carbonates and exchangeable which explains its mobility and bioavailability to plants. The bioavailability and mobility of metals in soil strongly depends on the extent of their sorption with solid phases. Partitioning of heavy metals between solid and aqueous phases is controlled by properties such as surface area. The study herein successfully relates the presence of toxic heavy metals to the extent of their sorption. A quantification of the speciation of heavy metals for soil in dumpsites of both vicinities, Sabo (named A) and Pakiotan (named B) in this study shows that the soils are highly contaminated in Cd and Zn [with concentration values greater than the standard minimum amount expected in dumpsite soil (USEPA, 2002)], some of the metals studied therefore, constitutes major health risk to the local population. These metals may pose danger to human and aquatic life, and such metals could contaminate surface water, groundwater and animal food chain. Therefore, steps should be taken

to check the accumulation of metals in those areas, as the toxic effects of these heavy metals fallout are of grave consequence to human existence.

REFERENCES

- Abdus-Salam, N., Ibrahim, M.S. and Fatoyinbo, F.T. (2011). Dumpsites in Lokoja, Nigeria: A Silent Pollution Zone for Underground Water. *Waste Management and Bioresource Technology*, 1: 21 – 30.
- Abeh, T., Gungshik, J. and Adamu, M.M. (2007). Speciation Studies of trace elements levels in sediments from Zaramagada stream in Jos, Plateau State, Nigeria. *J. Chem. Soc. Nig.*, 32 (2): 218 – 225.
- Adekola, F.A., Abdus-Salam, N., Bale, R.B. and Oladeji, I.O. (2010). Sequential extraction of trace metals and particle size distribution studies of Kanji lake sediment, Nigeria. *Chem. Spec. Bioavailab.*, 22 (1): 43 – 49.
- Ahumada, I., Mendoza, J. and Ascar L. (1999). Sequential extraction in soils irrigated with waste water. *Commun. Soil Sci. Plant Anal.* 30: 1057 – 1519.
- Chaudhary, S. and Benerjee D.K. (2008). Speciation of some heavy metals in coalfly ash. *Chem. Spec. Bioavailab.*, 19 (3): 95 – 102.
- Iwegbue, C.M. (2007). Metal fractionation in soil profiles at automobile mechanic waste dumps around Port-Harcourt. *Waste Management & Research*, 25 (6): 585 – 593.
- Eisler, R. (1986). Chromium hazard to fish, wild life and invertebrates: A synoptic review. U.S fish wild. *Serv. Biol. Rep.*, 85, 1 (6): 38 – 40.
- Evans, E., Ma, M., Kingston L., Lecharne, S. and Chowdhry, B. (1992). The speciation pattern of lead in street dusts and soils in the vicinity of two London schools. *Environ. Inter.*, 18: 153 – 162.
- Fayun L., Zhiping F., Pengfei X., Kokyo O., Xiping, M. and Wei, H. (2008). Contamination, chemical speciation and vertical distribution of heavy metals in soil of an old large industrial zone in northeast china. *Environ. Geol.* 57 (8): 1815 – 1823.
- Hickey, M.G. and Kittrick, J.A. (1984). Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.*, 13: 372 – 376.

- Horsfall, M. (Jnr.), and Spiff, A. (2005). Speciation and bioavailability of heavy metals in sediment of Diobu River, Port Harcourt, Nigeria. *Europ. J. Sci. Res.*, 6 (3): 20 – 36.
- Kotoky, P., Bora, B.J., Baruah, N.K., Baruah, J; Baruah, P. and Borah, G.C. (2003). Chemical fractionation of heavy metals in soils around oil installation. *Assam. Chem. Spec. Bio.*, 15(4): 115 – 125.
- Olajire, A.A., Ayodele, E.T., Oyediran, G.O. and Oluyemi, E.A. (2003). Levels and speciation of heavy metals in soils of industrial southern Nigeria. *Environ. Monit. Assess.* 85: 135 – 155.
- Robards, K. and Worsford P. (1991). Cd: Toxicology and Analysis. *A Review Analyst*, 116: 549 – 568.
- Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. (1993). *Environ. Org. Chem.* John Wiley and Sons, Inc., New York. 259 – 261.
- Smith S.R. (1996). Agricultural recycling of sewage sludge and the environment. Wallingford: CAB International.
- Tessier, A., Campbell, P.G.C. and Bisson, M. (1979). Sequential extraction procedure for the separation of particulate trace metals. *Anal Chem.*, 51: 844 – 851.
- Tokalioglu, S., Kartal S. and Birol, G. (2003). Application of a three -stage sequential extraction procedure for determination of extractable metal contents in highway soils. *Turk J. Chem.*, 27: 333 – 346.
- USEPA, (2002). Biosolids Applied to Land: Advancing Standards and Practices. National Research Council, National Academy Press, Washington DC, 282.
- Xian, X. (1989). Effect of chemical forms of cadmium, zinc and lead in polluted soils on their uptake by cabbage plants. *Plant Soil*, 113: 257 – 264.