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Mobility and Bioavailability of Pb, Cr, Zn, Cd, Mn and Cu from Waste Soils of Refuse Dumpsites in Kano Metropolitan City, Nigeria

[1]Abdallah S.A., [2]Uzairu A., [2]Kagbu J.A., [3]Okunola O. J.

[1]Hussaini Adamu Federal Polytechnic, Kazaure, Jigawa State Nigeria.
[2]Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.
[3]National Research Institute for Chemical Technology, Basawa, Zaria, Nigeria.

Abstract: The mobility and bioavailability of Pb, Cr, Zn, Cd, Mn and Cu in 10 waste soils of dump site of Kano metropolis was determined using a sequential extraction procedure in response to environmental concerns about increasing anthropogenic inputs in a fast-paced, urbanizing city. The average total extractable metals from the waste soils ranged from 95.25 - 251.21mg/kg, 43.09 - 83.12mg/kg, 175.24 - 345.95mg/kg, 30.05 - 70.12mg/kg, 115.11 - 376.23mg/kg and 54.16 - 130.30mg/kg for Pb, Cr, Zn, Cd, Mn and Cu respectively. The mean extractable metals in the control soils were all lower than those of the dumpsites. All the metals investigated had their highest concentrations in the residual fractions indicating that the metals were less bioavailable to the environment. The mobile phase of all the metals accounted for very low percentage of the total extractable metals. The overall order of mobility of the metals in the dumpsites followed the sequence: Cd > Mn >Zn > Pb > Cr > Cu. All the metals except Cd were within the standard limits for soils.

Key words: Bioavailability, Metals, Waste soils, Kano.

INTRODUCTION

Refuse generation, dumping and management have become a serious environmental problem in many urban areas in Nigeria (Olarinwoye *et al*., 2010). Many human factors such as technology, industrialization, agricultural practices, transportation, education and most importantly population increase are directly responsible for increase in refuse generation, which Kano in Nigeria is not an exception.

Kano is one of the largest and most populous cities in Nigeria. It houses more than 300 industries with an estimated population of 9.4 million inhabitants in 2006. It is situated at latitude 12^{o}N and longitude 8^{o}31'E. Being the commercial heart of Northern Nigeria it has attracted immigrants from other parts of the country and the neighboring countries. Due to the huge population municipal wastes generation is also on the increase.

Among waste deposited includes; plastics, metals, ceramics, foams, tiles, toys etc. it is a known fact that some of these products contain hazardous metals such as Ni, Pb, Cd, Cu, Zn and Hg (Omolaye *et al*., 2011), which perturb the distribution and concentration of these metals in the environment e.g underground water, soil and plants. Recent studies have also revealed the wastes dumpsite can transfer significant levels of these toxic and persistent metals into the soil environment (Cobbs *et al*., 2000; Udosen *et al*., 2006; Ebong *et al*., 2008). And eventually these metals are taken up by plants parts and transfer same into the food chain (Benson and Ebong, 2005). To culminate with this, in Kano, most of waste soils from dumpsites are used by farmers as organic manure. The study of mobility of metals is of crucial importance for the assessment of environmental quality of contaminated soils. This is because the mobility of the metals and their bioavailability in the contaminated soils depends strongly on their specific chemical forms (Fuentes *et al*, 2006). Hence it is pertinent to determine the mobile metals rather than the total metals in order to assess toxic effects and to study biochemical pathways (Gupta and Sinha, 2007). The method or scheme used extensively for the extraction of metals was that of Tessier *et al*. (1979) with some variations (Krishnamuri *et al*., 1995), Ma and Rao (1997). Though more time consuming, it furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of the metals.

Considering the above discussed facts, the objectives of the present study are to: determine physicochemical parameters of waste soil determine the concentrations of heavy metals in waste soils and assess the mobility and bioavailability of these heavy metals using sequential extraction.

Corresponding Author: Abdallah S.A., Hussaini Adamu Federal Polytechnic, Kazaure, Jigawa State Nigeria.

MATERIAL AND METHODS

Description of Sampling Areas:

Ten sampling dumpsites were selected. The location of the sampling stations was shown in Fig. 1. The control areas were sited from a distance of 20m away from the dumpsites relatively unaffected by the dump wastes. The sampling points comprised of Goron Dutse (GD), Kofar Na'isa (KN), Court Road (CR), Na'ibawa-'Yanlemo (NYL), Hauren Gidan Rediyo (HGR), Airport Road (AR), Brigade, (BG),Kofar Mata (KM), Hauren Legal (HL) and Kofar Gadon Kaya (KGK).

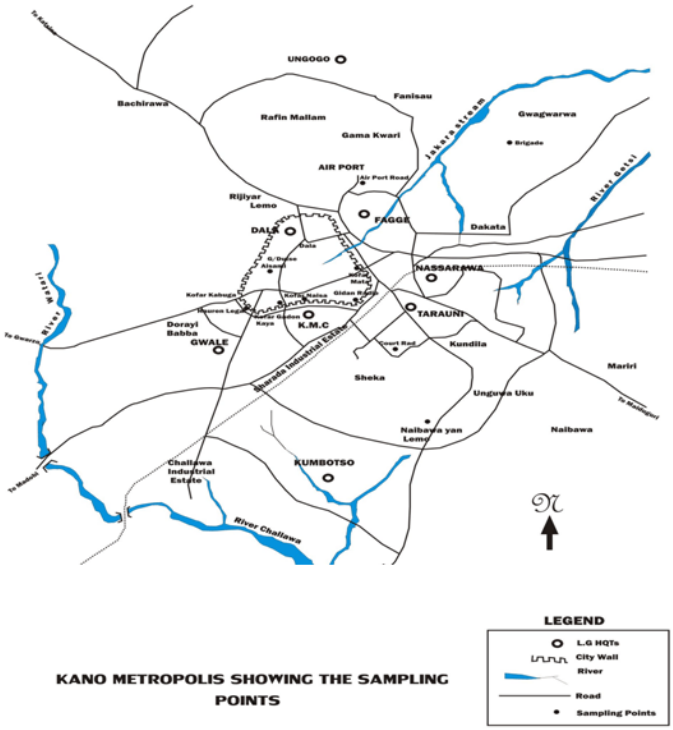

Fig. 1: Map of Kano metropolis showing the sampling stations.

Sample Collection:

Sampling was conducted based on the method described by Amusan (2005). Each sampling area was divided into four quadrants $5m^2$. Soil samples were picked from each quadrant while control samples were similarly collected 20m away from the up-slope of the dumpsites. The composite samples about 30g of the top soil (0-15cm) were taken and placed in labeled cellophane bags and conveyed to the laboratory for further treatment and analysis.

Sample Preparation:

The samples were air-dried in the oven at 30^0C overnight and homogenized using a clean acid washed porcelain mortar and pestle, and passed through a 2mm sieve to obtain fine fractions. The fine fractions (less than 2mm) were retained for analysis. The fine ground samples obtained were then stored in sterilized polythene bottles and placed in desiccators to attain constant weights pending analysis.

Quality Control:

All glassware, crucibles and plastic containers used for the experiments were washed with liquid soap rinsed with distilled water and soaked in 10% HNO_3 for 24 hrs and rinsed thoroughly with deionized water and dried in the oven at low temperature. The analytical results obtained were validated with spiked samples. The percentage recovery of metals obtained by the summation of sequential fractions in relation to the total metal content extracted with aqua-regia was computed. The analytical precision was confirmed with triplicates throughout the study.

Physico-chemical Properties of the Waste Soils:

Some physico-chemical parameters of the soil were determined. The pH (H_2O) measurement of the soil was determined by the procedure described by Bamgbose *et al*., (2000). The measurement was done with soil to water ratio (1:2.5 w/v) using a digital pH meter. The soil organic matter was determined using the wet digestion method (Walkley-Black 1934). Exchangeable cations were extracted by 0.1 M $BaCl_2$ and subsequently determined by AAS (Hendershot and Duquette, 1986). The available phosphorous was determined by the method described by Udo and Ogunwale (1978).

Sequential Extraction:

Sequential extraction was carried out on the principle of selective extraction proposed by Tessier *et al*. (1979), with some modifications. These included the use of $Mg(NO_3)_2$ instead $MgCl_2$ to extract exchangeable fractions because the chloride ion complex with metals (Shuman, 1985). The extraction of the oxidizable phase was undertaken after the extraction of the exchangeable phase. This allows the destruction of the organic matter which entraps the mineral materials and thus provides a better extraction of the phases that follow (Meguellati, 1982). For the residual fraction, combinations of aqua- regia: Hydrochloric acid- nitric acid (HCl-HNO_3) was used instead of the HF- $HClO_4$ (Sanchez *et al*, 1994; Maiz *et al*, 1997). Three sub-samples of 1g each of samples from the study and control areas were respectively subjected to sequential extraction separately. The procedure for this study is designed to separate heavy metals into six operationally defined fractions i.e. water soluble, exchangeable, carbonate bound, Fe – Mn oxide/hydroxide bound, organic bound and residual fractions (Ma and Rao 1997).

Table 1 gives the summery and comparison of the percentage recovery of the sequential extraction and the aqua-regia digestion. This is a useful technique for authenticating the acceptability and reliability of the analytical method adopted. In the present study the recovery of added metal ions obtained with spiked samples was found to be >93.75%. The range of percent recovery for the sequential extraction was between 93.75 – 105.96% while for the aqua regia the range of values was between 89.10 – 106.22%. Among all the metals Cd showed the highest percent recovery in both the sequal tial extraction and the aqua-regia digestion. The variations in the percentage recovery could probably be due to differences in leaching time, reagents and the total volume of extractant used (Ciba *et al*., 1999). Many similar ranges have already been reported in literature for sequential extraction (Albores *et al*, 2000; Okunola *et al*, 2007 and Uba *et al*, 2008).

Table 1: Comparison of percentage recoveries of metals.

Metal	Aqua-Regia Extraction	Sequential Extraction
Pb	95.01±0.35	90.11±0.23
Cr	93.75±0.30	89.10±0.15
Zn	99.91±0.20	91.51±0.42
Cd	105.96±0.17	106.22±0.29
Mn	102.93±0.16	96.07±0.34
Cu	103.78±0.31	101.07±1.32

RESULTS AND DISCUSSION

Characterization of the Refuse Dumpsites:

Table 2 summarized the results of refuse dumpsites characterization. The dumpsites were found to be littered with assorted wastes. Among the wastes, fabrics, polythene, plastics, (found in all the dumpsites), papers and metals (found in all dumpsites except GD and BG respectively), were most dominant in the dumpsites. Other important wastes included leaves, broken bottles, tiles, wood and ceramics while the least included foams, hairs, charcoal, glass and bones. These materials deposited at the dumpsites on daily basis interact with the soil and probably alter its physico-chemical properties (Uba *et al*, 2008).

Physico-chemical Parameters:

The distributions of some selected soil physico-chemical properties of the refuse dumpsites were summarized mean in Table 3. Soil pH is an important parameter that directly influences sorption/desorption, precipitation/dissolution, complex formation and oxidation reduction reactions. As observed by Mclean and Bledsoe (1992).The pH differed significantly among the dumpsites. The pH across the dump sites ranged from 6.90 – 9.35 units. These values are expected as most soils in the tropics have their ranging from acidic to slightly neutral (Alloway and Aryes, 1997). The values obtained in this research however suggested that the dumpsites soils were alkaline in nature. This may be attributed to the buffering effect of soil organic matter

against pH changes in addition to the release of basic cations during the organic matter decomposition. The results of the available phosphorus in the refuse waste soil ranged from 57.43 – 149.08meq per100 g.

Table 2: Characterization of refuse dumpsite wastes (percentage) in Kano Metropolis.

Sample	BG	KM	GD	AR	KN	NYL	CR	HL	HGR	KGK
Fabrics	3.10±0.10	49.88±0.94	14.03±0.06	53.17±0.06	26.93±0.98	8.40±0.10	9.37±0.21	16.72±0.08	8.57±0.06	0.85±0.05
Polythene	14.90±0.10	2.13±0.60	18.47±0.06	20.30±0.36	21.37±0.12	19.08±0.10	25.60±0.26	23.50±0.10	32.67±1.12	16.37±0.32
Plastics	16.03±0.06	4.70±0.26	23.83±0.14	13.53±0.49	18.53±0.47	26.53±0.06	28.43±0.06	33.20±0.10	38.37±0.32	21.97±0.29
Paper	1.90±0.10	5.33±0.21	-	2.57±0.06	6.27±0.15	3.80±0.50	7.20±0.20	6.63±0.29	11.27±0.21	5.07±0.31
Metals	-	6.98±0.10	8.00±0.10	4.28±0.08	8.30±0.00	3.77±0.74	22.43±0.40	11.30±0.10	-	6.33±0.29
Leaves	26.50±0.50	6.79±0.15	-	-	6.60±0,09	24.43±0.25	-	2.55±0.06	-	29.27±0.25
Bottles	-	2.07±0.06	-	-	5.53±0.12	-	-	-	2.96±0.12	-
Tiles	10.77±0.06	1.88±0.16	3.90±0.09	-	-	-	3.63±0.21	6.10±0.10	6.16±0.15	3.29±0.04
Wood	5.20±0.17	0.90±0.08	20.96±0.06	-	-	1.77±0.06	-	-	-	7.30±0.42
Foam	-	0.38±0.08	3.94±0.07	-	-	-	-	-	-	-
Ceramic	9.67±0.12	18.52±0.33	-	1.25±0.01	4.10±0.20	-	3.34±0.15	-	-	8.33±0.03
Hairs	-	-	-	1.27±0.12	-	-	-	-	-	-
Charcoal	-	0.44±0.01	-	2.02±0.00	-	-	-	-	-	-
Glass	-	-	6.87±0.05		2.37±0.10	-	-	-	-	0.63±0.04
Bones	12.03±0.06	-	-	1.61±0.04	-	2.32±0.15	-	-	-	0.59±0.05

Table 3: Some selected physicochemical properties of the soils from refuse dumpsites.

Dumpsite Location	pH	Organic Matter%	APmeq/100g	Exchangeable cations (Cmol/kg)						
				Ca	Mg	K	Na	Mn	Fe	∑CEC
GD	8.11±0.01	3.28±0.03	105.50±0.71	17.69± 0.29	11.14± 0.04	7.69±0.45	4.07± 0.22	87.01± 0.15	247.20± 0.13	374.78± 1.26
KN	7.55±0.07	7.16±0.06	84.43±0.60	28.33± 0.15	8.60± 0.28	4.30± 0.36	1.30± 0.14	59.93± 0.28	225.15± 0.69	327.61± 0.30
CR	7.63±0.04	3.81±0.04	112.03±0.04	16.00± 0.24	6.04± 0.08	6.42± 0.04	2.38± 0.04	136.40± 0.23	52.42± 0.04	219.86± 0.33
NYL	7.59±0.12	5.37±0.02	149.08±0.11	14.99± 0.11	2.34± 0.06	1.07± 0.01	0.78± 0.01	109.40± 0.16	231.39± 0.00	359.97± 0.09
HGR	7.70±0.00	1.66±0.01	85.73±0.04	16.67± 0.35	9.04± 0.04	5.52± 0.01	2.35± 0.04	123.29± 0.04	154.34± 0.08	311.21± 0.59
AR	7.58±0.03	3.57±0.00	124.58±0.11	13.42± 0.12	3.04± 0.12	2.7±	2.17± 0.11	73.09± 0.42	132.3± 0.21	226.7± 1.10
BG	6.90±0.00	1.96±0.06	91.9±0.14	14.19± 0.02	10.35± 0.11	13.86± 0.50	4.31± 0.18	69.36± 0.11	172.12± 0.16	284.16± 0.54
KM	9.35±0.07	3.30±0.01	62.75±0.32	14.25± 0.11	7.035± 0.01	5.725± 0.06	2.575± 0.05	71.04± 0.10	345.23± 0.15	446.05± 0.36
HL	8.25±0.07	3.13±0.11	57.43±0.46	17.00± 0.23	11.11± 0.18	9.22± 0.23	3.87± 0.03	43.98± 0.23	121.44± 0.07	206.62± 0.91
KGK	8.63±0.04	5.26±0.07	103.2±0.14	15.97± 0.20	13.44± 0.21	11.79± 0.04	3.70± 0.44	121.21± 0.16	187.88± 0.59	353.98± 0.82
Mean	7.93±0.69	3.85±1.66	97.66±27.60	16.95 ± 4.50	8.21± 3.61	6.83± 3.95	2.75± 1.20	89.47± 31.11	186.95± 80.81	311.09± 77.36
Range	6.90-9.35	1.66-7.16	57.43-149.08	13.42-28.33	2.34-13.44	1.07-13.86	0.78-4.31	43.98-136.40	52.42-345.23	206.62-446.05
Ctrl	7.03±0.93	2.03±0.79	48.21±26.80	14.58± 3.88	6.52± 3.21	3.06± 1.18	2.03± 0.99	52.94± 10.51	132.17± 58.10	211.22 ±61.80

Ctrl = Control

The high concentration of phosphorous contributes to good growth of plants (Uba *et al*, 2008). The organic matter (OM) content of the soil ranged from 1.66 – 7.16 % .The significantly higher OM contents of the soils might be attributed to the activities of the microorganisms involved in the organic matter decomposition thereby accumulating more organic matter in the soils. The mean OM content of the control site was significantly lower compared to the waste dump sites. The organic matter content of the soil plays an important role in adsorption reaction in the soil thereby preventing pollutants from reaching ground water sources (Alloway and Aryes, 1997). OM also plays important role in the total cation exchange site. The soils' concentrations of exchangeable cations (CEC) differ from dumpsite to dumpsite with a range of 206.62 – 446.05 $Cmolkg^{-1}$. This may not be unconnected to the heterogeneous nature of wastes received by different dump sites, which is expected to impact differently on soil properties.

Total Concentrations of Heavy Metals in Waste Soil:

Heavy metal content of waste soil samples are summarized in Table 4. The level of Pb in the study area ranged from 131.93 – 205.18$mgkg^{-1}$ while Cr and Zn ranged from 27.13 – 94.19 $mgkg^{-1}$ and 259.30 – 354.70 $mgkg^{-1}$ respectively. Cd has the least concentrations compared to the other metals with a range of 27.23 – 45.49 $mgkg^{-1}$. Other ranges of metal concentrations were 151.68 - 227.56 $mgkg^{-1}$ for Mn and 42.09 – 132.11 $mgkg^{-1}$ for Cu. The mean concentrations of the metals from the study and control areas (side by side) respectively were: Pb: 157.38, 40.52, Cr: 7.95, 6.95, Zn: 294.98, 64.07, Cd: 32.81, 5.19, Mn: 173.74, 86.12 and Cu: 68.48, 53.18 $mgkg^{-1}$. This indicated that the dumpsites had significantly higher heavy metals burden than the control areas. This agrees well with the findings of past researchers (Bamgbose *et al*., 2000; Eddy *et al.*, 2007; Ebong *et al*., 2008 and Uba *et al.*, 2008).

The profile of metal abundance in the study areas was: Zn>Mn>Pb>Cu>Cr>Cd. Among the six metals investigated, only Cd exceeded the European Commission (1986) permissible limit (2.0 - 3.0mg/kg). Nickel-cadmium batteries, cadmium- pigments, ceramics, glasses, paints and enamels, cadmium coated ferrous and non-ferrous products, cadmium stabilized polyvinyl chloride (pvc) products, cadmium alloys, cadmium electronics or electronic compounds are among anthropogenic sources of Cd in the environment (Baldini *et al.*, 2000). Values of 950mg/kg Mn, 100mg/kg Cr, and 75 mg/kg Zn were reported for uncontaminated soils (Sparkes, 2003). However, the values of concentrations of metals from waste soils reported by Uba *et al* (2008) were higher than those reported in this study.

Heavy Metal Speciation:

The sequential extraction of metals into operationally defined fractions is a useful technique adopted to assess the mobility and bioavailability of heavy metals in the waste soils. The results of the sequential extractions of six heavy metals Pb, Cr, Zn, Cd Mn and Cu from waste soils samples of the investigated areas were summarized in Figures.

Lead: The concentration levels of Pb in the six geochemical fractions of the refuse dumpsites soils are shown in Figure 2. The result revealed that the level of Pb in the residual fractions contained 39.51 (HGR) to 65.92% (CR) while the non-residual fraction contain 34.08 (CR) to 60.49% (HGR).

Table 4: Mean(±SD) concentrations (mg/kg dw) of some heavy metals in waste soils of refuse dumpsites.

Dumpsites	Pb	Cr	Zn	Cd	Mn	Cu
GD	95.25±0.01	43.09±0.09	184.85±0.37	44.13±0.13	115.11±0.10	54.16±0.04
KN	251.21±0.05	83.12±0.10	233.87±0.25	44.29±0.02	255.85±0.16	130.30±0.08
CR	221.20±0.16	60.24±0.06	245.79±0.44	69.94±0.16	313.28±0.04	115.31±0.01
NYL	189.03±0.03	61.14±0.07	283.85±0.17	60.17±0.05	331.18±0.06	101.09±0.07
HGR	236.27±0.08	55.17±0.07	216.90±0.19	34.92±0.31	301.90±021	95.10±0.00
AR	194.99±0.07	54.13±0.02	175.24±0.05	30.05±0.05	298.06±0.06	88.91±0.11
BG	173.04±0.03	51.1±0.10	179.71±0.32	31.10±0.10	264.06±0.05	93.67±0.00
KM	165.28±0.02	66.17±0.12	182.23±0.03	54.11±0.11	353.39±0.39	103.10±0.01
HL	201.17±0.06	72.05±0.05	205.85±0.16	70.12±0.12	376.23±0.10	114.77±0.23
KGK	246.15±0.05	70.04±0.04	345.95±0.06	48.02±0.13	341.10±0.09	113.08±0.02
Mean	197.36±46.55	61.63±11.63	225.42±54.77	48.69±14.75	295.02±73.55	100.95±20.63
Range	95.25-251.21	43.09-83.12	175.24-345.95	30.05-70.12	115.11-376.23	54.16-130.30
Ctrl	68.40±24.04	9.85±1.52	78.98±13.79	7.04±2.97	99.43±27.28	12.33±8.20
USEPA (1986) $mgkg^{-1}$	30-300	100	300	3	100-300	250

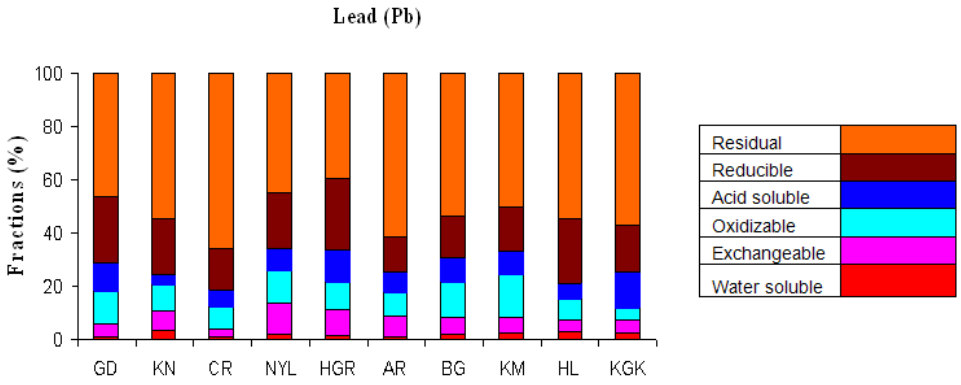

Fig. 2: Percentage of Pb in different chemical fractions of waste soils.

The highest level of Pb in the residual fraction is a reflection of the tendency of the metal to be less available to the environment. The residual fraction has been considered as the most stable, less reactive, and less bioavailable since it is occluded with the crystal lattice layer of the silicates and well crystallized oxide minerals (Terrus, 1995). The highest tendency of bioavailability of the metal is depicted at HGR (21.80%) and the least, (9.66% (CR). The general potential mobility and bioavailability of the metal in the six geochemical fractions follow the sequence: Residual>Reducible>Oxidizable>Acid soluble>Exchangeable>Water soluble. Similarly, the trend in the mobile metal abundance in the different refuse dumpsites soils was: HGR > NYL > KGK > GD > BG > AR > KM > KN > HL > CR. All the refuse dumpsites have metal concentration within the permissible limit (300mg/kg) set by USEPA (1986). Considering the mobile phase of the metals, the dumpsites might not be at risk but with years of accumulation, the level of the metal may reach and exceed the toxic limits.

Chromium: The results of extractable fractions of Cr are shown in Figure 3. The residual fraction contains the highest amount of Cr 51.25 - 71.13%. The next important fraction being the oxidizable phase has a mean percentage of 12.44% followed by the acid soluble phase 9.58%. The exchangeable fractions contain relatively low concentrations (4.18%) compared to the other fractions. This fraction is the most important from environmental point of view because it is the fraction that is bioavailable to the plants. The range of mobile fractions in the study areas contained 28.87 (HL) - 48.75% (KM) indicating that the metal will be readily available to the environment. The potential mobility and bioavailability of the metal in the refuse dumpsites

soils followed the trend: AR>HL>GD>KGK>CR>KN>NYL>HGR>KM>HL while the availability of the metal in the extracted fractions was in the order: Residual>Reducible>Acid Soluble>Oxidizable>Exchangeable >Water sol. The difference in the distribution pattern of the Cr may be attributed to the possible mobilization of the metal. The USEPA set limit of 100mg/kg in soil was not exceeded.

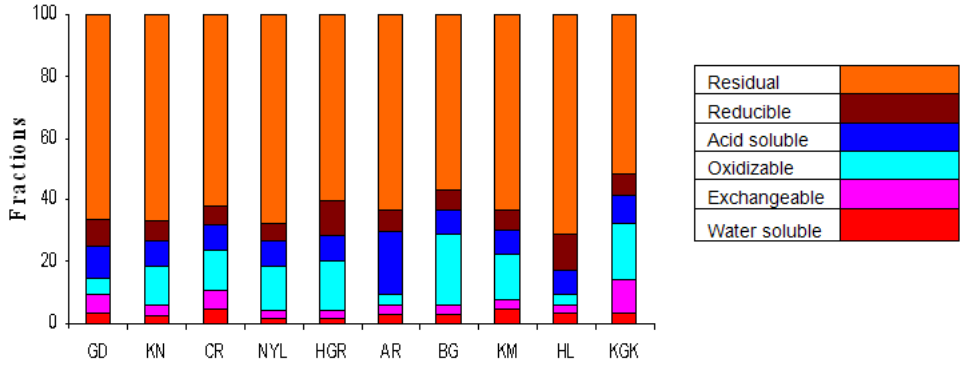

Fig. 3: Percentage of Cr in different chemical fractions of waste soils.

Zinc: The results of six geochemical fractions of Zn are shown in Figure 4. The metal was mostly concentrated in the residual fractions ranging from 30.05 to 51.79%. The relatively high percentage of the total Zn in the residual fraction probably indicates the greater tendency for Zn to become unavailable once it is in soils (Ma and Rao, 1997; Uba *et al* 2008). The amount of Zn in the residual fractions ranged from 30.05 - 51.71% while the range of Zn in the non-residual fraction fractions ranged from 48.29 to 69.95%. However the mobile phase contain only 13.01(CR) to 19.09% (BG). This is the amount that is potentially mobile. Other important fractions of the Zn are the reducible phase containing between 31.58 to 70.12%. The high concentration of the former may be linked to the high stability constant of Zn oxides (Kuo *et al*, 1983 and Ramos *et al* 1994). The trend of availability of the metal in the various fractions were in the order: Residual>Oxidizable>Reducible>Acid soluble>Exchangeable>Water soluble and similarly, the pattern of potential mobility and bioavailability in the various dumpsites were depicted as follows: BG>HL>HGR>AR>KM>KGK>KN=GD>NYL>CR. The level of zinc in all the metropolitan dumpsites were within the permissible critical limit set by USEPA (300mgkg^{-1}) except in KGK where it exceeded the limit.

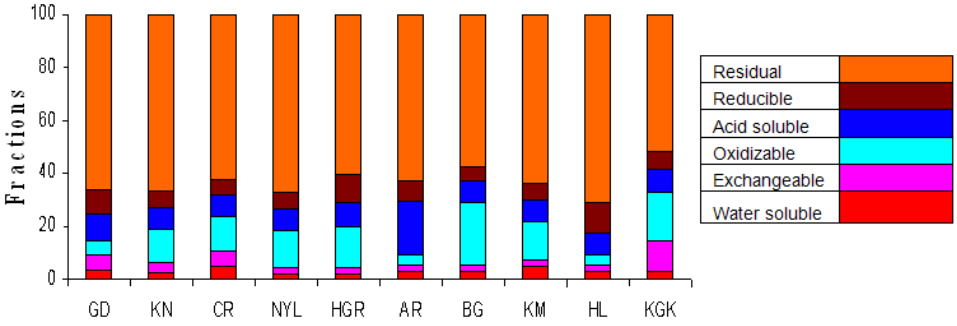

Fig. 4: Percentage of Zn in different chemical fractions of waste soils.

Cadmium: Figure 5 showed the distribution of the fractionation of Cd. The total extractable metal was above the USEPA (1996) set limit which is 3.0mg/kg in all the dumpsites. Cadmium is the least abundant metal in the refuse dumpsite in comparison to other metals studied. Cadmium batteries, metal scraps etc are being dumped from industrial, commercial and residential areas which might have contributed to the high concentrations of the metals. The range of mobile fractions was between 21.17 (CR) to 43.82% (KM) with an average of 29.62%. This metal fraction represented the fraction that is readily bioavailable to the environment (Xian, 1989; Kuo *et al*., 1983; Uba *et al*., 2008). The general orders of abundance of the extractable metals were: Residual > Oxidizable > Acid soluble > Reducible > Exchangeable > Water soluble. The potential mobility and bioavailability of this metal in the waste soils of the dumpsites were: KM>HL>NYL>KGK>AR>HGR>BG>GD>KN>CR.

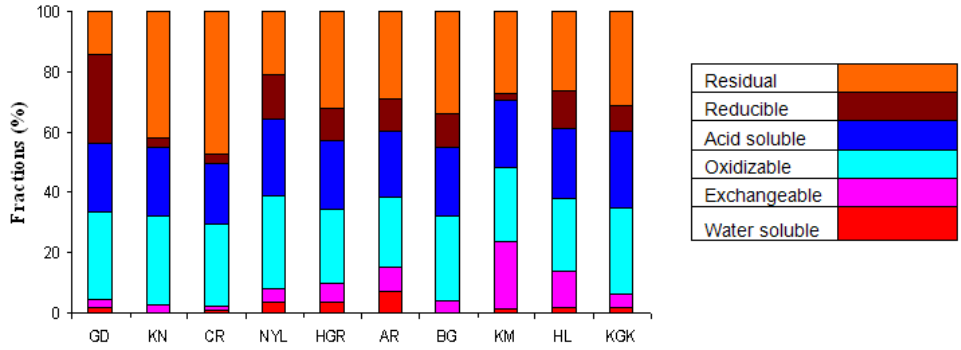

Fig. 5: Percentage of Cd in different chemical fractions of waste soils.

Manganese: Figure 6 shows the results of the extractable Mn fractions in the refuse dumpsites soils of the studied areas. The non-residual fraction contains high percentage of metals (75.04 (CR) to 85.41% (GD). Among the non-residual fractions the reducible phase ranked highest in concentration followed by the oxidizable phase.. The high percentage of Mn in this fraction may be due to the high precipitation of amorphous hydrous oxides of Mn during aging of the refuse dumpsite (Staeles *et al*, 2000). The distribution of this metal among the dumpsites followed the sequence: BG>HGR>NYL>AR>HL>KM>KN>HL>CR>GD and the general order of availability of the metals among the different extractable fractions followed the sequence: Reducible>Residual>Oxidizable>Exchangeable>Acid soluble>Water soluble. The levels of this metal have exceeded the USEPA (1986) set limit of 100 - 300mgkg^{-}1 in CR, NYL, HGR, KM, HL and KGK. The concentrations of this metal in all the refuse dumpsites soils were however within the set limit of uncontaminated soil of 950mgkg^{-1} (Sparks, 2003).

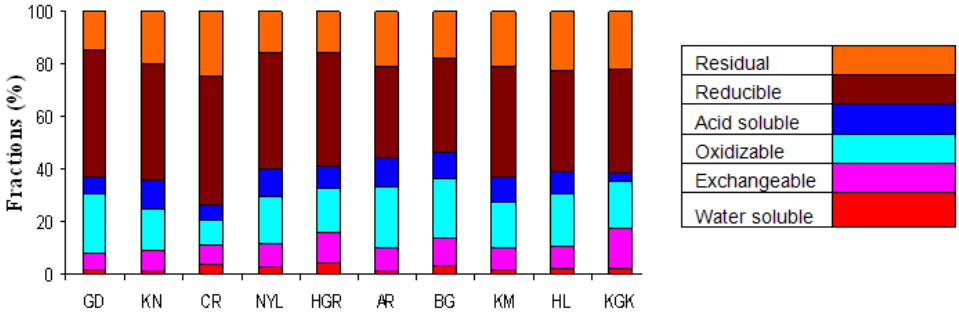

Fig. 6: Percentage of Mn in different chemical fractions of waste soils.

Copper: The results of copper in the various extracted fractions are presented in Figure 7. The level of the extracted copper in the soil samples of the ten metropolitan refuse dumpsites studied was below the set limit (250mg/kg) by USEPA (1986). The highest concentration of copper was recorded at KN (130.87±0.03) while the least concentration was recorded at GD, 55.54±0.03mg/kg. Terrus, (1995) reported that organic matter tightly holds Cu so much that its availability can be very low in organic soils. The general order of bioavailable Cu was Residual > Oxidizable > Reducible > Acid soluble > Exchangeable > Water soluble. Similarly, the level of mobile Cu in the dumpsites followed the trend BG>KGK>HL>KN>AR>CR>GD>HGR>KM>NYL. Only BG reflected a reasonable amount of the element in the mobile phase (15.92%). Most of the copper in the extracted wastes soil samples was presented in the residual fraction (23.72 to 62.59%). Gupta and Chen (1975) and Hickey and Kittrick (1984) also found that majority of copper in the soils and sediments to be associated with the residual fraction. In the case of HGR Cu was not found in the water soluble and exchangeable fractions.

Conclusion:

The results of this study indicated that physico-chemical parameters of the waste soils and the metal concentrations at the refuse dumpsites were significantly higher than the nearby control areas (20m away).The total extractable metals were all within the stipulated values set by USEPA (1986) except for Cd which

exceeded the limit. Generally, the metals depicted higher distribution in the residual fractions in all the refuse dumpsites with the overall order of mobility and bioavailability as: Cd > Mn > Zn > Pb > Cr > Cu. The low percent mobile fractions of the metals indicated low tendency of bioavailability and reactivity in the environment. However, heavy metals in the dumpsites may build up to high levels in the nearest future. There is therefore the need to monitor the levels of these metals in these areas to enable the evaluation of possible metal build-up.

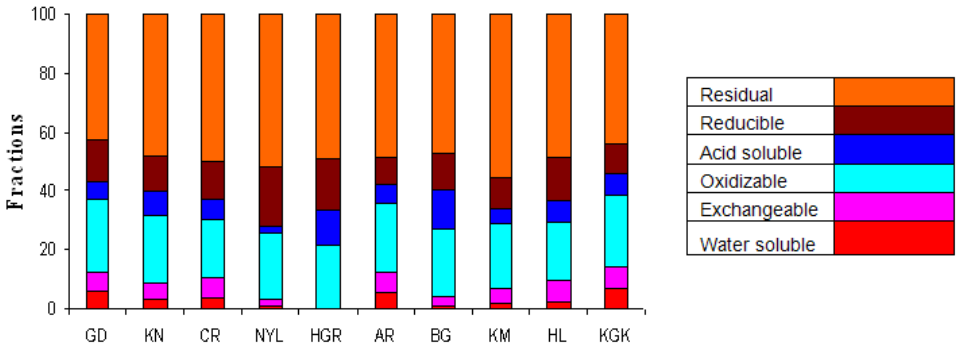

Fig. 7: Percentage of Cu in different chemical fractions of waste soils.

REFERENCES

Alloway, B.J. and D.C. Ayres, 1997. Chemical principles of environmental pollution, Second Edition, Blackie Academic and Professional, Chapman and Hall, London, pp: 190-216.

Amusan, A.A., D.V. Ige and R. Olawale, 2005. Characteristics of soil and crops uptake of metal in municipal waste dumpsites in Nigeria *J. Hum. Ecol.*, 17: 67-171.

Awofolu, O.R., 2005. A survey of trace metals in vegetation, soil and lower animals along some selected major roads in metropolitan city of Lagos. Environmental monitoring and assessment., 105: 431-447.

Bamgbose, O., O. Odukoya and T.O.A. Arowolo, 2000. Earthworms as bio-indicators of metal pollution in dumpsites of Abeokuta, Nigeria. *Revista de Biologia tropical*, 48 (1).

Fuentes, A., M.J. Saiez, M.I. Aguihar, A.B.P. Martins, I.J. Oitunio and V.I. Messegner, 2006. Ecotoxicity, phytotoxicity and extractability of heavy metals from different stabilized sewage sludges. *Environ. pollut.*, 143: 355-360.

Gupta, A.K. and S. Sinha, 2007. Assessment of Single Extraction Methods for the Predicition of Bioavailability of Metals to Brassica juncea L. (Var. vaibhar) grown on tannery wastes contaminated soil. *J. Hazard, Mater.*, 149: 144-150.

Hendershot, W.H. and M. Duquette, 1986. A simple barium chloride method for detrmining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.*, 50: 605-608.

Hickey, M.G. and J.A. Kittrick, 1984. Chemical partitioning of Cadmium Copper, Nickel and Zinc in soils and sediments containing high levels of heavy metals. *J. Environment Quality.*, 13: 372-376.

Kuo, S., P.E. Heilman and A.S. Baker, 1983. Distribution and forms of copper, Zinc, Cadmium, Iron, and Manganese in soils near a copper smelter. *Soil Sci.*, 135: 101-109.

Ma, I.Q. and C.N. Rao, 1997. Chemical fractions of Cd, Cu, Ni and Zn in contaminated soils *J. environment Qual.*, 26: 259-265.

Maiz, I., M.V. Esmoula and E. Millan, 1997. Evaluation of heavy Metal availability in contaminated soils by short sequential extraction procedure, The science of total environment., 206: 107-115.

McLean, J.E. and B.E. Bledsoe, 1992. Behaviour of Metals in Soils in ground water issue: EPA/540/S-92/018. U. S. EPA Robert S. Kerr Environ.Res. Laboratory, Ada, OK., pp: 1-20.

Meguellati, N., 1982. Mise au point d'un schema d'extraction selective des pollutants Metalliques Associes aux Diverse phases constitutive des sediments, these 3me cycle, universite de pau.

Odukoya, O.O., O. Bamgbose and T.A. Arowolo, 2000. Heavy metals in top soils of Abeokuta dumpsites. *Global J. Pure Applied Sci.*, 7: 467-472.

Okunola, O.J., A. Uzairu and G. Ndukwe, 2007. Levels of trace metals in soil and vegetation along major and minor roads in metropolitan city of Kaduna, Nigeria. African Journal Biotechnology., 6(14): 1703-1709.

Sanchez, G.R. and E. Millan, 1994. Ultrasonic bath digestion procedure for analysis of heavy metals in several reference materials. *Analysis*, 22: 222-225.

Shrivastava, S.K. and D.K. Banerjee, 2004. Speciation of metals in sewage sludge and sludge-amended soils. *Water, Air, Soil Pollut.*, 152: 219-232.

Shuman, L.M., 1985. Fractionation method for soil microelements. *Soil Sci*., 140: 11-22.

Sparks, D.L., 2003. Environmental Soil Chemistry 3rd Edition. Academic Press.

Staelens, N., P. Parkpian and 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.

Staessen, Z., 1994. Penal function and historical environmental cadmium position from Zinc smelters. Lacet 342: 152-157. in.

Stumm, W. and I.J. Morgan, 1981. Aquatic Chemistry. An introduction emphasing chemical equibilibra in natural water 2nd edition, John Wiley and sons New York.

Terrus, A., 1995. Distribution of differential fractions of Cd, Zn, Pb, and Cu in unpolluted and polluted soils. Water, Air and soil pollution, 83: 1-4.

Tessier, A., P.G.C. Campbell and M. Bisson, 1979. Sequential Extraction Procedure for the speciation of Particulate Trace metals. *Anal. Chem.*, 51(7): 844-861.

Uba, S., 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.

Udo, E.J. and J.A. Ogunwale, 1978. Laboratory manual for the analysis of soils, plants and water samples. Department of Agronomy University of Ibadan, pp: 45.

Udosen, E.A., E.I. Udoessien and U.J. Ibok, 1990. Evaluation of some metals in the industrial wastes from a paint industry and their environmental pollution implications. *Nig. J. Technol. Res.*, 2: 71-77.

Udosen, E.D., N.U. Benson, J.P. Essien and G.A. Ebong, 2006. *Int J Soil Sci*., 1: 27-32.

United States Environmental Protection Agency (USEPA)., 1986. Quality Criteria for Water. United States Environmental Protection Agency. Office of Water Regulations and Standards. Washington D.C., 20460.

Walkley, A. and I.A. Black, 1934. An examination of the Detjare method for Determining soil organic matter and a proposed modification of the chromic Acid titration. *Soil Sci*., 37: 29-36.

Xian, X., 1989. Effects of chemical forms of Cadmium, Zinc and lead in polluted soils on their uptake by cabbage plants. *Plant Soil.*, 113: 257-264.